

SOVIET PHYSICS USPEKHI

A Translation of Uspekhi Fizicheskikh Nauk

SOVIET PHYSICS USPEKHI

Russian Vol. 77, Nos. 3-4

JANUARY-FEBRUARY 1963

ELECTRON THEORY OF TRANSITION METALS. I

S. V. VONSOVSKIĬ and Yu. A. IZYUMOV

Usp. Fiz. Nauk 77, 377-448 (July, 1962)

CONTENTS

I. Introduction	548
1. Brief data on the electronic structure of transition element atoms	548
2. Some data on the electronic properties of transition metals	553
3. General qualitative ideas on the electronic structure of crystals containing transition element atoms	566
II. Elementary Electron Theory of Transition Metals	569
4. Band model of transition d-metal crystals	570
5. Model of interacting valence (outer) electrons and electrons of the inner unfilled shells [s-d(f) exchange model]	577
Literature. I	589
III. Properties of spin system of transition metal. 6. Hamiltonian of the electron system of transition metal. 7. Spin polarization of conduction electrons. 8. Indirect exchange interaction between electrons of spin-unsaturated shells via the conduction electrons. 9. Spin-wave theory of ferromagnetic metal. 10. Spin-wave theory of antiferromagnetic metal. 11. Magnetic relaxation and resonance in ferromagnetic and antiferromagnetic metals. 12. Magnetic scattering of slow neutrons in a ferromagnetic metal. IV. System of conduction electrons in a transition metal. 13. Energy of conduction electrons in a ferromagnetic transition metal. 14. Effective interaction between conduction electrons through the spin waves and the influence of this interaction on the superconducting state. 15. Condition for the existence of a superconducting state in a ferromagnetic metal. 16. Anomalous electric resistivity of ferromagnetic metal. V. Conclusion. Literature, II.	

BY transition metals, their alloys and compounds we mean crystalline bodies containing transition-group element atoms which have unfilled d or f shells. The distinctive features of the electronic structure of the isolated atoms should be conserved to some degree in the condensed (liquid and crystal) phases, and this leads to many singularities and to a great variety in the physical and chemical properties of these substances, as compared with bodies that contain no transition element atoms. This makes the transition metals, their alloys, and compounds interesting objects to the theoretical or experimental physicist engaged in the study of the structure of solids, their nature and physical properties, and the processes occurring in them under different external actions. Transition metals are also of prime importance in applications, since these substances play a leading role in modern technol-

ogy. It is sufficient to recall that the various steels, which are the "backbone" of technology, are alloys of iron, which is a transition element. One can also add that numerous magnetic materials, without which the most important branches of modern technology (electricity, radio, computer mathematics, etc) are inconceivable, must contain at least one transition-metal component. It is therefore understandable why these theoretical and practical aspects make the transition metals a timely and interesting object of scientific research.

From the physical point of view, the problem of transition metals, their alloys, and their compounds is a very extensive and complicated branch of solid state theory. In the present review we confine ourselves to a narrower problem, to the present day status of the theory of the electronic structure of pure transi-

tion metals, without touching upon their ionic crystal structure or the theory of their alloys and compounds, although in some cases we shall have to stop during the course of the exposition and discuss properties of these more complicated substances, too. Even in this more restricted formulation, the problem of transition metals is far from solved. Many unanswered questions still remain; many model representations, to which it becomes necessary to resort in the theoretical calculations, are of necessity quite approximate and sometimes even highly debatable. In spite of these circumstances, and perhaps precisely because of them, a summary of certain theoretical treatments used in the study of transition metal properties is of interest to physicists and engineers.

Much attention has been paid to transition metals in many books on quantum theory of solids^[1-4] and in reviews of general problems in the band theory of metals^[5-7]. We also call attention to a special review on transition metals and alloys written by Hume-Rothery and Coles^[8], in which much experimental material is cited, and in which structural properties of transition metals and alloys are also considered.

The present review differs noticeably both in contents and in the form of exposition from its predecessors on the theory of transition metals. The analysis is based on the notion of an unfilled and spin-uncompensated electron shell of the transition element atom, which leads to special properties of the electron system in the crystal lattice. The electron level density near the Fermi surface is always appreciably increased in transition metals, and when atomic ferromagnetic order arises in the crystal as a result of non-compensation of the magnetic moments, it becomes necessary to lift the spin degeneracy, i.e., to "shift" the energy bands* for the collectivized electrons with different spin projections. In the case of antiferromagnetic order, the spatial degeneracy is partially lifted for the conduction electrons. It is precisely these singularities of the electron structure of the transition metals that single them out as a special group of substances and bring about the entire specific nature of their physical and chemical properties; they can therefore be the subject of a special chapter in quantum solid state theory, namely the theory of transition metals. Much attention is paid in the present review to the effect of the "shift" of the energy bands of the conduction electrons with two different spin projections, whereas in preceding reviews principal attention was paid to the increase in the density of the electron levels near the Fermi surface. In the first part of the review (Chapters I and II) we present concise information on the electron structure of the transition group element atoms (Sec. 1); a brief summary is given of

the singularities of certain physical properties of transition metals (Sec. 2); a general qualitative treatment of the electron structure of transition metals is developed, along with a critical estimate of the models now employed in it (Sec. 3); this is followed by an exposition of the elementary theoretical treatment based on the band model of the crystals (Fig. 4), and on the so-called s-d exchange model (Sec. 5). The second part of this review is devoted to a development of a more rigorous quantum theory of transition metals, where we first consider the properties of the crystal spin subsystem (Chapter III), and then the conduction-electron subsystem (Chapter IV). This second part of the review can be regarded not only as a report of the specific results of the theoretical calculations, but also as an illustration of the new quantum-statistical methods (temperature Green's functions) employed in solid-state problems. The review concludes with a brief summarizing chapter V. On the whole, the review is not encyclopedic and consequently the attached bibliography, although covering the majority of basic papers on the theory of transition metals, cannot be regarded as exhaustive.*

I. INTRODUCTION

1. Brief Data on the Electronic Structure of Transition-element Atoms.

Although the transition-element atoms have many electrons, it is known^[9] that in the approximation of the centrally-symmetrical self-consistent field it is possible to retain for the states of the individual electrons of these atoms the same quantum characteristics as in the single-electron hydrogen atom, i.e., four quantum numbers: principal n , orbital l , magnetic m , and spin s . The state of a multielectron atom is determined above all by its electron configuration, i.e., by the number of electrons with given n and l . In accordance with the Pauli principle, not more than $2l(l+1)$ electrons can exist in each equivalent state (with given n and l); once this number is reached, we deal with a closed electron shell: $(nl)^{2l(l+1)}$. Table I shows the successive filling of the electron shells of these atoms.

For a complete description of the quantum state of the shell of a multielectron atom it is necessary to specify in addition to the electron configuration also the following total momenta: spin S , orbital L , and resultant $J = S + L$. Consequently, even if we disregard the fine structure of the terms (the magnetic interaction), states with the same configuration but different L and

*This effect is sometimes called in the literature, without complete justification, the "shift" of the Fermi surfaces of conduction electrons with two different spin projections.

*It must also be emphasized that the present review is devoted essentially to theoretical treatments of the physical properties of transition metals having a magnetic order, i.e., ferromagnetic and antiferromagnetic metals. Paramagnetic transition metals are discussed in much briefer form. Consequently the title of the review is in this respect somewhat broader than its content.

Table I. Successive filling of the electron shells of an atom

Configuration with given n and l								Total number of electrons in shell	Shell symbol
n \ l	s	p	d	f	g	h	k		
1	1s ²							2	K
2	2s ²	2p ⁶						8	L
3	3s ²	3p ⁶	3d ¹⁰					18	M
4	4s ²	4p ⁶	4d ¹⁰	4f ¹⁴				32	N
5	5s ²	5p ⁶	5d ¹⁰	5f ¹⁴	5g ¹⁸			50	O
6	6s ²	6p ⁶	6d ¹⁰	6f ¹⁴	6g ¹⁸	6h ²²		72	P
7	7s ²	7p ⁶	7d ¹⁰	7f ¹⁴	7g ¹⁸	7h ²²	7k ²⁶	98	Q

S have different energies, owing to the electrostatic interaction between the electrons. These energy differences usually range between 0.1 and 1.0 eV, which as a rule is several times smaller than the energy difference between levels with different electron configuration (approximately several eV). The sequence of levels with like configuration but with different L and S, arranged in ascending energy order, is determined by Hund's empirical rule (1927). According to Hund's rule, the minimum energy is possessed by the term with the largest value (for a specified configuration) of the summary spin S and the largest (for the same value of S) summary orbital momentum L. Qualitatively this rule follows from the requirement that the energy of the electrostatic interaction of the electrons in the atom, namely the exchange part of this interaction,* be a minimum. Figure 1 shows the level scheme for the iron atom, from which it is seen that as a rule levels with unlike configurations differ more in energy than levels within the same configuration.

The electron-shell filling sequence shown in Table I actually does not apply beyond potassium (K; Z = 19). In the potassium atom, as well as in the calcium atom that follows it (Z = 20), the states to be filled next are not the 3d states, which follow "in order" after the 3p states that are filled in the case of argon (Z = 18), but the next 4s states. Only in scandium (Z = 21) does a delayed filling of the ten-place 3d shell begin, and is

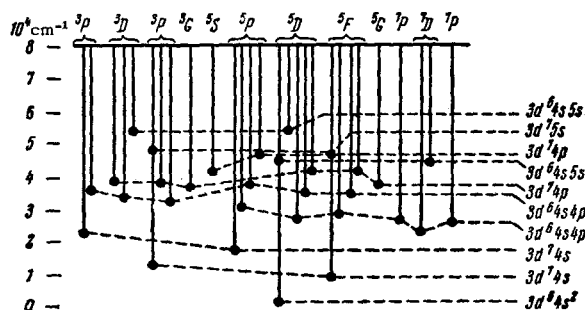


FIG. 1. Level scheme of iron atom after Hund.^[10] Terms with like electron configuration are joined by dashed lines (1 eV = 8067.5 cm⁻¹).

*See, for example, the second footnote on p. 264 of [9].

completed for the copper atom (Z = 29). Other violations of the simple sequence are observed in the filling of the 3d shell (iron group): for example, in the chromium atom (Z = 24) the configuration realized is 3d⁵4s in place of the "correct" configuration 3d⁴4s², whereas the 3d⁸4s² configuration of the nickel atom (Z = 28) is replaced in the copper atom not by the 3d⁹4s² configuration, but by 3d¹⁰4s. A delay in the filling of the 4d shell is observed in the elements from yttrium (Z = 39) to palladium (Pd; Z = 46) (the palladium group); a similar delay is observed for the 4f shell in the elements from lanthanum (La; Z = 57) to ytterbium (Yb; Z = 70) (rare earth group), for the 5d shell from lutetium (Lu; Z = 71) to platinum (Pt; Z = 78) (the platinum group), and finally for the 6d and 5f shells from actinium (Ac; Z = 89) to uranium (U; Z = 92), including the transuranic elements (the actinide group) (see Table II). It is thus precisely in the filling of the d and f electron shells that the normal sequence is violated. The elements in which the "delayed" filling of these shells takes place are those called the transition elements.*

The physical reason for the existence of internal unfilled groups in the shell of a multielectron atom is that the electron energy in such groups depends appreciably not only on the quantum number n, but also on l. For specified n, the energy increases with increasing l. The more the self-consistent field of the multielectron atom shell differs from the Coulomb field of the hydrogen atom, the more pronounced the dependence of the energy on l. It may therefore turn out to be energetically more favorable for the electron that is added on going from the element Z to the element (Z + 1) not to experience an increase in l (which is possible for a given n), but an increase in n with simultaneous decrease in l. Thus, for example, the states (n + 1)s and (n + 1)p can be energetically more favored than the states nd or nf. Using the approximate Thomas-Fermi statistical method,[†] it is possible to predict quantitatively the minimum atomic number (Z_l)_{min} with which the filling of a shell with specified l can begin. Elementary calculation shows that (Z_p)_{min} = 5(Z_d)_{min} = 21, (Z_f)_{min} = 58, etc, in splendid agreement with experiment.

Along with the energy singularities, the d and f shells have also "geometrical singularities" in the sense of the character of the distribution of the corresponding electron density. The electrons in the nd and nf states are as a rule closer in space to the atomic nucleus than the electrons in the (n + 1)s and (n + 1)p states, which have nearly the same energy. The reason

*The periodic table (including the transuranic elements) contains altogether 42 transition elements, of which 24 are d-metals from the iron, palladium, and platinum groups, 14 are rare earth metals, and 4 are actinides.

[†]See, for example, pp. 286-288 in [9], pp. 461-463 in [11], or the book [12].

Table II. The electronic configurations, the principal term, the radii of the incomplete shells, and the shells of the valence electrons of the transition elements and the distances between the ions, the nearest neighbors in the crystal lattice of the metal (data on interatomic distances and on the lattice type are based on the book by B. F. Ormont, *Struktura neorganicheskikh veshchestv (Structure of Inorganic Substances)*, Gostekhizdat, 1950).

a) Iron Group (3d)

(Electron shell configuration of argon: $1s^2 2s^2 2p^6 3s^2 3p^6$)

Z	Element	Electron configuration without argon shell	Principal term of atom	Radii of 3d and 4s shells (in Å)		Distance between ions in the metal (nearest neighbors) (in Å), type of lattice
				r_{3d}	r_{4s}	
21	Sc	$3d^4 4s^2$	2D	3.00	4.56	3.24 hcp (α) 3.204 fcc (β)
22	Ti	$3d^2 4s^2$	3F	2.36	4.35	2.900 hcp (α) 2.875 bcc (β)
23	V	$3d^3 4s^2$	4F	2.09	4.15	2.627 ₄ bcc
24	Cr	$3d^5 4s$	7S	1.96	4.98	2.493 bcc (α) 2.70 hcp (β)
25	Mn	$3d^5 4s^2$	6S	1.60	3.80	2.494 complex (α)
26	Fe	$3d^6 4s^2$	5D	1.44	3.39	2.4778 bcc (α)
27	Co	$3d^7 4s^2$	4F	1.30	3.51	2.507 hcp (α)
28	Ni	$3d^8 4s^2$	3F	1.19	3.40	2.4878 fcc
29	Cu	$3d^{10} 4s$	2S	1.14	3.70	2.5509 fcc

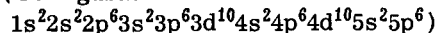
b) Palladium Group (4d)

(Configuration of Kr electron shell: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$)

Z	Element	Electron configuration without Kr shell	Principal term of atom	Radii of 4d and 5s shells (in Å)		Distance between ions in the metal
				r_{4d}	r_{5s}	
39	Y	$4d^5 5s^2$	2D	4.56	5.33	3.59 hcp
40	Zr	$4d^2 5s^2$	4F	3.75	5.08	3.18 hcp (α) 3.126 bcc (β)
41	Nb	$4d^4 5s$	6D	3.47	5.72	2.852 bcc
42	Mo	$4d^5 5s$	7S	2.98	5.42	2.72 bcc
43	Te	$4d^5 5s^2$	—	2.44	4.44	2.735 hcp
44	Ru	$4d^7 5s$	5F	2.32	4.92	2.693 hcp
45	Rh	$4d^8 5s$	4F	2.09	4.70	2.684 fcc (β)
46	Pd	$4d^{10}$	1S	4.35	—	2.7448 fcc
47	Ag	$4d^{10} 5s$	2S	3.29	4.32	2.883 fcc

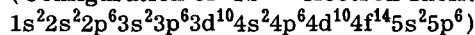
c) Rare Earth Group (Lanthanides, 4f)

(Configuration of xenon electron shell:



Z	Element	Electron configuration without Xe shell	Principal term of atom	Radii of 4f, 5d _a and 6s shells (in Å)			Distance between ions in the metal	
				q _{4f}	q _{5d}	q _{6s}		
57	La	5d6s ²	² D _{3/2}	—	5.33	5.88	3.71	Hexag. (α)
58	Ce	4f5d6s ²	³ H ₄	1.14	5.33	5.88	3.634	fcc (β)
59	Pr	4f ³ 6s ²	⁴ I _{9/2}	1.11	—	6.20	3.65	hcp (α)
60	Nd	4f ⁴ 6s ²	⁵ I ₄	1.05	—	6.20	3.662	Hexag. (α)
61	Pm	4f ⁵ 6s ²	⁶ H _{5/2}	1.00	—	6.20	3.642	fcc (β)
62	Sm	4f ⁶ 6s ²	⁷ F ₉	0.96	—	6.20	3.657	Hexag.
63	Eu	4f ⁷ 6s ²	⁸ S _{7/2}	0.92	—	6.20	—	—
64	Gd	4f ⁷ 5d6s ²	⁹ D ₂	0.85	5.33	9.80	4.084	bcc
65	Tb	4f ⁸ 5d6s ²	⁸ H _{7/2}	0.83	5.33	9.80	3.622	hcp
66	Dy	4f ¹⁰ 6s ²	⁵ I ₈	0.80	—	6.20	3.585	hcp
67	Ho	4f ¹¹ 6s ²	⁴ I _{15/2}	—	—	6.20	3.578	hcp
68	Er	4f ¹² 6s ²	³ H ₆	—	—	6.20	3.557	hcp
69	Tm	4f ¹³ 6s ²	² F _{7/2}	0.73	—	6.20	3.532	hcp
70	Yb	4f ¹⁴ 6s ²	¹ S ₀	0.70	—	6.20	3.523	hcp
							3.866	fcc

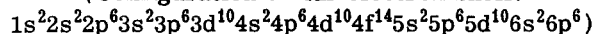
d) Platinum Group (5d)

(Configuration of Yb⁺⁺ electron shell:

Z	Element	Electron configuration without Yb ⁺⁺ shell	Principal term of atom	Radii of 5d and 6s shells (in Å)		Distance between ions in the metal	
				q _{5d}	q _{6s}		
71	Lu	5d6s ²	² D _{3/2}	5.33	9.80	3.509	hcp
72	Hf	5d ² 6s ²		4.35	9.33	3.14	hcp (α)
73	Ta	5d ³ 6s ²		3.72	8.40	2.854	bcc
74	W	5d ⁴ 6s ²	⁵ D	3.25	7.90	2.735	bcc (α)
75	Re	5d ⁵ 6s ²		2.86	7.35	2.755	hcp
76	Os	5d ⁶ 6s ²		2.56	6.88	2.725	hcp
77	Ir	5d ⁷ 6s ²		2.32	6.53	2.709	fcc
78	Pt	5d ⁹ 6s	³ F	2.22	7.51	2.769	fcc
79	Au	5d ¹⁰ 6s	² S	1.94	7.06	2.883	fcc

e) Actinide Group (5f and 6d)

(Configuration of Rn electron shell:



Z	Element	Electron configuration without Rn shell	Principal term of atom	Radii of 5f, 6d and 7s shells (in Å)			Distance between ions in the metal	
				q _{5f}	q _{6d}	q _{7s}		
89	Ac	6d7s ²	² D _{3/2}	—	—	—	—	—
90	Th	6d ² 7s ²	³ F ₂	—	5.80	~10	3.59	fcc
91	Pa	5f ² 6d7s ² (?)	⁴ K _{11/2}	—	4.8	~9	3.25	Tetrag.
92	U	5f ³ 6d7s ²	² L ₆	—	4.1	8.4	2.77	Complex (α)
93	Np	5f ⁴ 6d7s ² (?)	² L _{11/2}	1.11	5.88	~10	2.97	bcc (β)
94	Pu	5f ⁶ 7s ²	⁷ F ₀	—	—	—	—	—
95	Am	5f ⁷ 7s ²	⁸ S _{7/2}	1.11	—	6.2	—	—
96	Cm	5f ⁷ 6d7s ² (?)	⁹ D ₂	1.07	—	6.2	—	—
97	Bk	5f ⁸ 6d7s ² (?)	⁸ H _{17/2}	—	—	—	—	—
98	Cf	5f ¹⁰ 7s ² (?)	⁵ I ₈	—	—	—	—	—

Table III. Magnetic moments of trivalent ions of rare-earth elements

Z	Element	Number of 4f electrons	Principal term	g-factor	$\mu_{\text{theor. eff}}$ (in μ_B)	μ_{exp} (in μ_B)
57	La ⁺³	0	$1S_0$	0	0	0
58	Ce ⁺³	1	$2F_{5/2}$	$6/7$	2.54	2.51
59	Pr ⁺³	2	$3H_4$	$4/5$	3.58	3.53
60	Nd ⁺³	3	$4I_{9/2}$	$8/11$	3.62	3.55
61	Pm ⁺³	4	$5I_4$	$3/5$	2.68	—
62	Sm ⁺³	5	$6H_{5/2}$	$2/7$	1.55 *	1.46
63	Eu ⁺³	6	$7F_0$	0	3.40 *	3.37
64	Gd ⁺³	7	$8S_{7/2}$	2	7.94	8.07 ± 0.05 **
65	Tb ⁺³	8	$7F_6$	$3/2$	9.72	9.62 ± 0.05 **
66	Dy ⁺³	9	$6H_{15/2}$	$4/3$	10.64	10.67 ± 0.05 **
67	Ho ⁺³	10	$5I_8$	$5/4$	10.61	10.86 ± 0.2 **
68	Er ⁺³	11	$4I_{13/2}$	$6/5$	9.60	9.79 ± 0.15 **
69	Tm ⁺³	12	$3H_6$	$7/6$	7.56	7.35
70	Yb ⁺³	13	$2F_{7/2}$	$8/7$	4.53	4.50
71	Lu ⁺³	14	$1S_0$	0	0	0

*In the case of the Sm⁺³ and Eu⁺³ ions at room temperature, the condition that the energy difference of neighboring levels of the multiplet be small compared with kT is violated ($E_1 - E_2 > kT$), and consequently the formula for the magnetic susceptibility becomes more complicated and the formula for μ_{eff} differs from the ordinary formula $\mu_{\text{eff}} = g\sqrt{J(J+1)}$. This question was investigated in detail by Van Vleck.^[18a,b]

**See the experimental data on the measurement of paramagnetic susceptibility in these metals as presented by Arais and Miller (J. of Appl. Phys. 31, 325 (1960); by Arais and Colvin at the 6th Conference on Magnetism and Magnetic Materials of 14-17 November 1960, New York. Green, Levgold, and Spedding obtained $\mu_{\text{exp}} = (9.9 \pm 0.2)\mu_B$ for Er (Phys. Rev. 122, 827 (1961)).

for it is that the effective potential well for the d or f electrons is located closer to the nucleus than for the s and p electrons.* Therefore the region of "classically attainable" distances for the d or f states will also be closer to the nucleus of the atom, i.e., the d and f groups are closer to the nucleus.†

As long ago as in 1930, Slater^[13] proposed a semi-empirical method of calculating the effective radii of different electron shells of multi-electron atoms, which are regarded as spheres on the surfaces of which a maximum electron probability distribution density is attained; this distribution was determined with the aid of the approximate wave function of the electron in the self-consistent field of the atom.‡ By way of the first approximation, Slater chose for the radial part of the wave function of the electron the nodeless function

$$\varphi(\rho) = \rho^{(n^*-1)} e^{-\frac{Z-\sigma}{n^*}\rho}, \quad (1.1)$$

which at large distances (ρ —distance measured in Bohr radii $r_B = 0.5291 \times 10^{-8}$ cm) behaves asymptotically like a hydrogen wave function with "principal quantum number" n^* and with nuclear charge $(Z - \sigma)e$, where σ is the screening parameter. Slater has shown that best agreement with experiment is obtained by choosing $n^* = 1, 2, 3, 3.7, 4, 4.2, \dots$, in correspondence to the values of the true quantum number $n = 1, 2, 3, 4, 5, 6, \dots$ and by breaking up the electrons into shells:

$$1s; 2s, p; 3s, p; 3d; 4s, p; 4d; 4f; 5s, p; \dots$$

to determine the screening parameter. No account is taken whatever of the influence of the electrons in shells that are exterior to the given shell; each electron of a given shell contributes to the parameter a value equal to 0.35 (except for the first group, for which this fraction is 0.30); if the shell under consideration is s or p, then for this shell, each electron from the nearest neighboring internal shell with $(n - 1)$ introduces a fraction equal to 0.85, while the electrons from the following innermost shells introduce a fraction equal to 1.00; for the d or f shells this fraction is always 1.00.

With the aid of these rules it is possible to calculate the energies of the atoms and ions, and also the effective radii of different groups of their shells. In the last columns of Table II are given the values of the effective radii for the

*See, for example, p. 324 in the book [11].

†Inasmuch as most physico-chemical properties of the atoms are determined essentially by their valence electrons (s and p), which are farthest away from the nucleus, one can expect that differences in the number of the d and particularly f electrons, which are closer to the nucleus, will not lead to any noticeable differences in the indicated properties. A clear cut example of this are the rare-earth elements, which are very close to one another in their physico-chemical properties. This, naturally, does not pertain to those properties which are the direct consequence of the difference in the structure of the 4f shell of these elements, for example to their magnetic properties (see below).

‡These calculations were subsequently made more precise (see, for example, supplement to the Russian translation of [14], p. 424). For our purposes, however, Slater's approximate calculation is perfectly adequate.

internal $[(n+1)s]$ and unfilled (nd or nf) shells. It is seen from these data that the latter always have a considerably smaller radius than the former.

One of the most important features of transition-element atoms is the fact that their spin and orbital momenta are not compensated; this fact follows from Hund's rule and determines their paramagnetic nature. By way of an example, Table III lists the values of the magnetic moments of trivalent ions of rare earths as predicted by the theory and as observed experimentally. As regards the latter, the most accurate method for the determination would be to measure the magnetic susceptibility of rarefied monatomic gases of transition elements. In practice, however, these measurements entail great technical difficulties, since the temperature region where the gas phase of these substances exists is quite high, making the experiment exceedingly complicated. In addition, the measured effect itself becomes very small, since the paramagnetic susceptibility decreases with temperature in accordance with the Curie law, $\chi_p \sim 1/T$. Therefore to obtain experimental information on the magnetic properties of the transition element atoms it becomes necessary to measure their magnetic properties in the solid phase. Naturally, in a crystal each ion is under the influence of its own atomic environment, which can change appreciably the properties that characterize its free state (for more details see Sec. 2). One can expect, however, the deep 4f shell of ions of the rare-earth elements to be practically immune to noticeable influence of the neighboring atoms, owing to the good screening on the part of the outer $5s^25p^6$ group, at least when it comes to the values of the magnetic moments. The trivalent ions of the rare earths should therefore behave also in crystals like free ions, from the magnetic point of view. This assumption is well justified in practice, as can be seen from Table III. Unlike the atoms of the rare earths, the atoms of iron, palladium, and platinum have 3d, 4d, and 5d shells which lie closer to the periphery of the atom and therefore are not so strongly screened against the influence of the neighboring atoms in the crystal. This influence is primarily manifest in the so-called phenomenon of "quenching" of the orbital momenta of the d shells, and consequently in crystals the entire magnetism of the ions of this type is due essentially to the spin moments. Comparison of the theoretical moments with the observed ones* does not yield for these atoms as good an agreement as in the case of the rare earths. Even in this case, however, it is quite obvious that the magnetic properties of the atoms are determined practically completely by the momenta of the unfilled d shells.†

*A more detailed exposition of data on atomic paramagnetism can be found in books on magnetism [15-18], and also in [19].

†Another method of measuring atomic and ionic magnetic moments is the well known Stern and Gerlach experiment with an atomic beam passing through an inhomogeneous magnetic field.

2. Some Data on Electronic Properties of Transition Metals

In the condensed phase (liquid or crystal), the atoms of the transition elements come close to one another or to the atoms of other transition and non-transition elements (in alloys or compounds) and the distances between them are of the order of the atomic distances; the interactions between the atoms therefore become comparable in magnitude with the bonds between the electrons in the shells of the individual atoms. These interatomic interactions affect above all the valence electrons, the character of the motion of which is radically changed in the crystal. This is seen most clearly from a comparison of the entirely different optical spectra, which reflect the structure of the energy levels of the valence electrons in gases (line spectra) and crystals (continuous spectra). This change in the spectrum character indicates that the valence electrons experience complete collectivization in the metallic crystals and form an electronic Fermi liquid in which the ionic lattice of the crystal is "immersed." On the other hand, the electrons of the innermost filled atomic shells hardly change the character of their motion in the crystal. This is evident from the x-ray spectra produced by electronic transitions between levels of the internal shells, which practically do not change their line character on going from the free atom to the crystal.* On the other hand, the electrons of the unfilled d and f shells cannot be classified as either belonging to closed shells or as valence electrons. One can only expect the f electrons, being closer to the nucleus of the atom than the d electron, to move in a crystal more like the electrons of the inner shells, whereas the d electrons should experience to a greater extent the collectivizing action of the interatomic interaction in the crystal. This will be discussed in greater detail in Sec. 3 and in Chapter II. We mention here only the characteristic features of some physical properties of transition metals, which have a direct bearing on the electron system of the crystal.

a) Magnetic properties. As already indicated in Sec. 1, the atoms and ions of transition elements are always paramagnetic † in the free state, since by virtue of Hund's rule their electron shells have in the ground state a nonvanishing spin, nonvanishing orbital momentum or both simultaneously. Comparison of magnetic properties of isolated atoms or ions of transition ele-

*The observed broadening of the emission lines of the x-ray spectra, which is particularly large in the case of heavy-element atoms, is due to the reduction in the average lifetime of the corresponding excited states of the atom with absence of the electron at the deep inner levels [see also item d) below].

†This holds true for ions which do not completely lack an unfilled shell. In the case of ions which do not have such a shell (for example Sc^{+++} , Zr^{4+}), they are diamagnetic; on the other hand ions of transition element atoms in which an unfilled electron shell occurs can also be paramagnetic. Thus, for example, the divalent ions Cu^{++} , Ag^{++} , etc., are paramagnetic.

ments with the same properties of crystals containing these atoms in their makeup can serve as an important indicator of the changes that occur in the unfilled d and f shells of the condensed phase under the influence of interatomic forces.

The extensive experimental material on the magnetic properties of such crystals makes it possible to present, with sufficient reliability, the following classification by magnetic properties. We first discuss the 42 transition metals in pure form. We have here two different groups: 1) metals with atomic magnetic order, which in turn include: 1a) ferromagnets—Fe, Co, Ni (from the 3d metal group) and Gd, Tb, Dy, Ho, Er, and Tu (from the 4f metal and rare-earth groups); 1b) antiferromagnets—Cr, Mn (from the 3d metal group) and Ce, Pr, Nd, Pm, Sm, and Eu (from the 4f metal and rare earth groups); 2) paramagnetic transition metals—Sc, Ti, V (from the 3d metal group); Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd (from the 4d metal group); La, Yb (from the 4f metal and rare earth groups); Lu, Hf, Ta, W, Re, Os, Ir, Pt (from the 5d metal group); and Ac, Th, Pa, U (from the 6d and 5f metal and actinide groups).*

Ferromagnetic metals have below the Curie point (Θ_f) a spontaneous magnetization I_S , which reaches a maximum I_0 at 0°K ($I_S \equiv 0$ when $T \geq \Theta_f$). In antiferromagnetic metals, the crystal breaks up into two (or more) magnetic sublattices, which have at temperatures below the Neel point Θ_N spontaneous magnetizations I_{iS} ; however, the vector sum of I_{iS} taken over all the sublattices is equal to zero: $\Sigma I_{iS} = 0$. In the case of rare-earth metals with magnetic order, both ferromagnetic and antiferromagnetic states can be observed in neighboring temperature intervals. For example^[20,21], dysprosium is ferromagnetic from zero to $\Theta_f = 85^\circ\text{K}$ and antiferromagnetic from Θ_f to $\Theta_N = 175^\circ\text{K}$. Holmium is ferromagnetic from zero to $\Theta_f = 20^\circ\text{K}$ and antiferromagnetic from Θ_f to $\Theta_N = 132^\circ\text{K}$. Finally, erbium is ferromagnetic from zero to $\Theta_f = 19.9^\circ\text{K}$ and antiferromagnetic from Θ_f to $\Theta_N = 80^\circ\text{K}$. Above the Curie or Neel point, all the metals with atomic magnetic order lose this order and become paramagnetic with a susceptibility that obeys approximately the Curie-Weiss law†

*It should be noted that so far there are no sufficiently reliable data on the measurements of magnetic properties of several metals of the 3d, 4d, and 5d groups, the rare earths, and the actinides. In particular, there are some grounds for assuming that palladium and platinum are antiferromagnetic.^[164] It is possible that vanadium is also antiferromagnetic^[165], but final conclusions call for additional more careful investigations. A later paper by Barnes and Graham^[169] suggests, in contrast with ^[165], that vanadium is not antiferromagnetic.

†Investigations have shown that the actual dependence is more complicated. Recently K. P. Belov and A. V. Ped'ko observed (by magnetic measurements) that gadolinium has in the interval from $\Theta_f = 210^\circ\text{K}$ to $\Theta_N = 290^\circ\text{K}$ an antiferromagnetic state, with apparently helicoidal structure (gadolinium is in the ferromagnetic

$$\chi_p = \frac{C}{T - \Theta_p}, \quad (2.1)$$

if $T \gg \Theta_f$ or Θ_N ; here Θ_p is the paramagnetic Curie point, which in the general case differs from Θ_f or Θ_N in both magnitude and sign,* and C is the Curie constant.

Comparison of the magnetic properties of free atoms and crystals of transition elements with atomic magnetic order is simplest to carry out by determining the average atomic magnetic moments obtained from measurements on crystals. The sought-for information can be obtained in two ways. First, it is possible to determine the average moments for a crystal with magnetic order by dividing I_0 of the ferromagnet by the number of atoms per unit volume. In the case of an antiferromagnet it is necessary to determine for this purpose the sublattice saturation I_{i0} [for example by neutron diffraction^[22], see Item d) below]. These average moments should be compared with the moments of the free atoms or ions. Second, in the case when $T \gg \Theta_f, \Theta_N$, when the transition metals have no spontaneous magnetization and go over into the paramagnetic state, the effective atomic magnetic moments are determined, for example, by measuring the Weiss constants which are contained in expression (2.1) for the susceptibility; these should be compared with the moments of the free atoms.

Table IV lists the values of the average atomic moments calculated by the saturation method, for the presently known ferromagnetic and anti-ferromagnetic metals of the iron and rare-earth groups. From a comparison of these average moments with those of the free atoms, listed in the same table, we see that in the case of the iron group a noticeable difference exists between the two, something not observed for the rare-earth group metals; in addition, all the average atomic moments have fractional values greatly deviating from whole numbers.†

To determine the effective magnetic moments from measurements of paramagnetic susceptibility, in the case when the latter is given by (2.1), it is necessary to know the expression for the constant C . For isolated atoms (gases) theory yields the following formula:‡

state below Θ_f), in analogy with the other rare-earth metals Dy, Tb, Ho, Er, and Tu. The antiferromagnetism of gadolinium turns out to be very "weak" and is destroyed in a critical field $H_c \sim 15$ Oe. This apparently explains also why it remained unnoticed in earlier investigations. A final solution of this problem calls, naturally, for the performance of neutron diffraction investigations.

*See, for example, Item 4 of Sec. 25 in ^[15].

†The deviation of μ_{at} from μ_{av} in rare-earth metals is apparently due to the influence of the crystalline field on the states of the 4f electrons (see ^[47b,150] on this topic).

‡In the general case the paramagnetic susceptibility has a more complicated form than (2.2) even for gases of free atoms (see, for example, Sec. 9, Item A in ^[16]); we shall not discuss this in greater detail at present, however.

Table IV. Comparison of spin magnetic moments (in μ_B units) of isolated atoms of certain transition metals with the average atomic moments for the ferromagnetic and antiferromagnetic state of the crystal

Element	Spin magnetic moment of the isolated atom (in μ_B)	Average atomic magnetic moment of the crystal (in μ_B)
Cr	5	0.2–0.4
Mn	5	1.5
Fe	4	2.218
Co	3	1.715
Ni	2	0.604
Gd	7	7.12
Er	9	8–9?
Ho	10	4.0

$$C = \frac{N\mu_B^2 g^2 J(J+1)}{3k}, \quad (2.2)$$

where N is Avogadro's number, g is the Lande factor, μ_B is the Bohr magneton, and k is Boltzmann's constant. Thus, comparison with theory necessitates the knowledge of the quantum numbers J and the Lande factor. Measurements of the gyromagnetic ratio yield for metals of the iron group $g = 2$, i.e., the "quenching" of the orbital momenta mentioned in Sec. 1 does take place; therefore expression (2.2) assumes the simpler form

$$C = \frac{4N\mu_B^2 S(S+1)}{3k}. \quad (2.3)$$

Actually, however, the temperature variation of χ , say for nickel, cobalt, and iron, has been shown by experiment to deviate appreciably from the Curie-Weiss law when $T > \Theta_f$ ^[23]. Consequently, comparison with theory calls for a detailed investigation (see^[82], and also Sec. 4 below). The picture is simpler in the case of rare-earth metals, for example gadolinium and dysprosium, where the susceptibility follows (2.1) above the Curie point and where good agreement is obtained between theory and experiment for the constant C , using (2.2) or (2.3), if it is assumed that the ground states of the 4f shells of the gadolinium and dysprosium ions in the crystal are respectively 8S and $^6H_{15/2}$,* and therefore $J_{Gd} = 7/2$, $g_{Gd} = 2.0$ and $J_{Dy} = 8$, $g_{Dy} = 1.25$. Substitution of these values in (2.2) yields $C_{Gd} = 7.87$ and $C_{Dy} = 14.05$, whereas experiment yields 7.8 and 13.6–14.00, respectively.

In the case of the antiferromagnetic metals chro-

mium and manganese, neutron diffraction yields^[22] for the average atomic magnetic moments of the sublattice 0.2–0.4 for chromium and 0, 1, and 2 for manganese, respectively (in μ_B units).*

If we exclude the rare-earth metals, which apparently all have in practice magnetic atomic order at low temperatures,† then the majority of the transition metals have no magnetic atomic order,‡ and are paramagnetic in their behavior. Yet the paramagnetism of these metals has many peculiarities.^[24] One should note first that the magnitude of the atomic susceptibility at room temperature greatly exceeds in practically all these metals the corresponding values for alkali and alkali-earth non-transition metals (Table V), and is exceeded only by the rare-earth metals (when $T > \Theta_f$ or Θ_N). The temperature dependence of the susceptibilities of these substances is quite unique. In none of these metals does it obey the Curie-Weiss law (2.1). In some metals χ decreases with increasing temperature (V, Nb, Pd, Ta, Pt), and in others it increases (Ti, Zr, Mo, Ru, Rh, Hf, W, Os, Ir). Another characteristic feature is that elements of different groups, but located in the same column of the periodic table, have the same character of temperature dependence $\chi(T)$ (for example, $d\chi/dT > 0$ for Ti, Zr, Hf, or $d\chi/dT < 0$ for V, Nb, Ta), and on going from one column to the other the sign of the derivative $d\chi/dT$ changes (for example, Zr^+ , Nb^- , Mo^+ or Hf^+ , Ta^- , W^+). A definite correlation is also observed in the values of the susceptibility and the change in sign of $d\chi/dT$ with the values of the electronic specific heat [see item b) below]. In some cases a maximum (for example, Pd) or a minimum (Zr and Nb) is observed on the $\chi(T)$ curves. One must note, however, that investigations of the magnetic properties of paramagnetic transition metals (including rare-earth metals) vary in character, have been carried out under different experimental conditions, with differently prepared materials of different quality, and as a rule not on single crystals of high purity. Nor are there sufficiently detailed measurements in the field of low and super low temperatures, or simultaneous magnetic and neutron diffraction investigations.

Of appreciable interest are also investigations of the magnetic properties of ferromagnetic and antiferromagnetic alloys and compounds of transition metals, both with one another and with non-transition elements, since these observations can yield important informa-

*The complicated crystalline structure of manganese has not made it possible to obtain as yet reliable results, and consequently the authors of^[22] give three different values; it is also possible that ions with unequal moments are located in the different sites of the elementary cell of the manganese crystal.

†Although there are still no exhaustive data on all the elements of this group.

‡Here, too, there are not enough complete data for very low temperatures.

*I.e., both the Russel-Saunders (LS) coupling^[9,14] and Hund's rule^[10] hold true, and in addition the susceptibility of the conduction electrons can be neglected.

Table V. Atomic magnetic susceptibility of paramagnetic transition metals at room temperatures, χ_A , and the sign of its derivative $d\chi_A/dT$

Metal	$\chi_A \cdot 10^6$	$d\chi_A/dT$	Literature
Scandium	315	?	6
Titanium	156	+	2,3
Vanadium	255	-	4
Yttrium	491	?	6
Zirconium	119	+	2,3
Niobium	209	-	4,5
Molybdenum	82.5	+	4,5
Technetium	270	-	1
Ruthenium	44	+	7
Rhodium	101	+	8
Palladium	558	-?	8
Lutetium	?	?	
Hafnium	75	+	9
Tantalum	152	-	4,8
Tungsten	55	+	4,5
Rhenium	69	-	6,9
Osmium	9.5	+	7
Iridium	35	+	10,11
Platinum	189	-	8
Sodium	15.6		
Potassium	44		
Aluminum	16.7		

1. C. M. Nelson, Ph. D. Diss., Univ. of Tenn. (1952), cm.²⁷
2. C. F. Squire and A. R. Kaufmann, J. Chem. Phys. 9, 673 (1941).
3. L. Klemm, Z. Electrochem. 45, 354 (1939).
4. C. J. Kriessman, Revs. Mod. Phys. 25, 122 (1953).
5. W. J. de Haas and P. M. van Alphen, Proc. Acad. Sci. Amst. 36, 263 (1933).
6. H. Bommer, Z. Electrochem. 45, 357 (1939).
7. A. N. Guthrie and L. T. Bourland, Phys. Rev. 37, 303 (1931).
8. F. E. Hoare and J. C. Walling, Proc. Phys. Soc. B64, 337 (1951).
9. C. J. Kriessman and T. R. McGuire, Phys. Rev. 90, 374 (1953).
10. K. Honda, Ann. Phys. 32, 1027 (1910).
11. M. Horowitz and J. G. Daunt, Phys. Rev. 91, 1099 (1953).

tion on the electronic structure of the substances of interest to us. Not being able to dwell on this question in detail, we note only the most essential results which have a direct bearing on the subject of the present review. For example, in the case of alloys of ferromagnetic metals of the iron group (Fe, Co, Ni) appreciable deviations are observed from the rule of simple mixing for the average atomic magnetic moments. In the study of binary alloys of nickel with low concentrations of non-transition metals, when the alloy is still ferromagnetic, the following regularity was observed: replacement of each atom of nickel by an atom of another element of valence ν decreases the average atomic moment of the alloy p'_{all} (in μ_B units) by an amount νv , i.e.,

$$p'_{all} = p_{Ni} - \frac{\nu}{100} v, \quad (2.4)$$

where ν is the atomic percentage of additive in the alloy. A similar relationship but less clearly pronounced holds for cobalt alloys, too. On the other hand, in alloys based on iron substitution of each iron atom by an atom of a non-transition element of any valence decreases the average atomic magnetic moment of the alloy by $2.2 \mu_B$, i.e., by the average moment of pure iron:

$$p''_{all} = p_{Fe} \left(1 - \frac{\nu}{100}\right). \quad (2.5)$$

A more complicated law governs the variation of the average atomic moments in alloys of Fe, Co, or Ni with transition elements. The data for some alloys of this type are listed in Table VI, from which it is seen that in the case of alloys of Ni with Pd or Fe with Ru, which are in the same column of the periodic table and consequently have an electronic shell of similar structure, the average atomic moment of the alloy re-

Table VI. Change in average atomic moments Δp in alloys of iron, cobalt, and nickel with transition elements of the 3d, 4d, and 5d groups at an additive concentration of 1%*

Solvent	Additive	$\Delta p \cdot 100$	Solvent	Additive	$\Delta p \cdot 100$
Fe (3d)	Cr (3d)	-2.2	Ni (3d)	Ni (3d)	-0.93
	Mn (3d)	-2.2		Pt (5d)	+1.15
	Co (3d)	+1.2		Cr (3d)	-4.4
	Ni (3d)	+0.6		Mn (3d)	+2.4
	Ru (4d)	0.0		Fe (3d)	+2.8
	Rh (4d)	+1.0		Co (3d)	+1.2
	Pd (4d)	-0.20		Mo (4d)	-5.4
	Os (5d)	-1.6		Ru (4d)	-2.8
	Ir (5d)	+0.87		Pd (4d)	0.0
	Pt (5d)	+2.0		W (5d)	-5.8
				Pt (5d)	-0.6
Co (3d)	Mn (3d)	-4.8			
	Fe (3d)	+1.6			

*See Table 69 of [17], after L. Néel, Le Magnétisme, Réunion à Strasbourg, 1939 (1940).

Table VII. Average atomic (molecular) magnetic moment of compounds of transition elements

Compound	μ_{mol}	Literature	Compound	μ_{mol}	Literature
Fe ₂ B	3.82	1	MnBi	3.52	1
Fe ₃ C	6.045	1	Mn ₂ Sb	0.94	1
Fe ₄ N	8.88	2	Mn ₂ Sn	0.86	1
FeBe ₂	2.24	3	CrTe	2.39	1
MnAs	3.40	1	MnP	1.2	1
MnSb	3.53	1			

1. L. Néel, Le Magnétisme, Réunion à Strasbourg, 1939 (1940).
 2. Ch. Guillaud, H. Créveaux, Compt. rend. 222, 1170 (1946).
 3. V. Marian, Ann. de phys. (11) 7, 459 (1937).

mains the same as in crystals of pure nickel or iron. On the other hand, in an analogous alloy of nickel with platinum, the average moment of the alloy decreases upon addition of each platinum atom by an amount equal to the average moment of the pure nickel [see formula (2.5)]. A similar law is observed also in alloys of iron with chromium and manganese.

The average atomic moment of an alloy is greatly influenced by a phase transition of the order-disorder type. In some cases the moment may change by 100%, for example, in the alloys Fe₃Pt or Ni₃Mn (see Table 7 in [17]).

No less interesting are the magnetic properties of the intermetallic compounds. Table VII lists data for the average magnetic moments per "molecule" of several such compounds. An analysis of these data in conjunction with the results of measurements of other properties of the substances (electric conductivity etc.) is an essential stage in the study of the electronic structure of transition metals, their alloys, and compounds.

Recently tremendous experimental material has been accumulated on the determination of the average atomic magnetic moments in semiconductor ferrimagnets—ferrites^[25] with different crystalline structures (spinel, garnet, perovskite, magnetoplumbite, and others), and also in oxides, sulfides, selenides, and other nonmetallic compounds of transition elements. We are unable to dwell here on this question. We merely note that studies of the magnetic properties of these substances, and particularly the determination of the magnetic saturation, in conjunction with x-ray structural and neutron diffraction investigations, have yielded a fairly complete picture of the atomic distribution of the spin magnetic moments in these substances. Unlike pure metals and alloys (except for the rare-earth ones), ferrites and other nonmetallic compounds conserve to a considerable degree the magnetic characteristics of the free atoms or ions of the transition elements. Where necessary, we shall use below the data on the average magnetic moments of ferrites and other compounds.

No less interesting are the magnetic properties of paramagnetic alloys, in which atoms of transition elements participate. Unfortunately, in most cases the

investigations of these substances were sporadic and can therefore not be used for an analysis of the properties of their electronic structure.* Only in the very latest time did a more systematic study of the magnetic properties of dilute solutions of transition metals in diamagnetic solvents begin, for example solutions of Mn or Cr in copper, gold, and silver. In these solutions ferromagnetism and antiferromagnetism of apparently a very special type was observed at low temperatures (at very low concentrations of manganese and chromium atoms).^[26] This phenomenon is of great interest in the study of the nature of exchange interaction of electrons in transition metals and alloys† (see Sec. 5 below).

In conclusion it can be stated that the magnetic properties of transition metals, their alloys, and compounds are one of the most important ways of obtaining detailed information on the electronic structure of these substances and primarily on the distribution of the spin density of the electrons in the crystal lattice.

b) Electronic specific heat^[21,27]. Another type of important information on the details of the electronic structure of transition metal crystals is obtained by low-temperature measurements of the specific heats of these substances. As is well known, the specific heat of a normal metal is the sum of the specific heats of the ionic crystal lattice C_{lat} and of the system of collectivized electrons C_{el} . If the metal has in addition also atomic magnetic order or paramagnetism of the lattice, then it becomes necessary to add the magnetic specific heat C_{mag} to the other two terms. One must also bear in mind that at low temperatures certain transition metals are superconductors, and that the atomic nuclei may become oriented (see, for example [28] and Sec. 5); because of this it is necessary to take into account in most cases two additional terms,

*See, for example, the remark made on this subject in Sec. 5 of Ch. V, Part III of [17].

†Very recently most important experimental researches were reported on the magnetic properties of dilute alloys of ferromagnetic elements (iron and cobalt) in paramagnetic transition metals and alloys of the palladium group^[154,158-163]. The results of these researches are of very great interest for the entire problem of transition metals as a whole (see also Sec. 5 below).

Table VIII. Electronic specific heat (at 1°K) for different metals

Metal	γ exp, 10 ⁴ Joule-mole ⁻¹ deg ⁻²	Litera- ture	Metal	γ exp, 10 ⁴ Joule-mole ⁻¹ deg ⁻²	Litera- ture
Li	1.75	1	Ni	7.3	12
Na	1.37	1	Zr	2.89	7
K	1.97	1	Nb	8.7	13
Cu	0.686	2	Mo	2.1	14
Ag	0.66	3	Tc	8.3	15
Au	0.74	4	Ru	3.0	21
Zn	0.654	5	Rh	4.8	21
Cd	0.71	6	Pd	13.0	21
Ti	3.3	7	Hf	2.1	21
V	9.1	8	Ta	5.9	21
Cr	1.5	7	W	1.2	9
Mn	15.8	9	Re	2.3	21
Fe	5.0	10	Os	2.3	21
Co	5.0	11	Ir	2.9	21
			Pt	6.6	21
			La	8.4	2

1. L. M. Roberts, Proc. Phys. Soc. B70, 738 (1957).
2. J. Rayne, Aust. J. Phys. 9, 189 (1956).
3. P. H. Keesom, N. Pearlman, Phys. Rev. 98, 548 (1955).
4. W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite a. A. Wexler, Phys. Rev. 98, 1699 (1955).
5. W. H. Keesom a. J. N. van der Ende, Proc. Acad. Sci. Amst. 35, 143 (1932).
6. E. N. Samoilov, DAN SSSR, 86, 2,816 (1952).
7. Friedberg, Estermann a. J. Goldman, Phys. Rev. 87, 582 (1952).
8. R. D. Worley, M. W. Zemansky a. H. A. Boorse, Phys. Rev. 87, 1142 (1952).
9. N. M. Wolcott, Conf. de Phys. des Basses Temp., Paris (Paris, Inst. Int. du Froid), p. 286.
10. W. H. Keesom, B. Kurrelmeyer, Physica 6, 663 (1939).
11. G. Duyckaerts, Physica 6, 817 (1939).
12. W. H. Keesom a. C. W. Clark, Physica 2, 513 (1935).
13. A. Brown, M. W. Zemansky a. H. A. Boorse, Phys. Rev. 86, 134 (1952).
14. M. Horowitz a. J. G. Daunt, Phys. Rev. 91, 1099 (1953).
15. J. G. Daunt a J. W. Cobble, Phys. Rev. 92, 507 (1953).
21. Parkinson, Repts. Progr. Phys. (London) 21, 226 (1958).

C_{sc} and C_{no} . At first glance the task of separating these components in the experimentally observed overall specific heat of the metal may appear hopeless. However, the highly different character of the temperature dependence of the individual terms comes to the rescue here. In practice, in all metals the system of collectivized electrons is highly degenerate (the degeneracy temperature is $\Theta_{deg} \sim 10^4$ deg K). Consequently at room temperatures ($\sim 3 \times 10^2$ deg K) we have $C_{lat} \gg C_{el}$. However, at temperatures that are noticeably below the Debye temperature of the metal, where $C_{lat} \sim T^3$ and $C_{el} \sim T$, the inverse inequality, $C_{el} \gg C_{lat}$, may hold true if the other two terms C_{sc} and C_{no} are absent. In such a case one measures in practice only the electronic specific heat. From elementary electron theory^[2] we have for the case of strong degeneracy

$$C_{el} = \gamma T, \quad (2.6)$$

$$\gamma = \frac{\pi^2 k^2}{3} N(\xi_0), \quad (2.7)$$

where $N(\xi_0)$ is the number (density) of the electronic states per unit energy interval in one gram atom of the metal at the Fermi surface, and ξ_0 is the limiting Fermi energy at $T = 0^\circ K$.* It follows from (2.7) that

*Landau^[29] and Luttinger^[30] have shown that expression (2.7) for the coefficient γ remains valid also in the more rigorous theory of the Fermi liquid with account of strong interaction between the electrons

C_{el} is determined by the density of the electronic energy levels in the metal.* Table VIII lists experimental values of γ for certain normal metals, and also for the investigated transition metals of the iron, palladium, and platinum group and some of their alloys. It is seen from Table VIII that in transition metals γ is appreciably larger than in normal metals. We can therefore state by virtue of (2.7) that the level density of the electron states in these metals is also higher than in the non-transition metals. This is usually regarded as the most direct and convincing proof that the d electrons participate in the system of collectivized electrons of these metals. Figure 2a shows a curve plotted from the data of Table VIII, while Fig. 2b shows the dependence of the electron density $N(\xi_0)$ [calculated from formula (2.7)] on the total number ν of the d and s electrons per atom of investigated transition metal. From the form of the curves $N(\xi_0) = f(\nu)$ it follows, first, that a definite correlation exists between the densities for the metals of the 3d, 4d,

In the model of electron gas with quadratic dispersion law $\epsilon = \hbar^2 k^2 / 2m$ (ϵ - energy, $\hbar k$ - quasimomentum, $2\pi\hbar = h$ - Planck's constant, m - electron mass), the coefficient is $\gamma_0 = (4/3)(\pi k/h)^2 \times V_a (3N_a/\pi V_a)^{1/3} m$, where N_a is the number of electrons per atom and V_a is the atomic volume. An account of the influence of the crystalline field in the effective-mass approximation (m^) yields $\gamma = m^* \gamma_0 / m$. Attempts were also made to introduce correlation corrections into the value of γ , which reduce this quantity somewhat (see, for example, Table 2 on p. 409 of the review^[32]).

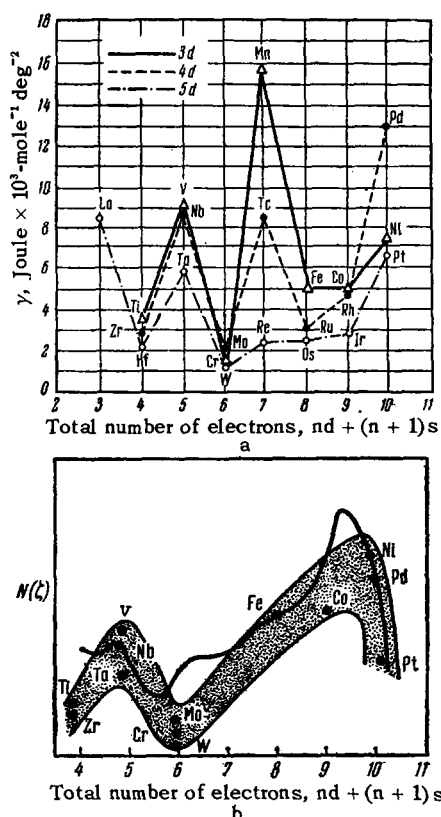


FIG. 2. a) Electronic specific heat (at 1°K) of transition metals.^[21] b) Continuous curve shows the density of the electron states $N(E)$ for the 3d band in copper as a function of the total number $3d + 4s$ of electrons after Krutter^[67] and Slater^[65]. The dots denote the magnitudes of this density, calculated by formula (2.7) using the experimental data for the electronic specific heat (see Fig. a).

and 5d groups, located in like columns of the periodic table, and second that these curves are not monotonic in character, but have maxima and minima. As was already noted above [see item a)] these maxima and minima are connected in regular fashion with the reversal in the signs of the derivatives of the paramagnetic susceptibility with respect to the temperature, $d\chi/dT$, and the value of the susceptibility χ itself. Very great interest attaches to a detailed investigation of several transition metal alloys of the Ti-V, V-Cr, Cr-Fe, Fe-Co, V-Fe, and Cr-Mn systems.^[31] The sharp maxima and minima for certain compositions of these alloys, and also for pure chromium, are striking.

The observed experimental facts obtained in measurements of the electronic specific heat will be discussed below (see Sec. 4 and elsewhere).*

As already noted above (see Sec. 1), the electronic structure of the rare earth element atoms has the following form: a closed xenon shell, an unfilled 4f shell, and finally, the $6s^2$ and $5d^1$ valence electrons (with

*We call attention also to special reviews on electronic specific heat^[21,27] and to^[31b].

stipulation that electron exchange is possible between the 4f and 5d states). The 4f electrons are reliably screened by the xenon outer closed shell $5s^2, 5p^6$ since the 4f shell has a smaller radius (see Table II). All this gives grounds for expecting that the 4f electrons are practically not collectivized in the crystal. Therefore their contribution to the specific heat of the rare-earth metal group is made not to the electronic component C_{el} , but primarily to the magnetic component C_{mag} , since it is precisely the 4f electrons that determine principally the magnetic properties of these metals, the ferromagnetic and antiferromagnetic properties as well as the paramagnetic ones. Naturally, the 5d electrons of the rare-earth metals will increase their electronic specific heat compared with normal metals. This can be seen, for example, in the case of lanthanum, which does not have any 4f electrons, but has 5d electrons in the valence band. The coefficient γ for lanthanum is $8.4 \times 10^{-3} \text{ Joule} \cdot \text{mole}^{-1} \text{ deg}^{-2}$ ^[21], which is comparable with the values of γ for transition metals of the d groups. In the case of the remaining rare-earth metals, the electronic component of specific heat has not yet been separated and the entire attention of the researchers was aimed at a study of the magnetic "anomalies." Figure 3 shows the temperature curves for the specific heats of Gd, Dy, Ho, and Er (for $T > 10^\circ\text{K}$), which are well correlated with the magnetic data for these metals (the Curie and Neel points!). It is obvious that for these metals it is necessary to continue to investigate the temperature dependence of the specific heat at lower temperatures ($T \lesssim 10-1^\circ\text{K}$). It is also important to note that investigations of the specific heat must be carried out with very pure specimens, single crystals as a rule, and must be accompanied by investigations of other properties of metals (primarily magnetic).

c) X-ray emission and absorption spectra.*^[33-35]

A study of the optical and x-ray line spectra of isolated

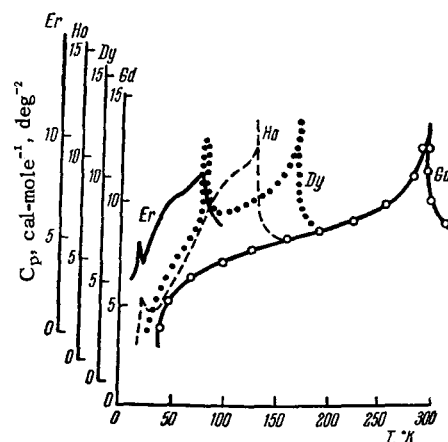


FIG. 3. Specific heats of gadolinium, dysprosium, holmium, and erbium. Different ordinates are used for each metal.

*See also Sec. 9 of Ch. III in^[1], Sec. 104 in^[2], Secs. 3.9, 3.91, and 3.92 in^[3], and pp. 103-111 in^[7].

atoms yields a direct and accurate picture of the structure of their electronic spectra. In the case of solid crystalline bodies, a study of the spectra of the emission or absorption of electromagnetic waves also yields important information on the structure of the electronic spectrum of these substances. Unlike the majority of other physical properties of crystals, which are determined either by the entire spectrum as a whole (binding forces, most magnetic parameters), or else by the character of the distribution of the electronic levels near the Fermi surface (specific heat, kinetic processes, etc.), the spectra of emission or absorption of electromagnetic waves can in principle disclose the entire structure of the energy spectrum of the crystal electrons. As was already noted above, it is precisely a study of the x-ray spectra of solids* that made it possible to state for the first time, from the experimental point of view, that the motion of the internal electrons in crystals has the same characteristics as that of free atoms (localization near the nuclei and line-type energy spectrum), while the external electrons are collectivized and become delocalized over the volume of the crystal, their spectrum having no longer a discrete but a band nature. Among the most convenient methods for the study of the energy spectrum of electrons in crystals are, for example, the spectra of emission of electromagnetic waves, obtained after the internal electrons are knocked out from the crystal (in an x-ray tube) and their places occupied by external collectivized electrons (Fig. 4a) from some energy band. The width (BC) of these bands may reach an order of 10 eV, so that we will have a continuous emission spectrum which (accurate to the natural width of the initial state level, where a vacancy exists on the internal level†) will reflect to some de-

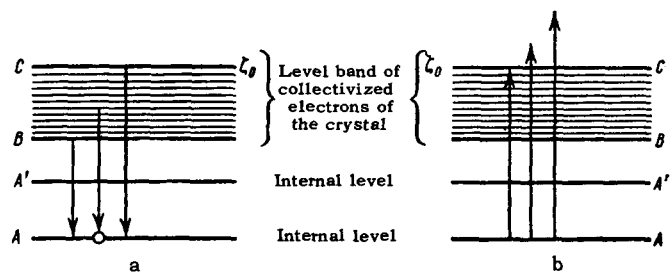


FIG. 4. Level scheme of x-ray spectra in emission (a) and absorption (b). ζ_0 - Fermi level at 0° K.

agree the characteristics of the filled part of the spectrum of the collectivized electrons that participate in the transitions. The wavelengths of these spectra are usually on the order of 100 Å and more, i.e., they lie in the soft x-ray region. The x-ray absorption spectra, which reflect the specific features of the electronic spectra of the crystal, are produced when any of the internal electrons is excited to the free levels of the energy bands of the collectivized states (Fig. 4b). We can thus expect the x-ray emission spectra connected with a given internal discrete (K, L, M, ...) level to have the form of a continuous band, the width of which is directly connected with the width (BC in Fig. 4) of the filled part of the energy band of the electron spectrum. At room temperatures that are low compared with Θ_{eq} , the emission band should have a sharply pronounced edge on the short-wave side, which corresponds to transitions (CA on Fig. 4a) of the electrons from the Fermi level ζ_0 . The absorption spectrum is likewise continuous, but its sharp edge is located on the long wave side (corresponding to the transition AC on Fig. 4b), which coincides with the short-wave edge of the emission band; on the short-wave side, on the other hand, there is no limitation on the absorption spectrum.

Figure 5 shows the results for emission and absorption K spectra of aluminum^[36a], which corroborate fully the picture described above. The ordinates of Fig. 5 represent the intensity $I(E)$ as a function of the energy E in eV in the case of the emission spectrum, and the absorption coefficient $\mu(E)$ for the absorption spectrum.* These "optical" characteristics of the spectra are directly related with the characteristics of the electronic spectra. Indeed, it is known from the quantum theory of radiation^[33-35] that $I(E)$ and $\mu(E)$ are determined by the product of two factors: the electron state density $N(E)$ in the band and the probability $P(E)$ of the corresponding transition from the initial states to the final one:

*The optical spectra of solids (in the visible and near ultraviolet region) also have certain specific features. However, as noted for example by the author of the review^[35] (p. 258), ... "The optical emission and absorption spectra in a solid correspond to transitions between two groups of levels, each of which belongs to a distribution $N(E)$, and the energies of which are not exactly determined. Although selection rules (for the quasi-momentum k) exist in this case, this cannot eliminate the fact that there is no one to one correspondence between the emitted and absorbed wavelengths of the light and a definite pair of levels in the electronic energy spectrum of the lattice. It follows therefore that it is impossible to resolve the level structures in the electronic energy spectrum bands of a solid with the aid of the optical emission and absorption spectra." In addition, the optical spectra of a solid are quite sensitive to the smallest variations in the structure of the surface.

†It is obvious that the reciprocal of the width of the x-ray level $(\Delta E)^{-1}$ can be defined as the theoretical limit of the resolution of the entire method used to determine the level structure in the bands, i.e., in the determination of the function $N(E)$. It must be recalled that the x-ray levels (when a "hole" exists on an internal level of the atom) broaden not only because of interactions within the crystal, but also because of radiation damping and probabilities of non-radiative transitions (Auger effect). This factor limits the region of

x-ray spectrum wavelengths to not higher than several Å, if we want the resolution to be on the order of 1 eV (for more details see Ch. 3 of^[33] or the end of Sec. 1 in the review^[35]).

*In Fig. 5 the energy is reckoned from the Fermi level ζ_0 (the point ζ_0); $I(E)$ and $\mu(E)$ are plotted in arbitrary units.

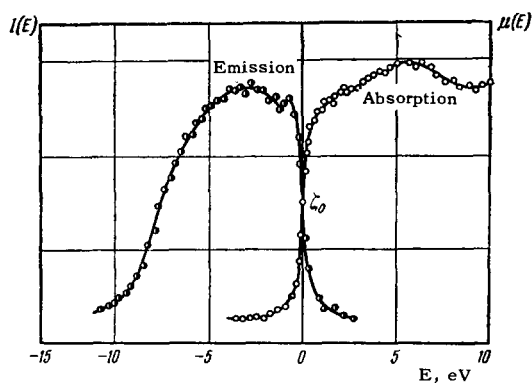


FIG. 5. Emission band and principal absorption edge of x-ray K spectra for aluminum.^[36a] ζ_0 —Fermi level.

$$I(E) \sim \omega^3 P(E) N(E), \quad E \leq \zeta_0, \quad (2.8)$$

$$\mu(E) \sim P(E) N(E), \quad E \geq \zeta_0. \quad (2.9)$$

The probability $P(E)$ is determined in turn by the square of the matrix element corresponding to dipole, quadrupole, etc. radiation, which has the form

$$\int \psi_0^*(\mathbf{r}) \hat{A} \psi(\mathbf{k}; \mathbf{r}) d\mathbf{r}, \quad (2.10)$$

where $\psi_0(\mathbf{r})$ is the electronic wave function of the atomic state (s, p, d, ...), $\psi(\mathbf{k}; \mathbf{r})$ is the wave function of the collectivized state (occupied in the case of emission and free in the case of absorption), and \mathbf{k} is the quasimomentum vector.

It is natural to expect that the peculiar electronic structure of the transition metals will lead also to specific peculiarities in their soft x-ray emission and absorption spectra. However, in view of the fact that the intensity in the emission spectrum or the absorption coefficient are proportional to the product of the probability of transition and the state density [see formulas (2.8) and (2.9)], we cannot say anything definite concerning the latter, until some assumptions or estimates of the transition probabilities are made. It is seen from (2.10) that the transition probability depends appreciably on the wave function of the electron and the lattice, which we do not know exactly, and all the more in the case of the transition metals. It must be noted that formula (2.10) implies also that the ordinary selection rules are approximately valid for the dipole and quadrupole radiation^[9-11], if we recall that the wave function $\psi(\mathbf{k}; \mathbf{r})$ in the lattice is approximated by a linear combination of the atomic functions of the s, p, or d states. In those cases when we deal with near-lying atomic levels and accordingly with "overlapping" energy bands in the crystal, it becomes necessary to take simultaneous account of functions of all the "overlapping" states in the expansion of $\psi(\mathbf{k}; \mathbf{r})$ in the atomic functions. However, not the entire state density $N(E)$ participates in the formation of the spectrum, but only the part of the density corresponding to the selection rules. Therefore, for example in dipole

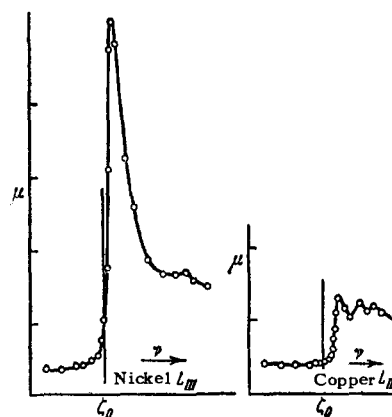


FIG. 6. Absorption x-ray L spectra for nickel and copper. The absorption μ is in arbitrary units, and the energy (frequency) in eV; ζ_0 corresponds to ~ 3 eV for nickel and 6.2 eV for copper.

x-ray K spectra, we cannot hope to single out in the case of the iron-group metals, with sufficient clarity, the participation of the 3d band alone (since the corresponding dipole atomic transition $s \rightleftharpoons d$ is forbidden by the selection rules). A simpler spectral picture can be expected in the case of L spectra (atomic transition of the $p \rightleftharpoons d$ type). Figure 6 shows an example where the absorption L spectra of soft x-rays are compared for the transition metal nickel and copper^[36b], from which it is seen that μ increases sharply in nickel near the absorption edge.

Emission spectra can also yield information on the total width of the energy band participating in the emission. Unfortunately, there is still a great disparity in the results obtained by various researchers.* Extensive and systematic experimental work is still necessary to obtain reliable results for the entire aggregate of transition metals, both of the 3d, 4d, and 5d groups and particularly for the rare-earth groups, which have hardly been investigated to date (see also Sec. 4 below, the remarks following Eq. (4.9)).

d) Determination of electron density in transition metals by methods of structural x-ray and neutron diffraction. The transition-metal properties listed above display the peculiarities of the magnetic characteristics and of the electronic energy spectrum in the crystals of these substances. No less important to the understanding of the nature of transition metals is detailed information on the spatial distribution of the electrons within the crystal. Theoretically it is possible to obtain this distribution from knowledge of the exact wave function of the electron system, since the square of its modulus does give the spatial distribution density of the electrons. From the general theory of electron motion in a self-consistent periodic field of a crystal lattice^[1-4] we know that the wave function should have the form of a plane wave which

*See, for example, the remark on p. 185 in [6].

is modulated in "step" with the lattice [see also (2.10)]:

$$\psi(\mathbf{k}; \mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u(\mathbf{k}; \mathbf{r}), \quad (2.11)$$

where the modulating factor $u(\mathbf{k}; \mathbf{r})$ has the same periodicity as the lattice, and its form is determined by the potential of the latter. From (2.11) we see that the electron density $\rho(\mathbf{r})^*$ in the crystal is determined by the modulating factor $u(\mathbf{k}; \mathbf{r})$:

$$\rho(\mathbf{r}) = |u(\mathbf{k}; \mathbf{r})|^2. \quad (2.12)$$

Unfortunately, we do not know as yet with any degree of accuracy not only the multielectron function of the electron system in the crystal, but also the single-electron function (2.11), so that an exact calculation of the density (2.12) is impossible. Much attention has been paid recently to this question, and several papers have been published in which attempts are made, using the Hartree-Fock method, to calculate as accurately as possible the electron density in transition metal crystals^[37]. † The most reliable information that can be obtained for the time being is from measurements of the atomic form factors in the determination of the scattering cross sections of x rays and neutrons in crystals. The atomic scattering form factor $F(\mathbf{q})$, as is well known^[9,11], is directly related to the density of the electron cloud of the atom $\rho(\mathbf{r})$:‡

$$F(\mathbf{q}) = \int \rho(\mathbf{r}) e^{i\mathbf{q}\mathbf{r}} d\mathbf{r}, \quad (2.13)$$

where \mathbf{q} is the change, resulting from the collision, in the momentum vector of the particle (photon or neutron) scattered by the atom. Inasmuch, as can be seen from (2.13), the form factor and the density are Fourier transforms of each other, we have in the limiting case of homogeneous density (free electrons: $\psi(\mathbf{k}; \mathbf{r}) \approx \exp[i\mathbf{k}\cdot\mathbf{r}]$ and $\rho = \text{const}$) $F(\mathbf{q}) = \delta(\mathbf{q})$, i.e., there is no scattering; in the opposite limiting case of maximally inhomogeneous electron distribution [$\rho(\mathbf{r}) = \delta(\mathbf{r})$], the form factor is independent of the scattering angle, $F(\mathbf{q}) = \text{const}$. It is obvious that in the most interesting intermediate cases $F(\mathbf{q})$ is some function of \mathbf{q} , and once this function is determined by experiment, it is possible to determine also $\rho(\mathbf{r})$ with the aid of (2.13).

It is therefore clear that measurement of the form factors in the scattering of x rays and neutrons in crystals, and particularly in crystals of transition

*Strictly speaking, the electron density in space should be determined by means of the exact multielectron function $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$; in this case the density function (2.12) is determined as the integral of $|\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2$, taken over the coordinates of all the $(N-1)$ electrons:

$$\rho(\mathbf{r}) = \int \dots \int |\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_1 \dots d\mathbf{r}_{N-1}.$$

†A bibliography of all the earlier investigations is listed in^[37].

‡In the case of x rays, $\rho(\mathbf{r})$ should be taken to mean the density of the electronic charge, while for neutrons it is the density of the uncompensated magnetic moments.

metals, their alloys, and compounds, is very important. Weiss and de Marco^[38] made the first attempt at an exact experimental separation of the form factor in crystals of pure metals of the iron group (Ti, V, Cr, Mn, Fe, Co, Ni, and Cu). These authors have set out to subdivide experimentally the electron density in the crystal into three parts: 1) the density of the filled shell such as of the argon atom, containing 18 electrons in all the investigated metals, 2) the density of the electrons whose radial distribution at the lattice sites recalls the atomic 3d electrons, and 3) the collectivized electrons (4s, p) with density close to homogeneous. The experimental technique of the experiment consists of measuring the absolute form factors and subtracting from them the contribution made by the closed shell having the configuration of argon, which is calculated by the usual method of the self-consistent field for the isolated atom. It is furthermore assumed here that the radial distribution of the 4s and 4p electrons in the crystals is such that their form factors are vanishingly small for all Bragg angles in the case of crystals of such high symmetry as the iron-group metals. Thus, after subtracting the contribution of the "closed argon shell" we are left only with the contribution from the localized 3d electrons. Using further the relation (2.13), we can determine the radial density of these electrons. As a result of processing their measurements, Weiss and de Marco obtained the following values for the numbers of the localized 3d electrons per site in the investigated crystals:

$$\text{Cr} - 0.2, \quad \text{Fe} - 2.3, \quad \text{Co} - 8.4, \quad \text{Ni} - 9.7, \quad \text{Cu} - 9.8,$$

the accuracy in each case being on the order of ± 0.3 electron. The results of the Weiss and de Marco experiments for the case of iron (2.3 3d electrons localized at the lattice site) were subjected to serious criticism on the part of many authors, from both the experimental^[39] and the theoretical^[40] points of view.* In particular, Batterman, Chipman, and de Marco made a very thorough measurement of the x-ray form factors for iron, copper, and aluminum, and found that for iron, unlike the results of Weiss and de Marco^[38], the number of localized 3d electrons per lattice site is not 2.3, but is closer to the value for the free atom. In this connection, there are no grounds for regarding the results obtained for all the investigated metals as final. Much tedious work still remains to be done. However, the very organization of such research is undoubtedly of timely interest for the entire problem of transition metals, and the first work done by Weiss and de Marco^[38], in spite of the error it contains in the case of iron, served as the starting point for a whole new trend in experimental and theoretical research on x-ray and neu-

*It must be noted that both the experiments themselves on the determination of the x-ray form factors in crystals and their interpretation involve very great experimental and theoretical difficulties.

tron form factors, and also initiated the search for more accurate theoretical methods of calculating the electron density in crystals (the Hartree-Fock method and others).

No less important information concerning the electron density in a crystal is obtained by studying the atomic form factors, using polarized beams of slow neutrons for diffraction studies of substances with atomic magnetic order. In accordance with general formula (2.13), the neutron scattering form factor, normalized to the number of electrons in a Wigner-Seitz cell^[1-4], is connected with the density of the uncompensated electronic spins by the formula^[41]

$$F_{\text{neut}}(\mathbf{q}) = \int_{\tau} \{A|\psi_{\uparrow}|^2 - B|\psi_{\downarrow}|^2\} e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}, \quad (2.14)$$

where $|\psi_{\uparrow}|^2$ and $|\psi_{\downarrow}|^2$ are the charge densities normalized per unit volume and per electron for the "right" and "left" spin projections, respectively, while A and B are respectively the numbers of the electrons with "right" and "left" spin projections; the integration is carried out over the volume of the Wigner-Seitz cell. The x-ray form factor is obviously

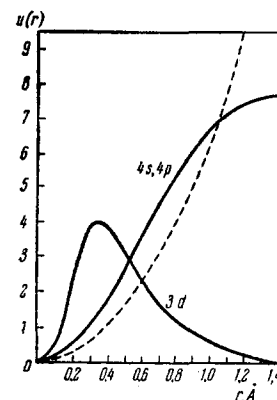
$$F_{\text{x-ray}}(\mathbf{q}) = \int_{\tau} \{A|\psi_{\uparrow}|^2 + B|\psi_{\downarrow}|^2\} e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}. \quad (2.15)$$

When $q = 0$ we have $F_{\text{neut}}(0) = A - B$, i.e., equal to the average atomic magnetic moment in μ_B units, and $F_{\text{x-ray}}(0) = A + B = Z$, i.e., the atomic number of the elements. It is assumed here that the contribution of the 18 electrons of the argon shell is the same as in the free atom. For F_{neut} , the argon shell makes a negligible contribution, since the approximate equality $A|\psi_{\uparrow}|^2 \cong B|\psi_{\downarrow}|^2$ is satisfied for it at all points of the cell.* In the case of the x-ray form factor (2.15), this contribution can be first calculated for the free atom by the self-consistent field method and then subtracted. Thus, formulas (2.14) and (2.15) yield the form factors due to the scattering of neutrons and x-ray photons by the 3d, and 4s or 4p electrons. Weiss and Freeman^[41], using new methods to calculate the form factors^[37], and also x-ray^[38] and neutron^[42] diffraction data, calculated the electron density for iron and nickel crystals.† Figure 7 shows curves for the electron density

*The intra-atomic exchange interaction, in the presence of a group with uncompensated spin (for example 3d or 4f), influences the radial distribution of the other groups even if their spin is compensated. This effect, as shown by calculations of^[41], is most significant for 3s, 3p, and 4s electrons, and increases the coherent magnetic scattering of the neutrons. Although the absolute magnitude of the form factor due to this effect is small, it cannot be neglected and may reach ~ 0.1 in electron units.

†Allowance is made here for the deviation of the electron density distribution from spherical symmetry near the crystal lattice sites, which leads to the appearance of "outgrowths" on the $F(\mathbf{q})$ curve. Later on we take account also of the influence of the crystalline field (of definite symmetry) on the 3d states (the distribution of the 3d levels, partial lifting of the degeneracy).

FIG. 7. Curves showing the radial distribution of the electron density with uncompensated spin in an iron crystal (curve 3d) and also for the electrons with compensated spin (curve 4s, 4p). The dashed curve corresponds to the radial distribution of the density for homogenous distribution of the charge in the crystal.^[41]



in an iron crystal with uncompensated spin (curves 3d), and also for the radial density with compensated spin (4s-4p). The same figure shows (dashed) the curve for uniform density, for which the form factor is equal to zero at all Bragg angles. Thus, according to^[41], the magnetic moment in the iron crystal is produced by a charge with density $2.2|\psi_{\uparrow}(3d)|^2$, localized at the lattice sites, and all the remaining 3d electrons (3.8 per site) form together with the two 4s electrons a nearly homogeneously distributed system of collectivized electrons with density $2.9[|\psi_{\uparrow}(4s, 4p)|^2 + |\psi_{\downarrow}(4s, 4p)|^2]$.

In the case of the nickel crystal, the situation is different. The spin density is the result here of 5.0 3d electrons with one spin projection (right hand) and 4.4 3d electrons with the other (left hand) projection. Figure 8 shows the distribution of the localized charge near the nickel crystal site. Furthermore, it was possible to establish by experiment that the 5.0 3d electrons in nickel have a radial density which is somewhat more compressed towards the center of the site than the 4.4 3d electrons with opposite spin projection. Figure 9 shows a plot of the difference of these densities.

It must be noted, however, that the theoretical interpretation given above for the experiments on neutron diffraction is limited by the fact that the self-consistent field method employed is approximate. Watson and Freeman^[43] pointed out that owing to effects of spin polarization, a measurable difference arises in the neutron and x-ray form factors, making

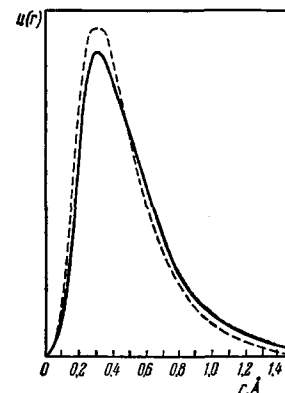


FIG. 8. Radial distribution of total charge at the site of the nickel lattice (continuous curve) and radial distribution of the spin density, normalized to the total density (dashed curve).^[41]

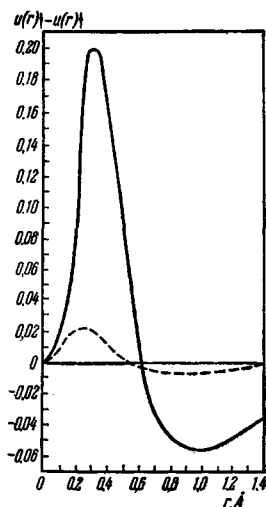


FIG. 9. Difference in charge density (per electron) for two spin projections for the free iron atom (continuous curve) and for the nickel crystal (dashed curve).

it difficult to obtain direct and detailed information on the distribution of the 3d electrons with the aid of the measured neutron (magnetic) form factors. In addition, these authors have called attention to still another difficulty that arises in the interpretation of the measurements of the form factors in experiments such as made by Weiss and de Marco^[38], a difficulty they discovered in an attempt to make the calculations more precise by the Hartree-Fock method and which consists in the fact that the theoretical interpretation of the form factor depends essentially on the degree of "ionization" of the atom in the crystal, which cannot be determined directly from these experiments. In connection with these investigations, interest attaches to the calculations made by Wood^[44], who showed that one-electron functions of the d band in the body centered cubic lattice of iron reduce the degree of delocalization on going from the "bottom" of the band to its "top." The author believes here that his calculations contradict the data of Weiss and de Marco^[38].

In conclusion we can emphasize once more that the question of the spatial distribution of 3d electrons in crystals of the iron group metals has not yet been solved with any degree of completeness.

e) Binding forces in transition metals. It is known from quantum theory of metals^[1-4] that the metallic bond is determined by the sum of the kinetic and potential energies of the electrons and ions of the crystal. Besides, the entire distinguishing feature of the metallic bond itself lies in the presence of conduction electrons with large Fermi energy and with wave functions that are nearly plane. The calculation is usually carried out, say for the alkali metals, under the assumption that there exist sufficiently "stiff" positively charged ions, which are immersed in an electron fluid. The interaction between the electron fluid and the ion determines the equilibrium distances between the ions (the constants of the crystal lattices), and the binding energy as a function of these distances, as well as the entire aggregate of elastic constants. Ex-

periment shows that the binding forces of the transition metals also single them out as a special group^[8]. If we choose as a measure of the binding forces the heat of sublimation, i.e., the energy necessary for complete dissociation of one gram molecule of solid metal into isolated atoms, the values obtained for the transition metals are four or five times higher than for the monovalent alkali metals. In addition, a comparison of the metals occupying the extreme right places in the transition periods (nickel, palladium, and platinum) with the neighboring precious metals (copper, silver, and gold) shows that the transition metals have high sublimation energies. These features of transition metals are again connected somehow with the active participation in the metallic bond of not only the conduction electrons, but also of the electrons of the unfilled d and f groups. However, this question will not be considered in greater detail here, since it is beyond the scope of the present review.*

f) Kinetic properties—electric conductivity. So far we have considered the statistically equilibrium properties of the transition metals. In the analysis of the kinetic effects connected with the transport of electrons in the crystal, the transition metals also have several specific properties. By way of an example let us consider the most typical kinetic phenomenon—electric conductivity. Table IX lists the values of the approximate specific electric resistivity of metals ρ (in units of 10^{-6} ohm-cm) at room temperature. Even from this essentially random comparison (inasmuch as the "room" temperature is not "identical" for the different metals) we can draw certain conclusions concerning the specific properties of transition metals. What is particularly striking are the very high values of ρ in the case of metals from the rare-earth group, which exceed by one or two orders of magnitude the values of ρ for monovalent noble metals copper, silver, and gold. An appreciable reduction in ρ is also observed as the d shell becomes filled, for example on going over from nickel to copper ($12.0 \times 10^{-6} \rightarrow 1.56 \times 10^{-6}$), from palladium to silver ($10.2 \times 10^{-6} \rightarrow 1.49 \times 10^{-6}$), and from platinum to gold ($9.81 \times 10^{-6} \rightarrow 2.04 \times 10^{-6}$). However, a much more distinguishing feature of transition metals are the anomalies in the temperature dependence of the specific resistivity, particularly in the case of ferromagnetic and antiferromagnetic transition metals. In Fig. 10a—d are shown, by way of an example, curves of the temperature dependence of specific resistivity for several metals of the rare-earth group and the iron group^[20,46-50]; for comparison we show in Fig.

*The reader can find details on this question in the books^[1-4] and in the review of Hume-Rothery and Coles^[5]. Notice should also be made of the work by Stern^[45], in which a theoretical calculation is made of the binding energy of metallic iron with body centered cubic lattice, to be sure under the assumption that the unfilled 3d group is in the singlet state.

Table IX. Specific electric resistivity ρ of transition metals at room temperature (300°K) in units of 10^{-6} ohm-cm in comparison with the electric resistivity of monovalent metals (normal) such as gold, silver, and copper

Element	ρ	Literature	Element	ρ	Literature
Sc	—		W	4.9	2
Ti	47.5	2	Re	18.9	2
V	58.8	2	Os	8.9	2
Cr	2.6	2	Ir	5.0	2
Mn	150.0	49	Pt	9.81	2
Fe	8.7	2	Au	2.04	2
Co	6.2	2	La	82	47 b
Ni	12.0	2	Ce	93	49, 20 a
Cu	1.56	2	Pr	70	47 b
Y	—		Nd	70	47 b
Zr	41.0	2	Pm	100	47 b
Nb	21.0	2	Sm	—	
Mo	5.03	2	Eu	90	47 d
Te	7.64	2	Gd	130	47 a
Ru	—		Tb	115	47 a
Rh	4.58	2	Dy	95	47 a
Pd	10.2	2	Ho	80	47 a
Ag	1.49	2	Er	90	47 a
Lu	55.0	20	Tu	70	47 a
Hf	32.1	2	Yb	30	47 d
Ta	14.0	2	Lu	55	20

10c a curve for the non-ferromagnetic palladium; this curve was artificially made to coincide with the curve for nickel in the region $T > \Theta_f$. It is seen from this comparison that at temperatures below the Curie point the electric resistivity of ferromagnets decreases much more rapidly upon cooling than in the case of non-ferromagnetic metals. At the Curie point there is a more or less clearly pronounced kink in the curve (maximum of the derivative $d\rho/dT$). Anomalies are also observed in the temperature variation of the specific electric resistivity at low temperatures, too.^[51,52] Unlike the alkali and noble metals, the temperature variation of $\rho(T)$ for transition metals obeys not the “ T^5 ,” but a different law: $aT + bT^2$. Anomalies in the temperature variation of the electric resistivity were observed in antiferromagnetic metals^[53], and also in antiferromagnetic and ferromagnetic semiconductors^[54] (in ferrites).

It is thus the task of the theory to explain the following two effects: 1) why is ρ generally larger for transition metals than for normal metals, and 2) what causes the temperature anomalies. The first question can be answered in a most general fashion using the elementary Drude-Zener formula for the electric conductivity σ ,^[1-4] by assuming that there are two types of carrier in the transition metal (for example from the group Fe, Pd, or Pt), namely the s and d electrons; then $\sigma = n_d e^2 \tau_d / m_d^* + n_s e^2 \tau_s / m_s^*$, where n_d and n_s —densities τ_d and τ_s —relaxation times, and m_d^* and m_s^* —effective masses for the d and s electrons, respectively. At first glance it may appear that σ should be larger in a transition metal (many carriers with $n_d > n_s$). This is not so, however, since we have for the d electrons a very large effective mass

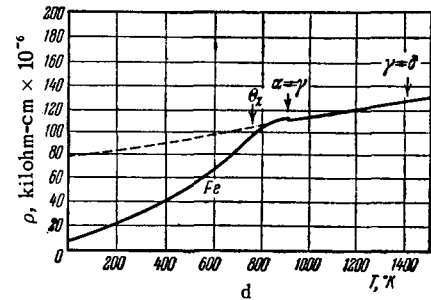
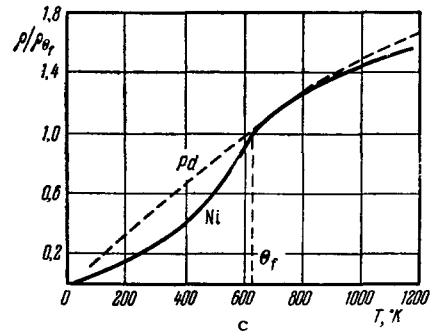
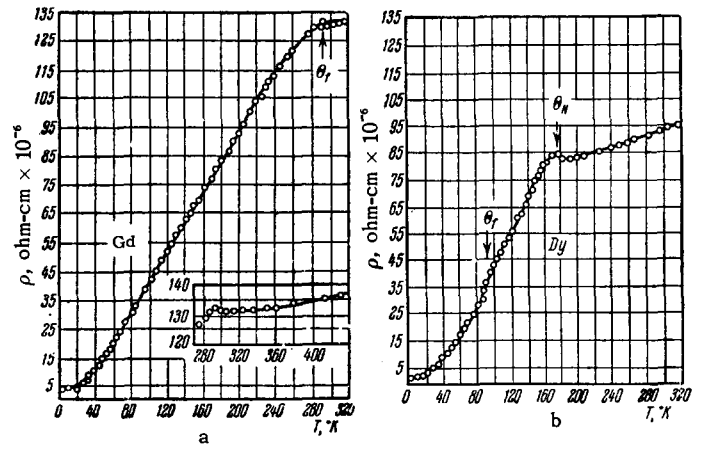


FIG. 10. a—Temperature dependence of the electric resistivity of gadolinium^[47a]; b—temperature dependence of the electric resistivity of dysprosium^[47b]; c—temperature dependence of the electric resistivity of nickel; the ordinates represent the relative resistivity; in addition to nickel, data are given for non-ferromagnetic palladium as a comparison^[48]; d—temperature dependence of the electric resistivity of iron; the $\alpha \rightleftharpoons \gamma$ and $\gamma \rightleftharpoons \delta$ phase transition points and the Curie point Θ_f are marked on the curve.^[49]

($m_d^* \gg m_s^*$, for example, in iron $m_d^* \sim 30 m_s^*$), owing to the narrowness of the d band, and also because the free path times τ_d and τ_s decrease very rapidly, so that there are many more possibilities in a transition metal for the scattering of the electrons participating in the current.

A more detailed discussion of the observed anomalies in the electric conductivity of transition metals will be given later (Secs. 5 and 16).

3. General Qualitative Ideas on the Electronic Structure of Crystals Containing Transition-element Atoms

In Sec. 2 we have explained some distinguishing features of the experimentally observed physical properties of transition metals. Let us summarize our findings briefly.

The most distinct features of the transition metals are the peculiarities in the magnetic properties, primarily in the realization of the ferromagnetic or antiferromagnetic magnetically-ordered states. From an analysis of some characteristic properties of these states we can establish an essential difference between transition metals with unfilled d or f shells. We shall henceforth, for the sake of brevity, call these d or f metals. Thus paramagnetism, which is the inherent characteristic of free atoms of say the rare-earth elements, is practically always realized in f metals. At high temperatures we deal with ordinary paramagnetism of the Curie-Weiss type. On the other hand, at low temperatures we practically always observe in these metals ferromagnetism or antiferromagnetism, and sometimes both [in different but adjacent temperature intervals, see item a) of Sec. 2]. The average atomic magnetic moment in these metals is practically the same as the moment of the free atom of the corresponding element. This indicates that, at least in the sense of magnetic characteristics, the unfilled 4f shell retains its atomic individuality also in a rare-earth metal crystal. The good screening of the 4f shells excludes their direct interaction in the crystal. Only indirect coupling is therefore possible, via the conduction electrons (5d and 6s), the wave functions of which are more or less uniformly "smeared out" over the crystal or else via the closed electron shell 5s², 5p⁶.

The situation is more complicated in d metals. From the very fact that the atomic magnetic moments have fractional values and the essential difference between these moments and the moments of the isolated atoms of the corresponding elements, in the case of ferromagnetic and antiferromagnetic d metals (Fe, Co, Ni, Cr, Mn), and also the total loss of magnetic activity, characteristic of free ions, it follows that in most crystals of these metals (Sc, Ti, V, all metals of the palladium and platinum groups) the quantum states of the former d shells of the atoms of these elements experience quite appreciable changes in the crystal. Another indication of this circumstance are the anomalously large values of the electronic specific heat of d metals, from which it follows that in these metals the electron densities near the Fermi surface are incomparably larger than in normal metals [see item b) of Sec. 2]. This is also indicated by the x-ray emission and absorption spectra [see item c) of Sec. 2]. It is therefore natural to assume that in a crystal the d electrons, whose wave functions overlap appreciably are not sufficiently screened and behave like d elec-

trons of isolated atoms, forming a unified collective group of crystal electrons, filling the states in the continuous energy band like the valence electrons of ordinary metals, except that this "d band" is appreciably narrower than the band of the valence s electrons, and the level density in this band is considerably larger, since the number of d states is five times larger than that of s states. At the same time, as we have seen above [item d) of Sec. 2], the d electrons are apparently unevenly distributed over the volume of the crystal, and their distribution is more likely to be the same as for isolated atoms. The situation observed here can therefore be arbitrarily described as a special kind of "superposition" of a crystalline energy collectivization, and the known conservation of the spatial localization at the individual lattice sites, characteristic of isolated atoms. This "superposition" can be clearly seen in the general form of the electron wave function in the periodic lattice field (2.11), which has the form of a plane wave modulated in step with the lattice. The plane-wave factor $\exp[i(\mathbf{k} \cdot \mathbf{r})]$ characterizes the collectiveness of the system, while the modulating factor $u(\mathbf{k}; \mathbf{r})$ characterizes the degree of localization at the individual lattice sites. In the case of d metals, the factor $u_d(\mathbf{k}; \mathbf{r})$ for the d electrons is apparently quite different from the atomic d functions, while in f metals, to the contrary, the function $u_f(\mathbf{k}; \mathbf{r})$ does not differ in practice from the f function of the isolated atoms (in the sense of the degree of spatial localization).

We thus arrive at the conclusion that there exist two types of transition metals, d and f, with which one must deal when an attempt is made to construct a quantitative atomic theory of transition metals. In addition, we are faced in the case of d metals with the question why some have magnetic order and others do not, i.e., it is necessary to ascertain the genesis of the exchange interaction which causes the existence of magnetic ordering in the crystals. Apparently, this genesis is somewhat different in the case of d and f metals.

In fact, as we have just noticed, in the case of f metals the 4f shells of the neighboring lattice sites do not overlap at all in practice, so that we can hardly assume a direct f-f exchange interaction to exist between them. On the other hand, the very existence of ferromagnetism and antiferromagnetism in practically all 4f metals indicates without any doubt that some exchange mechanism is realized in these metals.* As was already noted, one can suggest here two indirect mechanisms of such an exchange coupling—either through the conduction electrons (Zener^[55]), or through the electrons of the magnetically neutral 5s²5p⁶ shell^[56]. Consequently, in the case of f metals the electron system (on top of the internal filled shells which are "ascribed" to the ionic lattice) can be subdivided into

*Inasmuch as, say in gadolinium, the Curie point is $\Theta_f \sim 300^\circ \text{K}$, the energy of this interaction per atom is equal to $k\Theta_f \sim 10^{-14}$ erg, i.e., it is undoubtedly electrostatic rather than magnetic.

three subsystems: 1) the 4d and 6s conduction electrons, 2) the closed magnetically-neutral shell of $5s^25p^6$ electrons, and 3) the magnetically-active system of quasi-isolated 4f electrons. Such a subdivision must naturally be taken to have a rather arbitrary meaning, since a very noticeable interaction exists between these systems. First, the already mentioned indirect interaction, in which all three subsystems can actively participate. Second, the 4f electrons, which become spontaneously magnetized by interaction with the conduction electrons and with the $5s^25p^6$ closed shell can exert a reverse "magnetizing" influence primarily on the conduction electrons. In addition, each of the 4f shells, like the d shells, is under the influence of its surrounding "crystalline electric field," which has the symmetry properties of the given crystal (cubic, hexagonal, etc.). It is natural to assume the anisotropy of the electrostatic field in the crystal around each ion to lift the energy degeneracy for the f and d levels of the isolated atom, i.e., we deal with a Stark splitting of the f and d levels.* In rare-earth ions there is very strong spin-orbit interaction, which splits terms with different quantum numbers J by amounts on the order of $1,000\text{ cm}^{-1}$, so that J remains a "good" quantum number even in the crystal. Consequently, to clarify the magnetic and other properties of f metals, their alloys, and their compounds it is very important to know the "energy" spectrum of the ions and those internal crystalline fields which form this spectrum. One of the methods of investigating this spectrum are paramagnetic resonance studies, gyro-magnetic experiments, and also the determination of the atomic magnetic moments at 0°K .^[58]

From everything stated above with regard to the f metals, we can assume that in first approximation a quantitative quantum analysis of their electronic properties is best made by using the following "model." The crystal of the rare-earth metal is subdivided into an ionic lattice, in the sites of which are located ions with "free" 4f shell, subject to the action of the crystalline field of the given symmetry, and also spin-orbit and exchange interactions (of the Hund type, and also indirectly via the 5d6s and $5s^25p^6$ electrons). The electrons of the 4f shells can be regarded with sufficient justification as strictly localized at the lattice sites (we can neglect the crystalline level splitting characteristic of valence d electrons, since there is practically no "overlap" of the 4f functions and because of their "good" screening), as is the case with 5s and 5p electrons. The 5d and 6s electrons are fully collectivized and form a Fermi gas or liquid in

which the screened lattice of the trivalent 4f ions is immersed. The interaction between the localized 4f shells and the collectivized conduction electrons determines the entire aggregate of electronic properties of the f metals. Below, in Ch. II (Secs. 4 and 5), and also in the second part of the review (Ch. III and IV) we shall describe different "variants" in the development of these model representations concerning the electronic structure of the metals.

A more complicated problem is that of the electronic properties of d metals. This is connected primarily with the fact that in a crystal the less "deep" (in the spatial sense) d shells of the neighboring lattice sites experience already a noticeable overlap of their wave functions, and this in turn leads to a much sharper manifestation of the collective effects in the behavior of the d electrons in the crystal lattice of the d metals. Two obvious experimental facts—the sharp increase in the value of the electronic specific heat [see item b) of Sec. 2] and the appreciable difference in the magnetic characteristics of the isolated d atoms from those of d metals [see item a) of Sec. 2]—indicate without any doubt that such an assumption is indeed real. In other words, the d electrons in the metal experience to an appreciable degree the effect of crystalline collectivization. One can therefore no longer speak here of quasi-free d shells, but we must speak of a d band which furthermore cannot be regarded in a rigorous analysis as being completely an independent formation with respect to the energy band of the conduction electrons, as is usually done in the band theory of transition metals (see Sec. 4 below), assuming that the d and s bands simply overlap but retain in all other respects their individuality.

Recently Herring^[40] emphasized that the ordinary band theory of d-transition metals has two appreciable shortcomings: 1) it does not take into account the degeneracy of the d states, which leads to a "degenerate" d energy band in the crystal, and 2) it ignores the possibility of exact separation of the d and s bands in the crystal, connected with the fact that the former nd and $(n+1)s$ electrons of the isolated atoms in crystals of d metals form a unified collective, with a complex spatial distribution of the electron density, in which, to be sure, "echoes" of the atomic localization of the d electrons are conserved to a considerable degree [see item d) in Sec. 2]. On the whole, we deal with a Fermi liquid having a complicated dispersion law and a higher density of states near the Fermi surface. The account of the exchange and spatial correlations in such a system is essential in order to formulate a criterion for ferromagnetic or antiferromagnetic states in d metals.

In transition metals we are interested primarily in the active manifestation of paramagnetism of unfilled internal groups of the electron shell, characteristic of isolated atoms of the transition metals. Therefore in ascertaining the distinguishing features of the behavior

*Owing to the good screening of the 4f shell in the crystal, this splitting is one order of magnitude smaller in f metals than in d metals, and amounts to ^[57] several hundred cm^{-1} ; furthermore, this splitting decreases with increasing number x of electrons in the 4f shell (from 600 cm^{-1} for Ce^{+++} with $x = 1$ to 100 cm^{-1} in Yb^{+++} with $x = 13$).

of the electron system in such metals it is necessary to take into account the interaction between the electrons and the magnetic moments, which can form magnetically ordered states, either ferromagnetic or antiferromagnetic (for the latter one must make a distinction between the case of compensated antiferromagnetism or antiferromagnetism proper, and also uncompensated antiferromagnetism or ferrimagnetism) i.e., it is necessary to take into account the influence of this magnetic order on the entire set of electronic properties of the given substances.

In the case of ferromagnetism, the presence of spontaneous magnetization lifts the degeneracy in the conduction electron system with respect to the spin direction. This leads to a "displacement" of the energy bands of these electrons with different spin orientations, and also to a splitting of the internal levels of the ionic cores. Quantitatively this effect can be described in general form by including in the Hamiltonian of the electron system of the metal terms of the form $A_{sd}(\mathbf{r})\mathbf{m} \cdot \mathbf{s}$, where \mathbf{m} is the relative magnetization of the electron system, \mathbf{s} is the spin vector operator of the individual electron, and $A_{sd}(\mathbf{r})$ is a certain energy parameter, describing the exchange interaction between the electron and the magnetization, which in the general case is a function of the coordinates. In the particular case when the conduction electron system is treated as a gas of Fermi particles^[93] with complicated dispersion, the general form of the latter in the approximation which is "isotropic" in the spin terms is given by the formula

$$\varepsilon(\mathbf{k}, \sigma) = \varepsilon(\mathbf{k}) + A_{sd}(\mathbf{k})m_z\sigma, \quad (3.1)$$

where \mathbf{k} is the quasi-momentum vector and σ is the z-axis projection of the Fermi particle spin, while $\varepsilon(\mathbf{k})$ is the spin-independent part of the energy and $A_{sd}(\mathbf{k})$ is the exchange coupling parameter. The appearance of the second term in the right half of (3.1) does indeed describe the specific properties of the Fermi system in a metal with ferromagnetic order (see Sec. 5 below).

In the case of antiferromagnetism* the presence of the magnetic sublattice also influences the motion of the conduction electrons. Indeed, any collectivized electron going from the site of one sublattice to the site of another sublattice will move from a site with a spin of a certain value or a certain direction to a site having a different value or different direction of spin, but in transitions between sites of the same sublattice there will be no such changes in the spin at the sites. It is therefore clear that the state of the conduc-

tion electrons in a crystal with several magnetic sublattices should differ appreciably from the states in a crystal with a single sublattice or in a paramagnetic crystal. This difference reduces to the fact that in an antiferromagnetic crystal there is a partial lifting of the spatial degeneracy of the conduction electrons, inasmuch as the antiferromagnetic order leads to a change in the periodicity of the potential field (a lowering of its symmetry), in which these Fermi particles move. In this case there is no "shift" of the energy bands for electrons of different spin projections, but nonetheless an appreciable change can take place in the energy spectrum of the electrons (for example, splitting of the energy bands, similar to that arising in effects of atomic ordering in metallic alloys^[115]).

Summarizing, we can state that the presence of magnetic order in transition-metal crystals leads primarily to appreciable changes in the energy spectrum of the conduction electrons. Two principal effects are observed in this case: a) lifting of the degeneracy in the spin direction (ferromagnetic case) and 2) lifting of the spatial degeneracy (antiferromagnetic case).

A second important effect of the magnetic order on the conduction electron system is their scattering by the inhomogeneities of this order. Conduction electrons, participating in the electric or thermal current in a transition metal, are scattered not only by the thermal lattice vibrations (phonons) or by its static distortions, but also by collision with different dynamic and static magnetic inhomogeneities. Therefore the interaction mechanism which brings about these collisions differs from the phonon mechanism and from scattering on lattice defects, and the corresponding contributions to the kinetic coefficients (electric conductivity, thermal conductivity, etc.) in terms of the scattering probabilities will therefore have a specific temperature dependence (ferromagnetic anomalies) which is particularly pronounced near the Curie or Neel points, where one can expect a maximum effect of magnetic inhomogeneities.

One must also mention that in ferromagnetic and antiferromagnetic metals one observes galvanomagnetic phenomena of a specific character, for owing to the magnetic order in these metals an appreciable role is assumed by the spin-orbit magnetic interaction between the magnetization of the crystal and the current carriers in the crystal. The latter are under the influence of very strong local magnetic fields (up to 10^5 Oe and higher). All this leads to the appearance of spontaneous galvanomagnetic phenomena—the Hall effect, magnetoresistance, etc.

In connection with these strong local magnetic fields, mention should be made of the recently observed analogous fields (up to 10^6 Oe) acting on atomic nuclei in transition metals with magnetic order [see item f) of Sec. 5]. This raises the important problem of explaining in detail the genesis of these strong internal magnetic fields.

*If we exclude the fact that for uncompensated antiferromagnetism there exists the above-considered influence of the resultant magnetization of the crystal, which leads to a "shift" of the energy bands for electrons with positive and negative spins, but include on the other hand ferromagnetism of the ordered-alloy type, i.e., with sites that have magnetic moments that are different in value but are parallel.

We can also mention that magnetic order exerts an influence on the possibility of realization of a superconducting state in the electron system of the transition metal (see Sec. 14), on the possible occurrence of magnetic polarization of atomic nuclei (see Sec. 5), on the electron and nuclear magnetic resonances, etc.

So far we dealt with the influence of the magnetic order on the electron system of the transition metal crystal, i.e., we were interested so to speak in passive properties of this system. It was assumed here that the magnetic order already existed in the crystal, being brought about by some special forces of exchange nature. However, no interactions other than between electrons can occur in a crystal. Therefore the exchange which leads to a magnetic order of one type or another is an interaction between the very same electrons. Thus, the electron system is not only a passive partner with respect to the magnetic order, but must itself take active and direct participation in its establishment in the crystal. This, of course, manifests itself in different fashion in the case of d and f metals. In d metals the magnetic order is the result of the active influence of the exchange interaction in the system of collectivized electrons, in its struggle against the Fermi kinetic energy and the correlation energy, which counteract the establishment of such an order. In f metals, the exchange interaction occurs with active participation of the conduction electrons by an indirect exchange-coupling mechanism.

Finally, there is still another class of transition metals, namely paramagnetic metals, which have no magnetic order at any temperature, and also metals which have such an order but at temperatures above their Curie or Neel points. Various mechanisms of "absence" of atomic magnetic order are possible here: this may be the result of the Fermi energy counteracting the magnetization, or else the effect of thermal motion which breaks up the magnetic order. Naturally, in a rigorous formulation of the problem it is necessary to start from the exact Hamiltonian of the system of all the electrons, in which all possible interactions are taken into account. However, the great mathematical difficulties encountered in the theoretical treatment of such complicated systems as transition metals, make it necessary to follow the path of developing some approximate models. In spite of the apparent variety in such models, they can be reduced essentially to two main types: 1) the band model and 2) the model of interacting internal and external electrons.

In Ch. II we shall consider in greater detail two quantitative treatments of the transition d and f metals: one based on the elementary notions of the band model (Sec. 4) and the other on the basis of the so-called (s-d)-exchange model, also in an elementary form (Sec. 5). In the second part (Ch. III and IV) we shall develop more rigorous variants of the (s-d)-exchange model, and in the concluding Ch. V we shall

return once more to a general estimate of the status of the theory of transition metals.

To conclude this section, let us dwell briefly on investigations in which model attempts are being made to solve the problem of the electronic structure of 3d metals, their compounds, and alloys in which they are contained^[59,60,77,102,103,153,154]. Thus, for example, Wollan^[59] considers the question of the magnetic (exchange) coupling in crystals of compounds and pure 3d metals. This coupling is analyzed with the aid of the notion of "orbits," which arise as a result of the splitting of the 3d levels in the crystalline field. Goodenough^[60] introduces the hypothesis that there exists a certain critical distance ($R_C \sim 2.9 \pm 0.1 \text{ \AA}$); at distances $R < R_C$, the former 3d electrons of the atoms, whose orbits are oriented along the bonds, are converted into collectivized crystal electrons, and at distances $R > R_C$ they remain localized. Inasmuch as the wave function of the 3d electrons is anisotropic, we can expect a simultaneous realization of the localized and collectivized 3d electrons. The localized electrons obey the Hund rule^[10] and therefore play an active role in the magnetic properties of the crystal. Goodenough postulates further the existence of an internal exchange bond, and of antiferromagnetic ordering as a function of the degree of filling of the 3d shell etc. Assumptions of the same order are made also by Mott and Stevens^[102], Lomer and Marshall^[103], and Van Vleck^[77]. These papers do not therefore give a rigorous justification of the assumed hypothesis and are purely illustrative in character, aimed at indicating the "zoological" order in the physical properties of the transition metals, their alloys, and their compounds; this, nevertheless, is a necessary and quite useful (particularly from the practical point of view) stage in the development of the theory of transition metals and their compounds. Particularly instructive in precisely the latter meaning is the work of Goodenough et al^[153], in which a detailed analysis of the intracrystalline "fields" and their influence on the electron density of magnetoactive ions makes it possible to obtain several important indications of purely practical nature for a planned "construction" of new magnetic compounds with specified physical properties.

II. ELEMENTARY ELECTRON THEORY OF TRANSITION METALS

As we noted above, from the translational symmetry properties of the crystal it follows that the state of the electron in the self-consistent periodic field is described by wave function (2.11), which has the form of a modulated plane wave, in which, as it were, is contained a superposition of the tendencies of collectivization ($\exp[i\mathbf{k} \cdot \mathbf{r}]$) and localization [$u(\mathbf{k} \cdot \mathbf{r})$] of the electron in the crystal. Neither effect can be exactly evaluated at present, owing to the mathematical difficulties. It becomes necessary therefore to de-

scribe them artificially as effects that are in a certain sense distinct. It is in such an approximate approach that the foregoing model quantitative treatments were originated, namely the band model and the model of interacting external and internal electrons (s-d exchange model). In both models it is assumed from the very outset that it is possible to separate in a transition metal, albeit arbitrarily, two autonomous groups of electrons, one originating from the valence electrons of the initial atoms of the crystal and arbitrarily called the s-electron system (or the conduction electron system), and the other comes from the former electrons of the unfilled d or f shells of the initial atoms and is arbitrarily called the system of d (or f) electrons.* The s and d electrons are assigned different functions (2.11):

$$\psi_s(\mathbf{k}_s, \mathbf{r}) = e^{i\mathbf{k}_s \mathbf{r}} u_s(\mathbf{k}_s, \mathbf{r}), \quad (2.11a)$$

$$\psi_d(\mathbf{k}_d, \mathbf{r}) = e^{i\mathbf{k}_d \mathbf{r}} u_d(\mathbf{k}_d, \mathbf{r}). \quad (2.11b)$$

The function for the s electron, is chosen to be the same in both models. On the other hand, in choosing the function for the d electrons, these two models differ in that the function $\psi_d(\mathbf{k}_d, \mathbf{r})$ is approximated in them in different manners.

In the band model, principal attention is paid in (2.11) to the plane-wave factor ("free" completely delocalized electrons with $u(\mathbf{k}, \mathbf{r}) = \text{const}$). Only for the s and d electrons quantitatively different dispersion laws of type (3.1) are chosen:

$$\epsilon^s(\mathbf{k}_s, \sigma_s) = \epsilon^s(\mathbf{k}_s) + A_s(\mathbf{k}_s) m_z \sigma_s,$$

$$\epsilon^d(\mathbf{k}_d, \sigma_d) = \epsilon^d(\mathbf{k}_d) + A_d(\mathbf{k}_d) m_z \sigma_d.$$

It is assumed here that the functions ϵ^s , ϵ^d , A_s , and A_d are such that energetically the band for the s electrons is noticeably wider than the d band. These bands overlap and have a common Fermi surface. When the exchange interaction is sufficiently large the bands for the electrons with plus and minus spins can shift, and this leads to ferromagnetism.

In the s-d exchange model principal attention is paid in (2.11) for the d electrons to the modulating factor, which is approximated by a localized atomic function $\varphi_n(\mathbf{r})$ at the crystal lattice sites \mathbf{R}_n

$$u_d(\mathbf{k}_d, \mathbf{r}) \approx \varphi_n(\mathbf{r}) \delta(\mathbf{r} - \mathbf{R}_n) \delta(\mathbf{k}_d).$$

We therefore obtain for the wave function $\psi_d(\mathbf{k}_d, \mathbf{r})$ of the d electron $\varphi_d(\mathbf{k}_d, \mathbf{r}) \cong \varphi_n(\mathbf{r})$. For the wave function of the s electron, the same approximation is retained as in the band model [$u_s(\mathbf{k}_s, \mathbf{r}) \cong \text{const}$]. The dispersion law used for the s electrons has therefore in the zeroth approximation the usual band-theory form $\epsilon^s(\mathbf{k}_s)$, and the d-electron energy is identified with the

discrete atomic d levels, $\epsilon^d(\mathbf{k}_d) \cong E_d^0$. The d-band width connected with the transport of the charge in the crystal is thus equal to zero. In the higher first and second approximations account is taken of the electrostatic exchange interaction, both between the d electrons themselves and between the s and d electrons (s-d exchange coupling), which can ensure an atomic magnetic order in such a system.

In Sec. 4 below we describe briefly the band model of transition metals, while in Sec. 5 we discuss the s-d exchange model.

4. Band Model of Transition d-Metal Crystals

As noted above in the treatment of the electronic properties of d metals, it is necessary to allow for the appreciable influence of the crystalline state on the character of motion of the d electrons, which are subject to a noticeable collectivization effect. Consequently attempts to construct a band model for d metals began already long ago. Historically the first paper on the "collective model" as applied to ferromagnetism of metals is that of J. I. Frenkel^[61] (1928), who showed that ferromagnetism is possible in a gas of collectivized electrons if the absolute magnitude of the exchange energy of the magnetized electron gas is in a definite relation with the Fermi kinetic energy of this gas. This question was considered in greater detail by Bloch^[62] (1929). The latter work was criticized by Bethe^[63] and Wigner^[64b], who showed that in the zeroth approximation of perfectly free electrons ferromagnetism is possible only when the lattice constant exceeds a definite minimum boundary ($\geq 5 \text{ \AA}$), and in addition, perturbation theory was incorrectly used in Bloch's calculations, inasmuch as ferromagnetism is possible only in the limit in which the "perturbation," i.e., the exchange energy, is comparable with the "zero" Fermi energy, and finally, the calculations disregarded other correlation effects. The collectivized model of ferromagnetism found further development in the papers by Slater^[65], Stoner^[66], and Mott^[1,68], who attempted to improve the Frenkel-Bloch ferromagnetism criterion by making the band model of the transition metals more specific. Namely, they introduced the notion that in addition to the unfilled energy band of valence electrons (s and p) there exists in d metals also another unfilled band resulting from the splitting of the atomic d levels. It is assumed that the d band is noticeably narrower than the valence band (because of the smaller overlap of the d functions of the neighboring atoms in the crystal), but in view of the closeness of the energies of the nd, (n+1)s, and (n+1)p levels of the transition element atoms these bands must overlap and behave autonomously in all other respects. In particular, one can speak of "holes" in the d band and of "transitions" of electrons from the d to the s band, wherein the electrons and "holes" of the d bands are treated as quasi-free particles, which differ from the electrons

*We must emphasize here the entire arbitrariness of such a terminology: the s electrons comprise essentially the collectivized part of the electron density in the crystal, which is practically delocalized, while the d electrons are its localized and consequently less collectivized component.

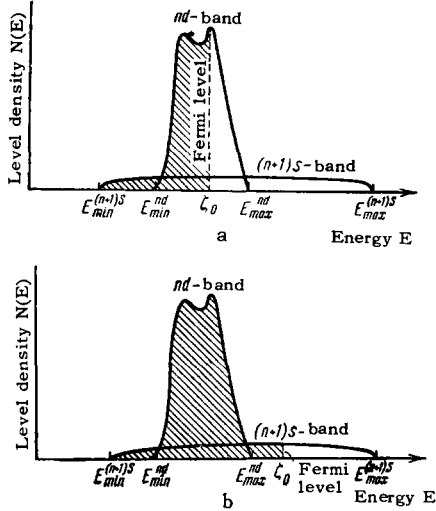


FIG. 11. Schematic representation of the distribution of electron level density in overlapping $nd - (n + 1)s$ bands. a – Case of transition metal; b – case of normal metal.

and “holes” of the valence band only in having a larger effective mass. Schematically such a picture is illustrated in Fig. 11a. Figure 11b shows a plot of the bands for a transition metal, say copper with filled d band. It is seen from this plot that the density of the energy levels in the d band is assumed to be appreciably higher than in the s band, this being due 1) to the narrowness of the d band and 2) to the larger number of d electrons per atom than s electrons. As we have seen in Sec. 2, this increased density of the electron levels in the transition metal at the Fermi surface does manifest itself in many anomalies of the electron properties of these crystals.

Specific calculations of the d band were first made by Krutter in 1935^[67], followed by Slater^[65], Mott^[68], Wohlfahrt^[69], and Fletcher^[70].*

By way of illustration let us show the more detailed calculation as given by Fletcher^[70]. It is known that the problem of determining the energy spectrum of an electron in the crystalline self-consistent potential field in the one-electron linearized approximation reduces to solving a Schrödinger equation of the type

$$\hat{H}\psi(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (4.1)$$

where Δ is the Laplace operator and $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{n})$ is the self-consistent periodic potential of the lattice: $\mathbf{n} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ is the lattice vector, with $n_1, n_2,$ and n_3 integers or half-integers and $\mathbf{a}_1, \mathbf{a}_2,$ and \mathbf{a}_3 the basic lattice vectors, while $\psi(\mathbf{r})$ and E are respectively the sought wave function and the electron energy. Usually some approximate method is used to solve (4.1)^[1-4]. Inasmuch as the d states, as was noted many times above, are less perturbed by the crystal-

*A review of these calculations was presented by Callaway in Solid State Physics (v. 7)^[6]. See also later papers by the same author on this subject^[71,72].

line “fields” than the valence electrons, we can use in this case the “strong coupling”* approximation to solve (4.1). In this approximation the wave function of the electron in the crystal is sought in the form of a series

$$\psi_m(\mathbf{k}; \mathbf{r}) = \sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}} \Phi_m(\mathbf{r} - \mathbf{n}), \quad (4.2)$$

where $\Phi_m(\mathbf{r} - \mathbf{n})$ is one of the five ($m = 1, 2, 3, 4, 5$) atomic wave d -functions[†] of the n -th lattice site. The summation in (4.2) is carried out over all the lattice sites, and \mathbf{k} is the quasimomentum of the collectivized electron in the lattice. The atomic d functions corresponding to the energy level E_d^0 have the form^[9,11,14,75] (for $\mathbf{n} = 0$)

$$\Phi_1(\mathbf{r}) = \left(\frac{15}{4\pi}\right)^{1/2} \frac{xy}{r^2} f(r), \quad \Phi_2(\mathbf{r}) = \left(\frac{15}{4\pi}\right)^{1/2} \frac{yz}{r^2} f(r),$$

$$\Phi_3(\mathbf{r}) = \left(\frac{15}{4\pi}\right)^{1/2} \frac{zx}{r^2} f(r),$$

$$\Phi_4(\mathbf{r}) = \left(\frac{15}{16\pi}\right)^{1/2} \frac{x^2 - y^2}{r^2} f(r), \quad \Phi_5(\mathbf{r}) = \left(\frac{5}{16\pi}\right)^{1/2} \frac{3z^2 - r^2}{r^2} f(r), \quad (4.3)$$

where $f(r)$ is the normalized radial d function of the isolated atom, while the numerical factors in (4.3) appear as a result of normalization of the angle parts of the functions. By virtue of the degeneracy of the atomic d functions, the correct zeroth approximation function for Eq. (4.1) in the crystal will be a linear combination of the solutions (4.2) with unknown coefficients $a_{mm'}(\mathbf{k})$:

$$\Psi_m(\mathbf{k}; \mathbf{r}) = \sum_{m'} a_{mm'}(\mathbf{k}) \psi_{m'}(\mathbf{k}; \mathbf{r}). \quad (4.4)$$

Substituting (4.4) in (4.1) and neglecting the inexact orthogonality of the functions (4.2) with respect to the indices m , we obtain from Eq. (4.4) for the determination of the coefficients $a_{mm'}(\mathbf{k})$, homogeneous algebraic equations, the conditions for the solvability of which will be the vanishing of the corresponding determinant of the system, from which we arrive at the following secular equation for the determination of the energy:

$$\|H_{mm'} - E\delta_{mm'}\| = 0, \quad (m, m' = 1, 2, 3, 4, 5), \quad (4.5)$$

where

$$\delta_{mm'} = \begin{cases} 0 & m \neq m', \\ 1 & m = m', \end{cases}$$

$$H_{mm'} = \frac{1}{\alpha_m \alpha_{m'}} \int \psi_m^*(\mathbf{k}; \mathbf{r}) \hat{H} \psi_{m'}(\mathbf{k}; \mathbf{r}) d\mathbf{r},$$

$$\alpha_m^2 = \int \psi_m^*(\mathbf{k}; \mathbf{r}) \psi_m(\mathbf{k}; \mathbf{r}) d\mathbf{r}. \quad (4.5')$$

*This is pointed out, for example, by Jones and Mott^[73]. However, Krutter^[67] and Slater^[65] used the cell method following Wigner and Seitz.

†As was already noted above [item c) in Sec. 2], the expansion (4.2) should strictly speaking be carried out directly in the $d, s,$ and p atomic functions, inasmuch as there is a single “hybridized” energy band in the crystal. However, for purposes of illustration, we are describing here a Krutter scheme of “individual” overlapping bands: $d, s,$ etc.

Using the smallness of the overlap integral for the d functions (4.3) and retaining in the integrals α_m only terms with $n = 0$, we obtain for the energy matrix

$$H_{mm'} = (E_d^0 + C) \delta_{mm'} + \sum_{n \neq 0} e^{ink} \int \Phi_m^*(\mathbf{r}-\mathbf{n}) [V(\mathbf{r}) - U(\mathbf{r})] \Phi_{m'}(\mathbf{r}) d\mathbf{r}, \quad (4.6)$$

where $U(\mathbf{r})$ is the potential of the isolated atom, and $C = \int \Phi_m^*(\mathbf{r}) [V(\mathbf{r}) - U(\mathbf{r})] \Phi_m(\mathbf{r}) d\mathbf{r}$ is the drop of the atomic d level due to the interaction between the electron of the given site with other lattice atoms. The energy in the band is measured usually from the level $E_d^0 + C$ and the nearest neighbor approximation is used in addition. To calculate the matrix elements (4.5) it becomes necessary to make specific assumptions concerning the form of the radial wave function $f(r)$, and also concerning the potential $V(\mathbf{r}) - U(\mathbf{r})$. The wave functions are usually chosen by the Hartree [see, for example, the calculation for the Cu^+ ion in [76]] or the Hartree-Fock method [2] for isolated ions (see, for example Cu^+ etc.), while the next approximation for the potential is $V(\mathbf{r}) = U(\mathbf{r})$ inside a sphere of radius equal to half the distance between the nearest neighbors, and $U(\mathbf{r}) = 0$ outside this sphere, where $V(\mathbf{r})$ is replaced by the potential of the atoms placed in the nearest neighboring sites. These simplifications enable us to obtain numerical values for the matrix elements (4.6). It becomes necessary then to solve the fifth-degree secular equation (4.5). One more simplifying assumption is made now. As first shown by Bethe [78], the atomic d level splits in the cubic electric field of the crystal into two levels, which are three-fold and two-fold degenerate, respectively. We can therefore expect in the cubic crystal not five but two d sub-bands, which will either overlap or will be separated by a forbidden energy gap. The number of states per atom in these two sub-bands will be six and four respectively. The wave functions corresponding to the first of the sub-bands (d_t) are the first three from (4.3), while the wave functions corresponding to the second sub-band (d_e) are the fourth and fifth from (4.3). Jones and Mott [73] indicated that, for example in a body centered cubic lattice where each atom is surrounded by eight nearest neighbors, the potential energy of the electron will be the lowest on the [111] axes. Inasmuch as the wave functions Φ_1 , Φ_2 , and Φ_3 have maxima, while Φ_4 and Φ_5 vanish along these axes, the d_t sub-band of the energies will lie lower than the d sub-band. For a face centered cubic lattice one can expect the positions of these sub-bands to be reversed.

If we assume such a splitting into sub-bands and neglect their interaction in first approximation, we can also neglect the matrix elements $H_{mm'}$ in (4.5) with $m = 1, 2, 3$ and $m' = 4, 5$. Then the fifth-degree equation (4.5) splits up into two, one cubic and one quadratic, thus greatly simplifying the solution. How-

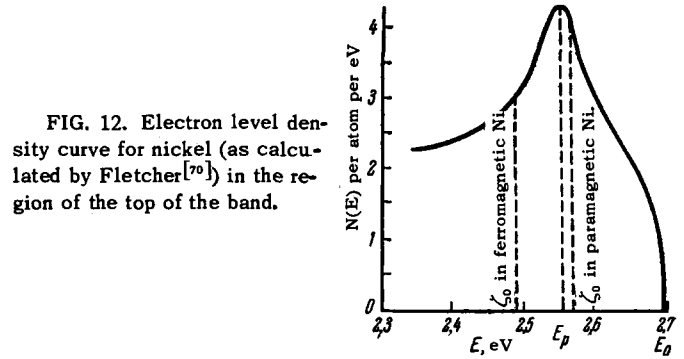


FIG. 12. Electron level density curve for nickel (as calculated by Fletcher [70]) in the region of the top of the band.

ever, for certain directions in k -space the secular equation (4.5) can be solved exactly. Using the approximate calculation scheme given above we can construct the equal-energy surfaces in the first Brillouin zone [1-4, 63] and then determine also the density of the energy levels in the band with the aid of the formula [1, 3]*:

$$N(E) \sim \int_{(E)} \frac{dS}{|\nabla E(\mathbf{k})|}. \quad (4.7)$$

Figure 12 shows the $N(E)$ curve for the "upper" part of the d band of nickel. The total width of this band as calculated by Fletcher [70] is 2.70 eV,† which is much less than the width of the $(n+1)s$ bands of real metals (approximately a fraction of an eV). From the $N(E)$ curve of Fig. 12 we see that the electron density in the d band has a peak near an energy value E_p somewhat lower than its upper edge E_0 .

After calculating the distribution of the levels in the d band, the question arises of the relative placement of the nd and $(n+1)s$ bands on the energy scale. To solve this problem we must solve in principle the problem of the crystal as a whole, making the expansion (4.2) more precise, and taking simultaneous account in it of all the external atomic functions nd , $(n+1)s$, $(n+1)p$, etc.‡ At the same time, whereas for metals with a closed d shell (copper, silver, gold, etc.) the relative placement of the $(n+1)s$ and nd bands is not so important (inasmuch as the Fermi surface passes "over" the "top" of the nd band), in transition d metals this question is of primary significance. Howarth [79], using the self-consistent field method, makes an attempt to give a more rigorous approximate estimate of the relative placement of the nd and $(n+1)s$ bands. Usually this question is solved by

*The integration in (4.7) is over a surface in k -space with specified energy $E = \text{const}$. This integral can be simply approximated by $N(E) \sim \Delta V_{\mathbf{k}}$, where $\Delta V_{\mathbf{k}}$ is the volume in k -space enclosed between the two equal-energy surfaces E and $E + \Delta E$; the integral can then be referred to the energy $E + (1/2)\Delta E \Delta V_{\mathbf{k}}$, which is determined by graphical integration.

†This value can be readily obtained from the energy difference $E_{1,2(k=\pi)} - E_{3(k=\pi)}$.

‡See also item c) of Sec. 2.

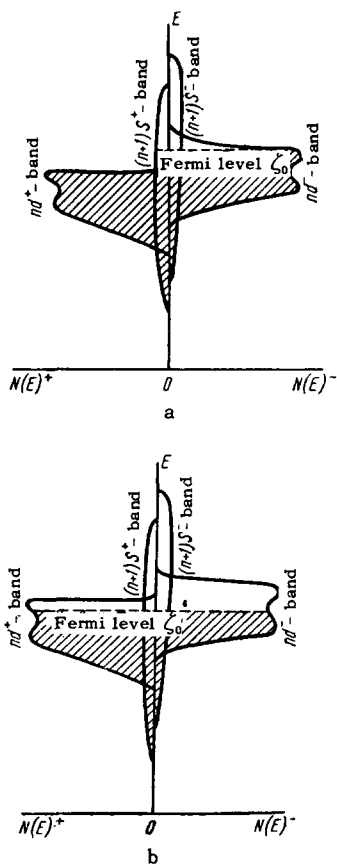
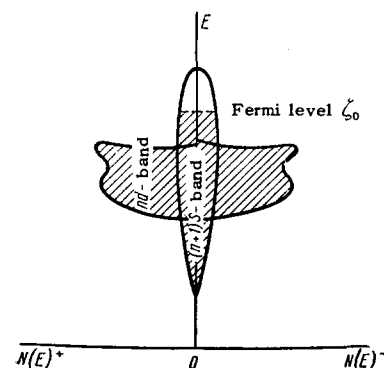


FIG. 13. Schematic diagram of the electron level density distribution in overlapping nd and $(n+1)s$ bands for two different spin projections (plus and minus) in transition d metals. a—Case when the Fermi level ζ_0 lies above the top of the sub-band for the plus spins; b—case when the Fermi level ζ_0 lies below the top of the sub-band for plus spins.

simple “fitting” of the placement of the bands to the known experimental data on the average atomic magnetic moments for ferromagnetic metals, or from the data on the electronic specific heat and paramagnetic susceptibility of paramagnetic metals (see below). Thus, for example, Fletcher^[70] (see Fig. 12) gives the Fermi level for ferromagnetic nickel by using the fact that the average atomic magnetic moment is $0.6\mu_B$, and assigning this moment only to 3d electrons (completely neglecting the polarization of the 4s electrons, see Sec. 5). In this case Fletcher is forced to postulate the lifting of the spin degeneracy in the 3d band, which now consists of two shifted 3d sub-bands for “right hand” and “left hand” spins (Figs. 13a and b). These two 3d sub-bands can be shifted relative to each other to such a degree and so located relative to the Fermi surface, that one lies below this energy level and is completely filled, while the second is left with 0.6 unfilled levels per atom from among the total number of five levels per atom for the given spin orientation (see Fig. 13a).^{*} In paramagnetic crystals of d metals, both d sub-bands for different spin projections are practically not shifted relative to each other, and the spectrum has an appearance shown schematically in Fig. 14.

^{*}In other cases the Fermi level can pass through both sub-bands for electrons with plus and minus spin projections (see Fig. 13b).

FIG. 14. Schematic diagram of electron level density distribution in overlapping nd and $(n+1)s$ bands for two different spin projections (plus and minus) in non-transition metals.



From Fig. 12, plotted in accord with Fletcher’s calculations for nickel, it is seen that the Fermi level ζ is to the left of the maximum of the $N(E)$ curve ($E_p > \zeta$). The point where the ordinate ζ crosses the curve of Fig. 12, i.e., $N(\zeta)$, makes it possible, in accord with (2.7), to compare theory with experiment by using the data for the electronic specific heat at 1°K . Namely, according to Fletcher, the value of γ from (2.7) should be $7.1 \times 10^{-3} \text{ J-mole}^{-1} \text{ deg}^{-2}$, while experiment yields a quantity that is somewhat larger, namely $7.3 \times 10^{-3} \text{ J-mole}^{-1} \text{ deg}^{-2}$, but at any rate of the same order of magnitude. It is also interesting to make a more detailed comparison of the values of the electronic specific heats over an entire series of transition d metals and their alloys, something already mentioned in item b) of Sec. 2.

In items a) and b) of Sec. 2 it was also noted that important information on the distribution of the levels in the d band can be obtained by studying the temperature variation of the Pauli paramagnetic susceptibility χ_p in nonferromagnetic d metals. From quantum theory of metals, neglecting the diamagnetic effect (the quantization of the orbital motion of the electrons in a magnetic field after Landau^[80]) we can obtain the following approximate expression for the paramagnetic susceptibility of a degenerate gas^[1-4,23]

$$\chi_p = 2\mu_B^2 N(\zeta) \left[1 + \frac{\pi^2}{6} (kT)^2 \left(\frac{d^2 \ln N(E)}{dE^2} \right)_{\zeta} \right]. \quad (4.8)$$

From (4.8) it follows that χ_p in transition metals at $T = 0^\circ\text{K}$ should as a rule be larger than for nontransition metals, inasmuch as $N(\zeta)$ in the former is larger than in the latter. As noted in item a) of Sec. 2, this is indeed observed.

Kriessman and Kallen^[23] give a detailed analysis of the data for the temperature dependence $\chi_p(T)$ of practically all the paramagnetic d metals (Ti, V, Cr, Mn, Zn, Hf, Nb, Ta, Mo, Ru, Rh, Ir, Os, Pd, Pt). For the low-temperature region, as compared with the temperature of the electron gas degeneracy in the metal, the function $N(E)$ can be expanded in powers of the small difference $E - \zeta$, so that (4.8) becomes

$$\chi_p = 2\mu_B^2 N(\zeta) + \frac{\pi^2}{3} \mu_B^2 \left\{ N''(\zeta) - \frac{[N'(\zeta)]^2}{N(\zeta)} \right\} (kT)^2. \quad (4.9)$$

It is seen from Eq. (4.9) that the temperature depend-

ence $\chi_p(T)$ is determined by the first and second derivatives of the function $N(E)$ on the Fermi surface. Usually the first term in the square brackets of the right half of (4.9) exceeds the second and therefore $d\chi/dT < 0$. A reversal of the sign of the derivative, i.e., $d\chi/dT > 0$, can occur only near the minima of the $N(E)$ curve, where $N'(E) = 0$. Thus, from the measured sign of the derivative $d\chi/dT$ we can determine whether the Fermi level lies near the minimum of the $N(E)$ curve or not. Thus, for example, in the case of Ti, Zr, Hf, Mo, W, Ru, Rh, Os, and Ir, when experiment apparently yields $d\chi/dT > 0$, ζ lies near the minimum of the $N(E)$ curve, while in V, Nb, Ta, Pd, and Pt the Fermi level lies away from the minima of the $N(E)$ curve. As was noted above [items a) and b) of Sec. 2], this agrees with the experimental data for the electronic specific heat, the values of which, for example, are appreciably lower for Ti than for Nb. Thus, we again verify how important it is to carry out a simultaneous experimental investigation of the electronic specific heat and the paramagnetic susceptibility for transition metals.*

It is quite tempting to use experimental data on the x-ray emission and absorption spectra to determine the distribution of the electron energy levels in the spectrum of the crystals. However, for the time being it hardly makes sense to attempt any numerical comparisons, except for the most general qualitative predictions referred to above [see item c) in Sec. 2], since we do not know the exact theoretical form of the function $N(E)$, nor do we know the theoretical values of the transition probabilities in (2.8) and (2.9), the equations which must be compared with experiment. Nonetheless, in principle, the x-ray spectral method of investigating the electron spectrum in d metals is one of the most promising and one must continue to develop it vigorously in both experimental and theoretical aspects.

An important and urgent problem is that of the occurrence and of the properties of the ferromagnetic and antiferromagnetic states in transition d metals. It is necessary to ascertain here the genesis of the ferromagnetic and antiferromagnetic state in d met-

*The correlation between the paramagnetic susceptibility χ_p and the level density at the Fermi surface can also be obtained by investigating the dependence of the susceptibility on the concentration in many alloys of transition paramagnetic metals with non-transition diamagnetic metals. Thus, for example, in alloys of the substitution type where the transition metal palladium is replaced by the nontransition metal silver^[155,1], a monotonic decrease in the susceptibility with increasing silver concentration is observed. At approximately 50% silver, the susceptibility becomes equal to zero and further increase in the silver concentration makes the susceptibility reach a constant negative value, equal to the diamagnetic susceptibility of pure silver. From these data we can conclude that in palladium we have on the average 0.5 "holes" per 3d band, which are indeed filled in the alloy when the silver concentration is 50%.

als, to establish a quantitative criterion for the possibility of occurrence or absence of magnetic spin ordering, to explain the influence of the "orbital magnetism" of the d states, and to present a quantitative explanation of the average atomic moments (their difference from the moments of the free atoms, and also their fractional character), to clarify the question of localization of the spin moments of d electrons in the crystal and the interaction effects between s and d electrons in the metal, and finally to explain the occurrence of spin waves as excitations of a definite type of the magnetically ordered state of the system of collectivized electrons.

The ordinary band model, in which the quasi-Coulomb and exchange interaction is considered as a perturbation, describes sufficiently well qualitatively the paramagnetic and ferromagnetic state of d metals. However, antiferromagnetism in d metals (Cr and Mn) still remain unexplained, as is the fact that the paramagnetic susceptibility of some of these substances below the Curie or Neel point follows the Curie-Weiss law (i.e., we deal not with a Pauli type of paramagnetism, but with a Langevin type). Below, following Friedel, Leman, and Olszewski^[81], we consider briefly the problem of ferromagnetism within the framework of the band theory.*

From the point of view of this model, ferromagnetism in an electron gas is possible when an energy "shift" δE occurs in the \pm sub-bands for the "right-hand" and "left-hand" spins respectively (see Fig. 14), owing to the "exchange" interaction. As a result of this shift, a total of ϵ electrons per atom will go over from the minus sub-band to the plus sub-band. This leads to an increase in the kinetic energy per atom $\epsilon \delta E$ (if ϵ is very small). The exchange energy of the metal is determined by the interaction of the electron pairs, and is therefore proportional to the square of the number of d electrons in each sub-band. We denote by n_+ and n_- the number of electrons (or holes) per atom in the \pm sub-bands; in the paramagnetic state we have $n_+ = n_- = n/2$. The change in energy on going from the paramagnetic into the ferromagnetic state is then equal to

$$\begin{aligned} \epsilon \delta E - \frac{1}{n} \left[\left(\frac{n}{2} + n\epsilon \right)^2 + \left(\frac{n}{2} - n\epsilon \right)^2 - 2 \left(\frac{n}{2} \right)^2 \right] E_{ex} \\ = \epsilon \delta E - 2n\epsilon^2 E_{ex} \end{aligned} \quad (4.10)$$

where E_{ex} is the average exchange energy per pair of nucleons. At the beginning of the iron group transition element series the 3d band is broader and is strongly "hybridized" with the 4s and 4p bands, and therefore the energy E_{ex} should be close to its value for the "free" electrons. To the contrary, for the end of this series, the 3d band becomes narrower and less

*Slater^[151] and Ledyard^[152] developed a treatment of antiferromagnetism within the framework of the collectivized electron model, somewhat different from^[81].

hybridized with the broad conduction band, so that in this case E_{ex} is closer to its value for the isolated atom. Because of this, an "average" estimate for E_{ex} yields a value 0.7 eV.^[32] It is easy to see that $n(\zeta_0) = n\epsilon/\delta E$. We introduce the dimensionless parameter

$$\xi = \frac{2\epsilon E_{\text{ex}}}{\delta E} = 2E_{\text{ex}} \frac{n(\zeta_0)}{n}. \quad (4.11)$$

From a comparison of (4.10) with (4.11) it follows that:

a) If $\xi > 1$, then the equilibrium state is ferromagnetic.

b) If $\xi < 1$, then the equilibrium state is paramagnetic.

It can be shown that the exchange interaction increases the paramagnetic susceptibility of the electron gas. Indeed, the exchange energy $-2n^2\epsilon^2 E_{\text{ex}}$ in (4.10) is proportional to the square of the magnetization $2n\mu_B\epsilon$, so that we can introduce an effective (molecular) field

$$H_m = -\frac{\partial(-2n^2\epsilon^2 E_{\text{ex}})}{\partial(2n\mu_B\epsilon)} = \frac{2n\epsilon E_{\text{ex}}}{\mu_B},$$

which is proportional to the magnetization. Further, by definition we have $\chi_{\text{p.exp}} = 2n\mu_B\epsilon/H$ (where H is the external magnetic field), and in accordance with the band model the susceptibility is [see formula (4.8)*]

$$\chi_{\text{p.band}} \cong 2\mu_B^2 \frac{n(\zeta_0)}{n} \quad (4.12)$$

and on the other hand

$$\chi_{\text{p.band}} = \frac{2n\mu_B\epsilon}{H+H_m}. \quad (4.12a)$$

From a comparison of these two formulas we get $H + H_m = n^2\epsilon/\mu_B n(\zeta_0)$, and in addition it is easily seen that $\chi_{\text{p.band}}(H + H_m) = \chi_{\text{p.exp}}H$. Using the expressions given above for $H + H_m$ and for H_m we get

$$\chi_{\text{p.band}} \frac{n^2\epsilon}{\mu_B n(\zeta_0)} = \chi_{\text{p.exp}} \left(\frac{n^2\epsilon}{\mu_B n(\zeta_0)} - \frac{2n\epsilon E_{\text{ex}}}{\mu_B} \right);$$

From this it is already easy to find that

$$\chi_{\text{p.band}} = (1 - \xi)^{-1} \chi_{\text{p.exp}}. \quad (4.13)$$

Formula (4.13) agrees with the experimental data [see item a) in Sec. 2], which give for $\chi_{\text{p.exp}}$ values that are greater than predicted by the elementary band model without account of exchange, if formula (4.12) is compared with that for the specific heat (2.6). The value obtained experimentally for the correction factor $(1 - \xi)^{-1}$ lies between two and three; we thus get from (4.11) $E_{\text{ex}} \sim 0.3-1.0$ eV; from studies of atomic spectra it is known that $E_{\text{ex}}^{\text{at}} \sim 0.4-0.8$ eV. The agreement is thus sufficiently good. The authors of [81] assume that for paramagnetic d metals E_{ex} lies between 0.5 and 1.0 eV.

The condition $\xi > 1$ necessary for realization of ferromagnetism requires that the level density $n(\zeta_0)$

at the Fermi level be high, and also that the average exchange energy E_{ex} also be high, something more easily satisfied for the d metals at the end of the series.

The foregoing calculations have the shortcoming that they have been carried out in the momentum (energy) space and that the distribution of the spins participating in the ferromagnetism in ordinary space is completely neglected. In all band-model calculations it is tacitly assumed that within the framework of this model we are dealing with complete spatial homogeneity of the electron density for both spin components (plus and minus). This would hold true were the wave function of the electrons to be a plane wave [$\rho(\mathbf{r}) = \text{const}$]. Actually, however, this is not the case in a real metal, especially for the former d electrons. As noted above, their wave function in the crystal is more likely to be close to a localized atomic d function than to a plane wave. It is therefore quite natural for the spin density in a ferromagnetic d metal to be inhomogeneous and localized at the crystal lattice sites. The crystalline collectivization effect alone makes whole-number values (in μ_B units) of the excess spin density for a given spin projection (plus or minus) unnecessary. From this elementary but perfectly rigorous analysis we immediately eliminate in principle the band-model "difficulty" mentioned above in the explanation of antiferromagnetism and Langevin paramagnetism. The difference between the Pauli ferromagnetism and antiferromagnetism lies in the fact that in the latter case the exchange (negative) interaction produces in the electron system an antiferromagnetism axis (quantization axis), which is "attached" by the magnetic forces to one crystal axis, whereas in the case of Pauli paramagnetism there is no such axis. At temperatures above the Curie or Néel points one can also expect a noticeable admixture of Langevin paramagnetism in ferromagnetic or antiferromagnetic d metals.*

In [81] the authors propose a concrete method for taking spin localization in space into account within the framework of the collectivized electron model. The main idea of this model is that the energy going to localization of the electron charge with one spin projection is compensated by the electrostatic repulsion of the electrons with the other spin projection. The condition for the stability of such localization agrees with the condition for the parameter ξ from (4.11).†

*Differences can be expected here, for example, between nickel and iron, inasmuch as in nickel the magnetic saturation is much smaller ($0.6 \mu_B$ per atom), and therefore the thermal motion will contribute more to the Pauli magnetism than to the Langevin magnetism, while in iron, to the contrary, the Langevin paramagnetism will play the greater role. In exactly the same manner, the scattering of the electrons on the "spin disorder" should have different characters in iron and in nickel [see item e) of Sec. 2].

†For details of the calculation we refer the reader to the original article [81].

*We note that $N(\zeta_0)$ in (4.8) is equal to $n(\zeta_0)/n$ in (4.12).

On the whole it can be stated that the band theory gives a satisfactory qualitative description of the electron properties of d metals. However, from the quantitative point of view the situation turns out to be much less clear. Most unsatisfactory are all attempts at a quantitative determination of the specific expressions for the density function $n(\xi_0)$ and for the estimated "width" of the d band; the account of the "interaction" of the nd band with the $(n+1)s$ and $(n+1)p$ bands is in practice not clear at all. Yet it has been known for a long time from the calculation of the wave functions and energies of the d levels of isolated atoms that the latter are much more sensitive to the least variations of the potential than are the valence electrons. An account of the exchange and Coulomb interactions is carried out as a rule in an incorrect form. There is still no clear-cut answer to the question of the spin waves within the framework of the ordinary band model. This question was first considered qualitatively for ferromagnetic metals by Herring and Kittel^[84]. This same problem was considered in greater detail, within the framework of the Bohm and Pines^[83,32] collective description of the interaction of the electrons in a metal, in an extensive research by Shimizu^[82], who obtained a more accurate criterion for the realization of the ferromagnetic state (in particular, ferromagnetism turns out to be possible in real crystals only for Fermi particles with very large values of effective mass).

Shimizu also considered the question of spin waves within the framework of the band model (see Sec. 8 in^[82]), but he artificially postulated there localized states for the atomic carriers of the magnetic moment. Abrikosov and Dzyaloshinskii^[86] considered in a very interesting paper, within the Landau theory of the Fermi liquid^[29], the question of the dispersion law for magnetic excitations (spin waves), and have shown that this law is quadratic in first approximation. They used in the Fermi-particle energy a term similar to the second term in (38.1), describing the interaction between the spins of these particles and the magnetization of the system. Izujama^[85] considered the question of spin waves within the framework of the band approximation, relating these magnetic excitations with the bound states in a system of Fermi particles (of the exciton type). Vonsovskii and Kobelev^[87], on the basis of the temperature Green's functions (see Part II of the present review, Secs. 9–11), took into account the influence of the magnetization density fluctuations in a system of collectivized electrons of a ferromagnetic metal. They have shown in this case that at temperatures $T \ll \Theta_f$ the spontaneous magnetization of the ferromagnetic metal decreases first because of the temperature dependence of the Fermi distribution function of the atomic carriers of magnetism (the d-band electrons) $I_F(T)$ and, second, owing to the occurrence of spin inhomogeneities—spin waves

$I_{s,w}(T)$. In the case of a fractional value of atomic moments and a quadratic Fermi-particle dispersion we have

$$I_F(T) \sim -aT^2, \quad I_{s,w} \sim -\beta T^{3/2}. \quad (4.14)$$

Analogous results were obtained by Edwards^[156], but by a different method.

We note here only one circumstance. One might think that all the calculations based on the band model, similar to the Fletcher calculation described above^[70], have no real meaning whatever, inasmuch as the band model is too crude an approximation, in which the very significant interactions in the system of collectivized electrons are neglected. Nonetheless, it is precisely now that a situation has arisen in metal theory, that calculations by means of even so imperfect a band model are of real physical interest and can be fruitful. The point is, as shown by a phenomenological approach to the treatment of the properties of Fermi systems with arbitrary sign of dispersion in real metallic crystals, developed in the well known papers of I. M. Lifshitz and his co-workers^[93], that a study of several effects in a magnetic field (oscillations of magnetic susceptibility, magnetoresistance, Hall effect, etc.) makes it possible to construct the form of the Fermi surfaces in metals from experimental data. This affords a possibility of exact verification of the corresponding calculations of these surfaces, obtained as a result of the use of model representations of the band theory. Thus, the approach proposed by I. M. Lifshitz has placed on the firm ground of quantitative verification the calculations of the Fermi-surface shape, level densities, etc., which were frequently made without suitable checks within the framework of the band model of metals (see also Pippard's review on the point^[157]). This is precisely why we made it possible to make room in the present review to a description of band model calculations (see also Chapter 5).

In spite of all the indicated essential shortcomings of the band model quantitative calculations, it has one important advantage, namely that the former d and valence electrons are considered in the crystal, in principle, as a single collectivized Fermi-particle system. This makes it possible to obtain a natural explanation for the fractional nature of the average atomic moments, and also the fractional numbers of the conduction electrons per lattice site. The band model affords also a fair qualitative explanation of the regularities in the x-ray spectra of transition metals. One should add also the already mentioned success of this model in explaining large values of the electronic specific heat and paramagnetic susceptibility of d metals.

At the same time, the band model has several principal difficulties and shortcomings. The major among these is the postulation of sharply autonomous existence of d and s bands in the energy spectrum of the

system and the artificial "sticking" of these bands to the common Fermi surface. In addition, in the ordinary band treatment one ignores in practice the spatial inhomogeneity of the electron density in the crystal (which follows already from the statistical correlation of the electrons in space, i.e., from the antisymmetrical character of the total wave function of the Fermi system). This leads to failure to take into account the individuality of the spin states of the electrons in the crystal, does not permit an explanation of the experimentally measured neutron and x-ray form factors, and practically eliminates the possibility of quantitatively describing the kinetic coefficients due to various types of "collisions" between the electrons and neutrons on the one hand and the spin (magnetic) inhomogeneities on the other.

Thus, it can be stated on the whole that the band model, while emphasizing the localization of the d electrons in the crystal, greatly impoverishes their magnetic properties which are connected to a considerable extent with the appreciable conservation* of a localized electron charge density distribution and particularly the density distribution of the magnetic moments of the former d electrons in the crystal. This model can therefore be employed with certain justification in the case of d metals, but it is little suitable for an explanation of the physical properties of f metals. (We shall return to an estimate of this model and compare it with another approach in the theory of transition metals at the end of the next Section 5).

5. Model of Interacting Valence (Outer) Electrons and Electrons of the Inner Unfilled Shells [s-d(f) Exchange Model] [90-92]

a) From the general considerations developed above (Secs. 3 and 4), we can see an obvious specific singularity of the electronic energy spectrum of the d and f transition group metals. In the case of d metals this reduces, in the language of the band model, to the fact that both the former valence (s, p) electrons and the electrons of the unfilled inner d-shells of the isolated atoms participate to an equal extent in the formation of the Fermi surface. This leads as a rule to an increased electron-level density near the Fermi surface, something that manifests itself both on the equilibrium statistical properties of the metal (specific heat, paramagnetic susceptibility, etc.) and on the kinetic coefficients (electric conductivity, heat conduction, etc.), which can greatly differ both in magnitude and in the temperature variation from the corresponding quantities for normal metals (see Secs. 2 and 4). The second major feature of transition metals and of their alloys and compounds is that they can have perfectly unique magnetic properties, such as

*In so far as one can visualize the case of a localized distribution of the spin (magnetic) density with an almost homogeneous distribution of the electron charge density.

atomic magnetic ordering (ferromagnetic or antiferromagnetic state), which is a direct consequence of the spin non-saturation of the unfilled d or f groups of the electron shell of the transition element atoms. However, in d metals the perturbation due to the intercrystalline interactions can hinder the realization of magnetic order, and then we deal with Pauli paramagnetism. Atomic magnetic order, which is most typical for f metals, influences not only the magnetic but also the electrical, optical, thermal, and other properties of the metals in the formation of which the principal role is played by conduction electrons, as in paramagnetic metals of the transition and normal groups. The existence of "magnetic anomalies" for nonmagnetic properties of transition metals with atomic magnetic order indicates that a definite connection exists between the "magnetic" electrons participating in this order, and the conduction electrons. This raises the important question of whether it is possible to distinguish in a crystal between conduction electrons and "magnetic" electrons. Do not all the former valence electrons and the electrons of the unfilled d or f shells form a single collectivized system—an electronic Fermi liquid which flows over the positively charged ionic lattice of the metal? Of course, in the case of a crystal one cannot speak in the literal sense of s, p, d, or f electrons, inasmuch as there is a strong interaction among them. However, a study of the x-ray and neutron form factors (see Sec. 2) gives us an undisputable right to relate the spin (magnetic) density not with the entire density of the electron charge, but only with that part which is localized near the lattice sites; on the other hand, the density of the electrons which essentially determine the conductivity and other nonmagnetic electronic properties of the metal turns out to be more or less homogeneous over the volume of the crystal. This experimental fact does indeed justify, at least from the qualitative point of view, the aforementioned subdivision of the transition metal crystal electrons into conduction and "magnetic" electrons. Using the analogy with the isolated atoms, we can retain also the names for these electrons (s, p, d, and f) although these terms must of course be assigned a different physical content. In connection with the problem under consideration, two other questions arise: 1) do the "magnetic" electrons have noticeable mobility in the crystal and 2) do the conduction electrons participate in the atomic magnetic order, either by making a direct contribution to the spontaneous magnetic moment of the crystal (in the case of ferromagnetism) or to the sub-lattice magnetization (in the case of antiferromagnetism), or else by influencing the magnetic order via their interaction with the "magnetic" electrons. These questions were answered in part in Secs. 3 and 4; it was emphasized there that account must be taken of the qualitative difference between the d and f metals. In the case of f metals one can answer the first question in the negative, since,

for example, the 4f electrons of the rare earth metals retain practically the same properties that are characteristic of isolated atoms, and can therefore be conditionally "ascribed" to the "immobile" ionic lattice of the rare earth metal. To the contrary, the two parts of the first question should be answered in the case of f metals in the affirmative: the conduction electrons are magnetized by the inner 4f electrons, which have a resultant magnetization, and also participate actively in the very genesis of the magnetic order, inasmuch as the exchange interaction between the 4f layers of neighboring crystal ions has the character of an indirect exchange with the decisive participation of the conduction electrons. In the case of d metals, the answer to the first question should be in the affirmative, since the d electrons have a perfectly noticeable mobility, albeit smaller than that of the s electrons, and therefore participate in transport phenomena in metals. The answer to the first half of the second question is the same as for f metals, while the answer to the second half, if not in the negative, is that in any case one can think that the s electrons do not play a decisive part in the formation of the exchange coupling in d metals.

Taking these considerations into account, we must describe the electron system of a transition d or f metal with atomic magnetic order by means of a scalar function $\rho(\mathbf{r})$, which determines the summary electron (charge) density in the crystal, and a vector function of the electron spin density $\mathbf{s}(\mathbf{r})$. The symmetry properties of the former coincide with the crystal-chemical symmetry of the metal, while the symmetry properties of the latter coincide with its magnetic symmetry. In addition, it is necessary to take into account also the momentum density function $\mathbf{P}(\mathbf{r})$ describing the non-localization of the electrons in the crystal. These functions are quantum mechanical operators, so that to obtain the statistical-thermodynamic characteristics of the electron system of the crystal it is necessary to determine the mean statistical values of these operators by means of the well known rules of quantum statistics^[88]

$$\rho(\mathbf{r}) = \frac{\text{Sp}[\hat{\rho}(\mathbf{r})\hat{W}]}{\text{Sp}\hat{W}}, \quad \mathbf{s}(\mathbf{r}) = \frac{\text{Sp}[\hat{\mathbf{s}}(\mathbf{r})\hat{W}]}{\text{Sp}\hat{W}}, \quad \mathbf{P}(\mathbf{r}) = \frac{\text{Sp}[\hat{\mathbf{P}}(\mathbf{r})\hat{W}]}{\text{Sp}\hat{W}}, \quad (5.1)$$

where $\hat{W} = \exp(-\hat{H}/kT)$ is the density matrix operator and \hat{H} is the Hamiltonian operator of the system.* Naturally, a rigorous calculation of the functions (5.1) entails great mathematical difficulties, making it necessary to use approximate methods for the solution of the problem.† We consider below an approximate treat-

*Sp is the matrix trace (spur) operator, i.e., the sum of all its diagonal elements; in our case these are the sums of the diagonal elements of the matrix of the product of two operators $\hat{\rho}\hat{W}$, $\hat{\mathbf{s}}\hat{W}$, and $\hat{\mathbf{P}}\hat{W}$, and also of the operator \hat{W} alone.

†For a possibility of a more general solution of the problem see Ch. III-V below.

ment of transition metals having atomic magnetic ordering. We do not delve deeply into the genesis of the latter, paying principal attention to a clarification of the influence of the magnetic ordering on the conduction electrons.*

b) We first stop to discuss the indirect exchange interaction via the conduction electrons, following Zener's elementary analysis^[55]. (A more rigorous solution is given in Secs. 7 and 8.) The energy of direct d-d or f-f exchange per lattice site can be written in first approximation in the form $-\frac{1}{2}A_{dd}(ff)S_{d(f)}^2$, where $A_{dd}(ff)$ is the parameter of direct d-d or f-f exchange interaction, and $S_{d(f)}$ is the average value of the relative magnetization of the d or f electrons per lattice site. The energy of the s-d(f) exchange per site will be equal to $-A_{sd(f)}S_{d(f)}S_s$, where S_s is the mean value of the relative magnetization of the conduction electron per site, and $A_{sd(f)}$ is the s-d(f) coupling parameter. The addition to the Fermi energy brought about by the magnetization of the conduction electrons is $\frac{1}{2}A_F S_s^2$, where $A_F = N\mu_B^2/\chi_p$, and $\chi_p = 2\mu_B^2 N(\zeta_0)$ is the ordinary Pauli paramagnetic susceptibility.† Thus, the total energy of the crystal per site, which depends on S_s and $S_{d(f)}$, is

$$E(S_{d(f)}, S_s) = -\frac{1}{2}A_{dd}(ff)S_{d(f)}^2 - A_{sd(f)}S_{d(f)}S_s + \frac{1}{2}A_F S_s^2. \quad (5.2)$$

Inasmuch as the entropy of a strongly degenerate gas of the s electrons in metals is very small^[1-4], the equilibrium values of the magnetizations S_s and $S_{d(f)}$ can be obtained from the requirement that (5.2) have a minimum value under the condition that $|S_s| \leq S_{s, \max}$ and $|S_{d(f)}| \leq S_{d(f), \max}$. One of the possible solutions has the form

$$S_s = \frac{A_{sd(f)}}{A_F} S_{d(f)}, \quad S_{d(f)} = S_{d(f), \max}. \quad (5.3)$$

The ratio $A_{sd(f)}/A_F$ amounts to $\sim (10^{-13}-10^{-14})/10^{-12} \sim 0.1-0.01$, and therefore the magnetization of the s electrons amounts to $\sim 1-10\%$ of the total. Substituting (5.3) in (5.2) we obtain the equilibrium energy of the s + d(f) system

$$E_{\min}(S_{d(f)}) = -\frac{1}{2} \left[A_{dd}(ff) + \frac{A_{sd(f)}^2}{A_F} \right] S_{d(f)}^2. \quad (5.4)$$

The quantity in the square brackets of (5.4) is the effective parameter of exchange between the inner electrons that interact with the conduction electrons

$$A_{\text{eff}} = A_{dd}(ff) + \frac{A_{sd(f)}^2}{A_F}. \quad (5.5)$$

The elementary analysis shows that the s-d or s-f

*We shall assume that either a d-d (or f-f) exchange is possible in the system of "magnetic" electrons of the metal, or else indirect exchange via the conducting electrons and the closed shells (see Sec. 3).

†In the case of a quadratic dispersion for the s electrons $\chi_p \approx (3/2)N\mu_B^2/\zeta_0$, and consequently $A_F \sim \zeta_0$.

exchange coupling can lead to an effective exchange coupling between the inner electrons, defined by the parameter

$$A_{\text{ind}} = \frac{A_{sd(f)}^2}{A_F}. \quad (5.6)$$

This indirect coupling parameter is always positive in the present approximation and therefore contributes to ferromagnetic spin order. The direct d-d or f-f exchange coupling can be of either sign. Consequently, if $A_{dd(ff)} > 0$, then only ferromagnetism is possible in the transition metal, while if $A_{dd(ff)} < 0$, then to obtain ferromagnetism the condition $A_{\text{ind}} > |A_{dd(ff)}|$ must be satisfied, otherwise only antiferromagnetism is possible. In those cases when the direct exchange is vanishingly small, the atomic magnetic order is determined entirely by the indirect exchange coupling via the conduction electrons.

It should be recalled that in 4f metals it is possible to have also an indirect exchange coupling with participation of the closed $5s^25p^6$ shell (of the Kramers type, see Sec. 3). A more detailed discussion of the results obtained will be postponed to Secs. 7 and 8, and we now turn to an examination of the effects connected with the magnetization of the conduction electrons.

c) In the general phenomenological treatment of ferromagnetic metals or semiconductors^[90] the electron system is regarded as a continuous medium, characterized by magnetic-moment and momentum densities $\mathbf{I}(\mathbf{r})$ and $\mathbf{P}(\mathbf{r})$, respectively. Subdividing approximately the electron system into two subsystems of s and d or of s and f electrons, and introducing consequently the four functions $\mathbf{I}_s(\mathbf{r})$, $\mathbf{I}_{d(f)}(\mathbf{r})$ and $\mathbf{P}_s(\mathbf{r})$, $\mathbf{P}_{d(f)}(\mathbf{r})$, we can write for the Hamiltonian of the system

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{d(f)} + \hat{\mathcal{H}}_s + \hat{\mathcal{H}}_{sd(f)}, \quad (5.7)$$

where $\hat{\mathcal{H}}_{d(f)}$ is the Hamiltonian of the d(f) subsystem, which depends only on $\mathbf{I}_{d(f)}$ and $\mathbf{P}_{d(f)}$, $\hat{\mathcal{H}}_s$ is the Hamiltonian of the s subsystem, a function of \mathbf{I}_s and \mathbf{P}_s only, and finally $\hat{\mathcal{H}}_{sd(f)}$ is the Hamiltonian describing the interaction of the subsystem, and depends on all four functions.* Such a general formulation of the problem does not predetermine the question of the genesis of the exchange coupling in the d(f) subsystem, which should be explained during the course of the solution of the problem itself. However, we are not interested here in this question, since we are investigating the effects exerted by the "magnetization" produced by the "magnetic" electrons on the spectrum and kinetic effects of the conduction electrons. In this case we can choose as the zeroth-approximation Hamiltonian the sum of the first two terms in (5.7), when the influences of the s subsystem and of the d(f) subsystems in $\hat{\mathcal{H}}_{d(f)}$ and in $\hat{\mathcal{H}}_s$ respectively are disre-

*If we take into consideration also magnetic interactions, then (5.7) contains additional terms that depend on the external and internal magnetic fields.

garded. Such a choice of the zeroth approximation is suitable if the following conditions are satisfied:

$$A_{sd(f)} \ll \zeta, \quad A_{sd(f)} \ll A_{dd(ff)}. \quad (5.8)$$

The first condition of (5.8) signifies that the s-d or s-f exchange coupling is small compared with the Fermi energy, and is always satisfied. The second condition, namely that these couplings be small compared with the direct exchange, may not be satisfied, for example by virtue of the smallness of the overlap of the d shells, and particularly the f shells of the neighboring lattice sites. Consequently when the second condition in (5.8) is violated, the indicated choice of zeroth approximation signifies that one can regard independently, on the one hand, the influence of the magnetization of the d(f) subsystem on the conduction electrons (their polarization) and the reaction of the magnetized s electrons on the d(f) electrons, and, on the other side, the influence of the s-d or s-f coupling on the genesis of the strong indirect exchange between the spins in the d(f) subsystem.

We choose as the perturbation energy of the problem under consideration the Hamiltonian* $\hat{\mathcal{H}}_{sd}$ and seek the correction to the zero-point energy $\hat{\mathcal{H}}_s$ of the conduction electrons. We are likewise uninterested in their reaction on the d(f) subsystem (see Chapters III and IV below). The conduction electrons in the metal will be regarded as a Fermi-particle gas with arbitrary dispersion (see^[93]). The energy density operator of such a quasiparticle, with allowance for the perturbation, has the form

$$\hat{\mathcal{H}}(\mathbf{r}) = \hat{\mathcal{H}}_s(\mathbf{r}) + \hat{\mathcal{H}}_{sd(f)}(\mathbf{r}) = \hat{\mathcal{H}}_s(\mathbf{r}) - B(\mathbf{r})(\hat{S}_{d(f)}(\mathbf{r})\hat{S}). \quad (5.9)$$

The operator †

$$\hat{\mathcal{H}}_{sd(f)}(\mathbf{r}) = -B(\mathbf{r})(\hat{S}_{d(f)}(\mathbf{r})\hat{S}), \quad (5.10)$$

which describes the isotropic (s-d) or (s-f) exchange interaction is chosen in the form of a very simple invariant, namely the scalar product of the relative magnetization vector $\mathbf{S}_{d(f)}(\mathbf{r})$ of the d(f) subsystem and the spin vector \mathbf{S} of the conduction electron. The first term in (5.9) satisfies the invariance requirements relative to translation by the period $\mathbf{a}_{c,c}$ of the crystal-chemical lattice, $\hat{\mathcal{H}}_s = (\mathbf{r} + n\mathbf{a}_{c,c}) = \hat{\mathcal{H}}_s(\mathbf{r})$. The same condition should hold for the coefficient in the operator (5.10), namely $B(\mathbf{r} + n\mathbf{a}_{c,c}) = B(\mathbf{r})$. However, the entire operator (5.9) may not be invariant under such translations, inasmuch as the operator (5.10) is invariant under translations by the period of the elementary magnetic

*This solution method was first proposed by S. P. Shubin^[90] and was further developed by one of us jointly with E. A. Turov.^[92,92]

†Strictly speaking, we should use in (5.10) not $\mathbf{S}_{d(f)}$ but the total magnetization of the s + d system. However, by virtue of (5.3) the difference between the latter and $\mathbf{S}_{d(f)}$ is a small quantity ($\sim A_{sd}/\zeta_0$), and can be disregarded in the approximation used in (5.10).

cell $\mathbf{q}_{m.c.}$, which in general may not coincide with the crystal-chemical cell, for generally speaking

$$\mathbf{S}_{d(f)}(\mathbf{r} + \mathbf{q}_{c.c.c}) \neq \mathbf{S}_{d(f)}(\mathbf{r}).$$

The energy operator of the entire system of s electrons is given by the expression

$$\hat{\mathcal{H}} = \sum_{\sigma} \int \hat{\psi}^*(\mathbf{r}, s) \hat{\mathcal{H}}(\mathbf{r}) \hat{\psi}(\mathbf{r}, s) d\mathbf{r}. \quad (5.11)$$

The integration is carried here over the entire volume of the crystal, and the summation is over two values of the spin variable ($\sigma = \pm 1/2$); $\hat{\psi}(\mathbf{r}, s)$ is the quantized wave function of the s electron—Fermi particle (see Sec. 118 of [75]). If we confine ourselves to the first approximation and average over the states of the inner electrons, then we can show [89] that the dispersion law for the conduction electrons has the form

$$\epsilon_{\mathbf{k}}^{\sigma} = \epsilon_s^0(\mathbf{k}) - \frac{1}{2} (1 + \sigma_s \mathbf{m}_{d(f)}) \beta(\mathbf{k}), \quad (5.12)$$

where $\epsilon_s^0(\mathbf{k})$ is the energy of the s electron as a function of the quasimomentum \mathbf{k} (arbitrary dispersion law) without allowance for the interaction with the $d(f)$ subsystem; σ_s ($\sigma_s = \pm 1$) is the magnetic moment of the s electron in μ_B units; $\mathbf{m}_{d(f)}$ is the relative magnetization of the inner electrons; $\beta(\mathbf{k})$ is the energy parameter of the s - $d(f)$ interaction, connected with $B(\mathbf{r})$.* The scalar product in (5.12) is equal to $+\mathbf{m}_{d(f)}$ or $-\mathbf{m}_{d(f)}$, depending on whether the direction of the s -electron spin projection does or does not coincide with the vector $\mathbf{m}_{d(f)}$.† Formula (5.12) is valid, properly speaking, only for low temperatures (small deviation of $\mathbf{m}_{d(f)}$ from absolute saturation at 0°K). However, (5.12) can be approximately extended also to the region of high temperatures (close to the Curie point), where the assumption that the magnetization $\mathbf{m}_{d(f)}$ is close to its saturation is no longer valid. The justification for it is the fact that the term with $\mathbf{m}_{d(f)}$ in (5.12) is a small addition to the first term [it is linear in the smallness parameter A_{sd}/ζ_0 , see (5.8)]. It is known further from metal theory that the conduction electrons remain degenerate up to temperatures on the order of $10,000^\circ\text{K}$ ($\zeta \gg kT$). It is precisely for this reason that (5.12) can be used for the conduction electrons in ferromagnetic metals up to the Curie points, taking $\mathbf{m}_{d(f)}$ to mean the average statistical value of the magnetization as a function of the temperature.

Formula (5.12) can be illustratively treated as follows: as a result of the s - d or s - f exchange interaction, the s -electron spin is acted upon by a strong molecular quasimagnetic field, the magnitude of which is on the order of the Weiss molecular field, and therefore the spin degeneracy is lifted in the s -electron gas. It is also important to note that the appearance of a term with $\sigma_s \mathbf{m}_{d(f)}$ in (5.12) is connected not with the

crude model representations, but follows from the general theory and that the obtained molecular field, acting on the s electrons, greatly depends on the states of the inner electrons. The result, for example near the Curie point where the magnetization $\mathbf{m}_{d(f)}$ depends sharply on the temperature, is a noticeable redistribution of the momenta (in the region of the Fermi energy) of the electrons in the "gas" of the ferromagnetic-metal conduction electrons, unlike in nonmagnetic metals, and their effective mass should change in addition. Using the customary formal definition of the latter, $m^* = \frac{\hbar^2}{a^2} \left(\frac{\partial^2 E(\mathbf{k})}{\partial k^2} \right)^{-1}$, we obtain from the dispersion law (5.12)*

$$m_{\sigma}^*(\mathbf{k}) = \hbar^2 [a(\mathbf{k}) + \beta'(\mathbf{k})(\sigma_s \mathbf{m}_{d(f)})]^{-1} a^{-2}, \quad (5.13)$$

where a is the lattice parameter, $\alpha(\mathbf{k})$ a quantity on the order of the Fermi energy ζ , and $\beta'(\mathbf{k})$ is on the order of the s - $d(f)$ exchange parameter. In the approximation of a quadratic dispersion law

$$\epsilon_{\mathbf{k}}^{\sigma} = \alpha_0 - \beta_0 (\sigma_s \mathbf{m}_{d(f)}) + \frac{1}{2} [\alpha_1 + \beta_1 (\sigma_s \mathbf{m}_{d(f)})] k^2, \quad (5.14)$$

where α_0 , β_0 , α_1 , and β_1 are independent of the quasimomentum, we obtain in place of (5.13)

$$m_{\sigma}^* = \hbar^2 [\alpha_1 + \beta_1 (\sigma_s \mathbf{m}_{d(f)})]^{-1} a^{-2}. \quad (5.15)$$

If we take into account the anisotropic exchange interaction [94], we obtain for the effective-mass tensor in place of (5.15) [95]

$$\begin{aligned} m_{\sigma_{\perp}}^* &= (\hbar/a^2) \{2[\alpha_1 - \sigma_s (\beta_1 + R)]\}^{-1}, \\ m_{\sigma_{\parallel}}^* &= (\hbar/a^2) \{2[\alpha_1 - \sigma_s (\beta_1 - 2R)]\}^{-1}, \end{aligned} \quad (5.16)$$

where $m_{\sigma_{\perp}}^*$ and $m_{\sigma_{\parallel}}^*$ are respectively the "longitudinal" and "transverse" terms of the effective mass relative to the magnetization direction, and R is a certain linear combination of the quasi-Coulomb and exchange parameters of the magnetic interaction ($\mathbf{m}_{d(f)} = -1$).

To estimate the influence of the magnetization effect on the thermodynamic properties of the ferromagnet it is necessary to consider one of the thermodynamic potentials, for example the free energy F . Its determination is facilitated by the fact that the energy (5.12) is the same for all the states of the $d(f)$ electrons with specified magnetic moment $\mathbf{m}_{d(f)}$. F can therefore be written in the form [91, 15, 16]

$$F = F_0(m_{d(f)}, T) + F_1(m_{d(f)}, m_s, T), \quad (5.17)$$

where F_0 and F_1 are respectively the free energy of the $d(f)$ electrons without account of the s - $d(f)$ exchange and of the s electrons with account of this ex-

* $\beta(\mathbf{k}) = \int \psi^*(\mathbf{k}, \mathbf{r}) B(\mathbf{r}) \psi(\mathbf{k}, \mathbf{r}) d\mathbf{r}$, where $\psi(\mathbf{k}, \mathbf{r})$ are the wave functions of the electron in the crystal.

†Formula (5.12) was first derived in [91, 92].

*We can also use a more consistent definition of the effective mass, by considering the motion of the s electron of the ferromagnetic metal in the external magnetic field. [93]

change. The latter can be replaced simply by virtue of the energy of the Fermi gas of the s electrons, in view of the degeneracy. We introduce the notation

$$n = n_+ + n_-, \quad m_s = \frac{n_+ - n_-}{n}, \quad (5.18)$$

where n is the total number of the s electrons per unit volume, n_+ and n_- are respectively the numbers of these electrons with right hand and left hand spin projections, and m_s is their average relative magnetization in μ_B units. The energy density of the degenerate gas is^[1-4,63,15,16,91]

$$\frac{3}{5} (n_+ \zeta_+ + n_- \zeta_-), \quad (5.19)$$

where ζ_+ and ζ_- are respectively the Fermi energies for the right-hand and left-hand electrons, equal to

$$\zeta_+ = \frac{\hbar^2}{2m_s^*} \left(\frac{3n_+}{4\pi} \right)^{2/3}, \quad \zeta_- = \frac{\hbar^2}{2m_s^*} \left(\frac{3n_-}{4\pi} \right)^{2/3} + \beta_0 m_{d(f)}. \quad (5.20)$$

Using (5.14), (5.15) and (5.17)–(5.20) we obtain accurate to constant terms

$$F(m_{d(f)}, m_s, T) = F_0(m_{d(f)}, T) + n[-\beta_0 m_s m_{d(f)} + \lambda(\alpha_1 + \beta_1 m_{d(f)})(1 + m_s)^{5/3} + \lambda(\alpha_1 - \beta_1 m_{d(f)})(1 - m_s)^{5/3}], \quad (5.21)$$

where $\lambda = (3\pi^2)^{5/3} (10\pi^2)^{-1} \sim 3$. From the condition that (5.21) be a minimum we can determine in principle the equilibrium values of the magnetizations $m_{d(f)}$ and m_s . If we use the smallness of the ratios β_0/ζ_0 and β_1/ζ_0 ($\ll 1$), we obtain

$$m_s = c m_{d(f)}, \quad c = \frac{3}{2} \left(\frac{\beta_1}{\alpha_1} - \frac{3}{5} \frac{\beta_0}{\alpha_1} \right) \sim 0.1 - 0.01. \quad (5.22)$$

Inasmuch as the coefficient c is in first approximation independent of T , $m_{d(f)}$ and m_s near the Curie point have the same temperature dependence $\sim (\theta - T)^{1/2}$, as shown in^[91,15].

The expressions obtained make it possible in principle to explain one of the possible causes of the fractional nature of the atomic magnetic moments of ferromagnetic metals^[15,91,96]. Indeed, those values of atomic moments which satisfy the minimum of (5.21) even at 0°K need not be integers (in units of μ_B). This fractionality at 0°K and the fractionality at higher temperatures, determined in terms of the Curie constants (see Sec. 2) will manifest themselves, generally speaking, in different ways. To be sure, this “fractionality effect” is of course not the only one and may even be the principal one (see Secs. 2–4 and Ch. 5).

To explain the nature of the “anomalies” of the kinetic coefficients in ferromagnetic metals (and also in paramagnetic transition metals) there are two causes of specific “anomalies” compared with the same properties of normal metals. First, owing to the presence of (at least) two sorts of current carriers (for example, the s and d electrons) and to the increased level density, additional opportunities for the scattering of carriers occur at the Fermi sur-

face (s - d transitions after Mott^[66] and scattering by magnetic inhomogeneities^[4,98,99]). All this can make its own additive contributions to the electric resistivity. Second, the kinetic coefficients may also be influenced by a change in the energy spectrum of the s electrons in transition metals, which have magnetic order (ferromagnetic or antiferromagnetic). This may lead to a different temperature dependence even in the phonon part of the specific electric resistivity. Indeed, for example in the case of high temperatures (compared with the Debye temperature of the metal) in a ferromagnetic metal, the collision time (relaxation time) of the conduction electrons τ_f depends on the temperature not only because of the collisions between the electrons and the phonons, the number of which varies with the temperature, but also because of the dependence of the chemical potential ζ_0 of the electrons on the temperature via the magnetization [see formula (5.2)]. As is well known^[1-4,63] the time τ_f is inversely proportional to the mean square of the amplitude of the thermal vibrations of the lattice (which indeed yields the ordinary phonon dependence on the temperature $\tau_f = 1/T$), and also the density of the electron states near the Fermi surface, which in turn is inversely proportional to the energy gradient $|\nabla_{\mathbf{k}} \epsilon_{\mathbf{k}}^{\sigma}|_{\zeta}^{-1}$ in the quasimomentum space near the same surface [see (4.7)]. Finally, τ_f is also directly proportional to the square of the quasimomentum at the Fermi surface $k_{(\epsilon=\zeta)}^2$. As a net result, the phonon relaxation time for the conduction electrons of a ferromagnet will be

$$\tau(\zeta_{\pm}) = \frac{A'}{T} [k_{(\epsilon=\zeta_{\pm})}]^{-2} (\nabla_{\mathbf{k}} \epsilon_{\mathbf{k}}^{\pm})_{\zeta_{\pm}}^{\pm}, \quad (5.23)$$

where A' incorporates all the constants that are independent of T and of $(m_{d(f)} + m_s)$. The quantities $k_{(\epsilon=\zeta_{\pm})}$ can be defined in terms of the corresponding Fermi-gas densities^[1-4,63]

$$k_{(\epsilon=\zeta_{\pm})} = h \left(\frac{3n_{\pm}}{4\pi} \right)^{1/3}. \quad (5.24)$$

For the energy gradient we obtain by virtue of (5.14) and (5.24)

$$\nabla_{\mathbf{k}} \epsilon_{\mathbf{k}}^{\pm} = h (\alpha_1 \pm \beta_1 m_{d(f)}) \left(\frac{3n_{\pm}}{4\pi} \right)^{1/3}. \quad (5.25)$$

Substituting (5.24) and (5.25) in (5.23) we obtain

$$\tau^{\pm}(\zeta) = \frac{A}{T} (\alpha_1 \pm \beta_1 m_{d(f)}) (1 \pm \frac{1}{3} m_s), \quad (5.26)$$

where A is independent of T . With the aid of the Drude formula [see item f) in Sec. 2] $\sigma_{\pm} = n_{\pm} e^2 \tau^{\pm}(\zeta) / m_{\pm}^*$ for s electrons with different spin projections we can, by using the foregoing formulas, obtain an expression for the ferromagnetic “anomaly” of the electric resistivity (more accurately, its phonon part) of ferromagnetic transition metals, due to the change in the energy spectrum of the conduction electrons. This additional resistance is equal to

$$\frac{\Delta \rho}{\rho_0} = c' (m_{d(f)} + m_s)^2, \quad (5.27)$$

where ρ_0 denotes the "normal" phonon resistance and c' is a constant. It is meaningful to compare this formula with experiment in conjunction with the contribution to the electric resistivity due to the additional scattering of the carriers by the magnetic inhomogeneities (and also, generally speaking, in an account of the s - d transition^[68]). These processes have been considered in many papers^[1,49,98-103] and we shall treat this question in greater detail in Sec. 16 of Ch. IV. See also^[87].

Within the framework of the same simple considerations it became possible to explain one of the causes of ferromagnetic anomalies and other properties of metals such as optical^[104], magneto-optical^[105], photoelectric^[106], thermoelectronic^[107], absorption of sound^[108], x-ray spectra^[109], and paramagnetic susceptibility^[110].

d) The results obtained for the calculation of the effects of "magnetized" conduction electrons in ferromagnetic metals can be generalized to include ferromagnetic semiconductors^[111,112]. In this case formula (5.12) for the conduction-electron dispersion laws signifies that the activation energy (the gap ΔE) and the width of the conduction band or the effective mass of the current carrier show different dependence on the magnetization of the semiconductor for different carrier spin projections. For example, if the state with $k = 0$ corresponds to the lowest energy (the "bottom" of the conduction band^[112]), then according to (5.14) the activation energy is

$$\Delta E = \alpha_0 - \beta_0 (\sigma_s m_{d(f)}), \quad (5.28)$$

where $\alpha_0 = \Delta E_0$ is the activation energy of the paramagnetic state ($m_{d(f)} = 0$). It is seen from (5.28) that regardless of the sign of the s - d (f) coupling parameter, the conduction band is split into two sub-bands owing to the lifting of the spin degeneracy of the carriers. We can therefore expect from the most general considerations the appearance of ferromagnetic anomalies on going through the Curie point for those properties of the semiconductor, which depend on the activation energy of the elementary excitations. The electric conductivity of a ferromagnetic semiconductor in the paramagnetic region depends on T in accord with the formula

$$\sigma_p = A_p \exp\left(-\frac{\Delta E_0}{kT}\right), \quad (5.29)$$

where A_p is the pre-exponential factor, which depends weakly on T . Below the Curie point we have in place of (5.29), by virtue of (5.28)

$$\sigma_f = A_p e^{-\Delta E_0/kT} [c_1 e^{\beta_0 m_{d(f)}/kT} + c_2 e^{-\beta_0 m_{d(f)}/kT}], \quad (5.30)$$

where c_1 and c_2 depend weakly on T and where $c_1 = c_2 = 1/2$ when $m_{d(f)} = 0$. The asymptotic behavior of $\ln \rho_f$ ($\rho_f = \sigma_f^{-1}$ is the electric resistivity) at tempera-

tures considerably below the Curie point ($m_{d(f)} \rightarrow 1$ and $\beta_0 \gg k\Theta_f$) yields*

$$\ln \bar{\rho}_f = \ln(A_p \bar{c}_1) + \frac{(\Delta E_0 - \beta_0)}{kT}, \quad (5.31)$$

where the superior bar denotes the asymptotic value and in the paramagnetic region

$$\ln \rho_p = -\ln A_p + \frac{\Delta E_0}{kT}. \quad (5.32)$$

Thus, in going over from (5.31) to (5.32) we must have an increase in the slope of the line $\ln \rho = f(1/T)$ (see Fig. 15a-d). From the size of this decrease $\Delta E = -\beta_0$ we can determine directly the exchange interaction parameter ($\beta_0 > \Delta E_0$), the sign of the temperature coefficient of electric resistivity may even reverse, i.e., the conductivity may become metallic (Figs. 15c and d). The straight-line portion of the $\ln \bar{\rho}_j$ curve given by (5.31) can be extrapolated to the Curie point Θ_f and the value of $\ln \rho_p$ for the same point subtracted from the resultant quantity; this yields

$$\delta = \ln \bar{\rho}_f\left(\frac{1}{\Theta_f}\right) - \ln \rho_p\left(\frac{1}{\Theta_f}\right) = -\left[\ln \bar{c}_1 + \frac{\beta_0}{k\Theta_f}\right]. \quad (5.33)$$

Thus, the asymptotic line (5.31) will have, in addition to the kink at the Curie point, also a jump δ relative to the $\ln \rho_p$ line. The direction of this jump is determined by the sign of the expression in the right half of (5.33). Inasmuch as the second term in the bracket is always greater than zero, the sign of δ is determined by the quantity c_1 . The experimental curves of the type shown in Fig. 15a were clearly observed by Belov et al^[54a] in manganese ferrites. A kink in the $\ln \rho$ curve near the Curie point was observed in several ferrites earlier by Komar and Klyushin^[54a]. In some of these, a weak bending of the type of Fig. 15a could

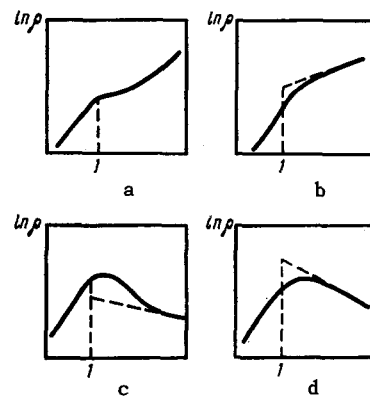


FIG. 15. Various types of "anomalies" in the specific electric resistivity of ferromagnetic semiconductors. The abscissas are Θ_f/θ .

*For the sake of being specific it is assumed that $\beta_0 > 0$. When $\beta_0 < 0$ it is necessary to replace in (5.31) c_1 by c_2 and β_0 by $|\beta_0|$. The physical result will be the same.

be noted. In the ferrites in which only a kink was observed, there probably exist anomalies of the type of Fig. 15b. Apparently, an anomaly of the type of Fig. 15c was observed in copper-zinc ferrite also by Suchkov^[54a]. Anomalies of the type of Figs. 15b-d were found by Folger^[54a] in ferromagnetic compounds of manganese with perovskite structure, namely magnetites.

The formulas obtained for ferromagnetic metals and for semiconductors with a single magnetic sublattice were generalized to include both atomic and polar antiferromagnetic semiconductors^[112,113] and also ferrites^[113,114,112] containing two and more magnetic sublattices.

In a ferromagnetic metal, the s-d(f) exchange interaction leads to a magnetization of the conduction electrons, while in the case of an antiferromagnetic metal, the influence of the spin system on the s electrons has a different character. By virtue of the s-d(f) exchange, the localization of the s electron with different spin projections near the sites of different magnetic sublattices is no longer energetically equivalent. Because of this, an appreciable change takes place in the dispersion law for the s electrons, analogous to that occurring in the theory of binary ordered alloys^[115]. As shown by Irkhin^[116], in the case of an antiferromagnetic metal with two collinear and equivalent magnetic sublattices (in the strong coupling approximation of the band theory, and also for the case of high temperatures, i.e., near the Néel point Θ_N), the dispersion law for the s electrons has the form

$$\left. \begin{aligned} \epsilon_1(\mathbf{k}) &= L - \frac{1}{2} (\mu^2 \lambda^2 + 4 \left| \sum_{\mathbf{h}} L(\mathbf{h}) e^{i\mathbf{k}\mathbf{h}} \right|^2)^{1/2}, \\ \epsilon_2(\mathbf{k}) &= L + \frac{1}{2} (\mu^2 \lambda^2 + 4 \left| \sum_{\mathbf{h}} L(\mathbf{h}) e^{i\mathbf{k}\mathbf{h}} \right|^2)^{1/2}, \end{aligned} \right\} \quad (5.34)$$

where μ is the relative magnetization of the sublattice of the d or f electrons ($\mu \ll 1$), while L , λ , and $L(\mathbf{h})$ are the parameters of the s-d(f) exchange; L and $L(\mathbf{h})$ contains also quasi-Coulomb terms of the s-d(f) coupling. It follows from (5.34) that in the paramagnetic region ($\mu \equiv 0$) the ordinary dispersion law holds true for the s electrons of the band model. At temperatures below the Neel point ($T < \Theta_N$) we have $\mu \neq 0$ and in accordance with (5.34) a gap of forbidden energies, of width $\sim \mu|\lambda|$, is formed at the center of the energy band of the s electrons of the antiferromagnetic metal. Inasmuch as the magnetizations of the sublattices vary rapidly with temperature near Θ_N , one can expect in this temperature region sharp antiferromagnetic "anomalies" of different physical properties, including also the electric conductivity. We can separate here two limiting cases^[116]: 1) the Fermi surface is located exactly at the center of the conduction band (prior to its splitting)* and 2) the

Fermi surface is located near the edge of the conduction band.

In the former case, the energy gap produced below the Néel point will separate the free sub-band from the completely filled one (5.34), which should lead simultaneously, on going through the Néel point, to a transition from the metallic to the semiconductor state. Taking into account only the exponential part of the dependence of the electric conductivity [see, for example, (5.29)] on T and using (5.33), we have

$$\sigma \sim \exp \left[-\frac{\mu(T)\lambda}{2kT} \right]. \quad (5.35)$$

It is seen from (5.35) that the activation energy in this case depends itself on T . This should distort somewhat the ordinary semiconductor variation of the electric conductivity with T , particularly near Θ_N .

In the second limiting case one can use the effective-mass approximation (see^[1-4,63]) and carry out the usual band-theory calculation of the electric resistivity for high and low temperatures. This yields^[116]

$$\left. \begin{aligned} \varrho &= \alpha T + \beta \mu^2(T) T & (T \gg \Theta_D), \\ \varrho &= \alpha' T^5 + \beta' \mu^2(T) T^5 & (T \ll \Theta_D), \end{aligned} \right\} \quad (5.36)$$

where α , α' and β , β' are quantities independent of T , and Θ_D is the Debye temperature. The first terms in (5.36) make the ordinary phonon contributions to the electric conductivity, while the second have arisen as the result of a change in the energy spectrum of the s electrons upon appearance of antiferromagnetic ordering.*

In the case of arbitrary location (and shape^[95]) of the Fermi surface in the antiferromagnetic metal, the effects that are characteristics of the two limiting cases considered above will be superimposed on each other in some manner. The results obtained here are in sufficiently good qualitative agreement with the experimental data, for example for manganese^[53a]. The crudeness of the developed calculation does not enable us, naturally, to speak of a quantitative comparison between theory and experiment in the case of the phenomenon considered.

Turov and Irkhin^[112] extended these calculations to the case of antiferromagnetic semiconductors and to ferromagnets, while Giterman and Irkhin^[114] calculated the case of antiferromagnetic polar crystals. We refer the readers to the original articles for details of these calculations.

In the low-temperature region, ferromagnetic and antiferromagnetic metals have an additional electric resistivity and heat resistivity that are specific to them and are due to collisions of the s electrons with the ferromagnons, which can exceed in magnitude the

*This case is possible, for example, in a body-centered cubic lattice in which there is one s-electron per atom.

*Here, as in the case of ferromagnetic metals, we must bear in mind the existence of other possible causes of the antiferromagnetic anomalies in the kinetic effects (see^[49,98-102]). In addition, at low temperatures ($T \ll \Theta_D$) the condition $\mu \ll 1$ may no longer be satisfied (see also Sec. 16 below).

phonon resistivities, in a definite temperature interval, owing to the specific dependence on T . The idea of the existence of this effect was first advanced in [117,118]; more detailed calculations were made in [119]. It was shown by Turov's detailed investigations [120-122] that the ferromagnon part of the electric resistivity ρ_{fm} is represented in the general case by a complicated function and can be only approximately given as a sum of two terms:

$$\rho_{fm} = a_1 T + a_2 T^2, \quad (5.37)$$

where a_1 and a_2 are quantities independent of T . This question will be considered in greater detail in Sec. 16 of Ch. IV.

e) To conclude this section let us consider still another problem connected with s-d(f) exchange, namely the influence of the spin and electron systems of a transition metal on the atomic nuclei of its ions, the so-called phenomenon of orientation of atomic nuclei in crystals, due to interaction between the magnetic moments of the electron orbits and spins, on the one hand, and nuclear magnetic moments on the other. In isolated atoms this interaction leads to a hyperfine structure (hfs) of the spectral lines and is therefore called the "hyperfine" or hfs coupling [58,123]. Methods of microwave spectroscopy, and particularly paramagnetic resonance, make it possible to investigate the hfs coupling in solids, too, and this yielded rich information on the electronic structure of ions in various compounds [58,167,168]. Inasmuch as in ferromagnetic crystals the resonance lines are usually very broad, it is difficult to resolve the hfs components for them. Therefore in ferromagnetic metals and alloys use is made of other experimental methods for determining the hfs. At the same time, knowledge of the hfs coupling for ferromagnets and antiferromagnets, particularly metallic ones, can yield in principle important information on the state of the electrons responsible for the magnetic atomic order. In a ferromagnetic crystal, owing to its spontaneous magnetization M_S at $T < \Theta_f$, each atomic nucleus is situated in a certain effective magnetic field H_{eff} , which has the same value and direction inside the ferromagnetic domain.* If the nuclei have magnetic moment μ_{nuc} and a spin quantum number I , then $(2I + 1)$ orientations of the nucleus relative to H_{eff} are possible, and the energy differences for each two neighboring orientations are $\mu_{nuc} H_{eff} / 2I$. At high temperatures all the nuclear spins are randomly distributed over all possible orientations. At low temperatures, however, $kT \lesssim \mu_{nuc} H_{eff} / 2I$, all the nuclear spins will be parallel to H_{eff} , i.e., total orientation of the nuclei takes place within the volume of each ferromagnetic domain. Inasmuch as the degree of nuclear polarization depends

*This field, which has essentially an intra-atomic character, must not be confused with the interatomic exchange field, which is responsible for the ferromagnetic order in the crystal.

in a known manner on the Boltzmann factor, H_{eff} can be determined if the nuclear polarization, μ_{nuc} , I , and T are known. At the present time there are three experimental methods for the determination of H_{eff} in ferromagnets.*

1) Determination of H_{eff} by measuring the anisotropy of gamma or beta radiation. In this method use is made of the fact that the gamma or beta rays emitted by decaying radioactive nuclei are anisotropic. At high temperatures, when the nuclear spins have random orientations, the overall intensity of the radioactivity from the specimen is isotropic. At low temperatures, on the other hand, when the distribution of the nuclear spins relative to the spontaneous magnetization M_S of the ferromagnet electrons becomes ordered, the radiation in the domain becomes anisotropic, and if the specimen is magnetized to saturation the overall radiation from the specimen will also be anisotropic. By way of a measure (factor) of the anisotropy one chooses the quantities

$$\epsilon_{\gamma, \beta} = \frac{W_{\gamma, \beta} \left(\frac{\pi}{2} \right) - W_{\gamma, \beta} (0)}{W_{\gamma, \beta} \left(\frac{\pi}{2} \right)},$$

where $W_{\gamma, \beta}(\Theta)$ is the intensity of the gamma or beta radiation in a direction making an angle Θ with M_S .† Using the formula for the angular distribution of the gamma or beta rays [128], we can obtain an approximate expression for $\epsilon_{\gamma, \beta}$ (see [127c]):

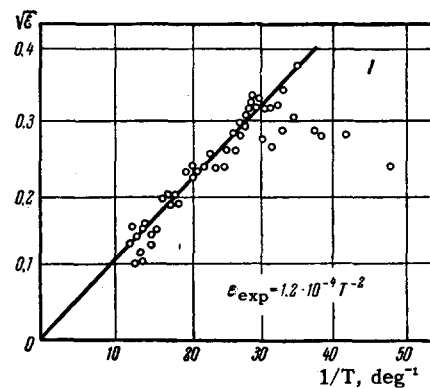


FIG. 16. Temperature dependence of the anisotropy factor of gamma radiation from radioactive oriented nuclei in a crystal. [127b]

*The idea of this method was first advanced by Khutsishvili [124]. The first experiments on the measurement of the anisotropy of gamma radiation of polarized nuclei were carried out by Alekseevskii and Shchegolev [125] and by Zavaritskii (see [124b]), and also by a group headed by Kurti [126] for Co^{60} in polycrystalline and single-crystal cobalt specimens at $T \sim 0.03-0.08^\circ K$. Samoĭlov, Sklyarevskii, and Stepanov [127] extended this method to the case of polarization of nuclei of diamagnetic elements in a ferromagnetic crystal, and also by using measurements of the beta-radiation anisotropy.

† Inasmuch as $W_{\gamma}(\pi) = W_{\gamma}(0)$, to observe the summary anisotropy of the gamma radiation it is sufficient for the ferromagnetic specimen to contain domains with only the 180° type of neighborhoods even in the demagnetized state.

$$\varepsilon_\gamma = \text{const} \left[\frac{\mu_{\text{nuc}} H_{\text{eff}}}{kT} \right]^2, \quad \varepsilon_\beta = \text{const} (I+1) \frac{v}{c} \left[\frac{\mu_{\text{nuc}} H_{\text{eff}}}{kT} \right], \quad (5.38)$$

where the constants depend on the character of the radioactive decay of the nuclear spin^[127c], v is the velocity of the beta particle, and c is the velocity of light. It is seen from (5.38) that the anisotropy of the gamma radiation makes it possible to determine the value of H_{eff} , while the anisotropy of the beta radiation determines also the sign of this field. Experiment^[125,126,127] has confirmed formula (5.38). Figure 16 is a typical plot of $\sqrt{\varepsilon}$ vs. $1/T$ ^[127b]; the values obtained for H_{eff} are $\sim 10^5$ – 10^6 Oe.* The measured anisotropy of the beta radiation for Co^{60} nuclei in an alloy of cobalt with iron have shown that H_{eff} is negative (relative to M_S)^[127].

2) Determination of H_{eff} by measuring the additional specific heat connected with the polarization of the nuclei in the crystals. This specific heat C_{on} reaches a maximum at $KT_1 \sim \mu_{\text{nuc}} H_{\text{eff}}/2I$, and when $T > T_1$ it has the form (see supplement to^[129]).

$$\frac{C_{\text{on}}}{R} \cong (I+1) I \left(\frac{\mu_{\text{nuc}} H_{\text{eff}}}{kT} \right)^2. \quad (5.39)$$

Inasmuch as all other contributions to the specific heat (from the lattice, from the conduction electrons, and from the spin waves) are vanishingly small below 1°K, the experiment yields in practice the value of C_{on} , from which H_{eff} is determined.† Figure 17 shows a C/R curve for terbium in accordance with the data of^[133]. From this we obtain for H_{eff} a value 5700 kOe.‡

*Figure 16 shows the average scatter of the experimental points; the latter fit quite well the line $\sqrt{\varepsilon} = \sqrt{1.2} \times 10^{-2} T^{-1}$ up to a temperature 0.04°K. The deviations from this line at lower temperatures are apparently due to the maximum of C of cobalt, which does not give the specimen enough time to cool to the temperature of the salt.^[127b]

† The first indications concerning the use of this method were given by Heer and Erickson,^[130] who made the first experiment with cobalt^[131] and found a value of 183 kOe for H_{eff} . Arp, Kurti, and Peterson^[132] repeated these experiments and found $H_{\text{eff}} = 200$ kOe. Kurti and Safrata^[133] measured C for the rare-earth metals gadolinium and terbium. No C_{on} component was found for Gd, probably owing to some additional specific-heat anomaly which has not yet been explained. In the case of Tb one observes clearly a rise in the C/R curve (see Fig. 17) below 1°K, connected with the nuclear polarization. The field H_{eff} was determined from (5.39) and found to be 5700 kOe. It can be compared with the value $H_{\text{eff}} = 6100$ kOe obtained from paramagnetic resonance experiments^[134] for terbium ethyl sulfate. It is clear therefore that in a metal and nonmetallic salt the hfs interaction is practically the same (the small difference can be attributed to different distributions of the electron density in the 4f group of the Tb ion). Consequently, the role of the conduction electrons in the formation of H_{eff} is apparently not very large.

‡ The curve of Fig. 17 gives the sum of the lattice ($\sim T^3$), ferromagnon ($\sim T^{3/2}$) and oriented-nuclei ($\sim 1/T^2$) specific heats; the corresponding distribution is shown in Fig. 17.

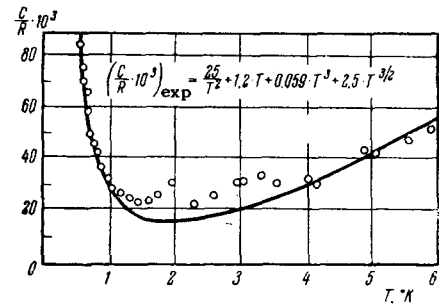


FIG. 17. Temperature dependence of the specific heat of terbium at low temperatures. The summary specific heat is made up of the lattice specific heat ($\sim T^3$), that of the conduction electrons ($\sim T$), of the ferromagnons ($\sim T^{3/2}$) and the nuclear component C_{on} (after^[133]).

The values of H_{eff} determined by any of these two methods can be compared, for example, with the value of the same field obtained in paramagnetic salts for the same ions, by studying the variation of this field with changing composition of the investigated alloy or with changing crystal structure.*

3) Determination of H_{eff} from the Zeeman nuclear multiplet produced by H_{eff} in measurement of the Mössbauer effect. The resonant absorption of gamma quanta in crystals, discovered by Mössbauer^[135] in 1956, has already been used in many practical ways to study many physical phenomena (see, for example, the reviews^[136]), including the determination of the magnitude and the field H_{eff} acting on the atomic nuclei in ferromagnetic crystals. In the case of the 14.4-keV gamma radiation from Fe^{57} , occurring in the decay of Co^{57} , the spectral line has a very small natural width, so that the hfs can be resolved for the 14.4-keV transition^[136,137]. These experiments yielded $H_{\text{eff}} = 3.33 \times 10^5$ Oe. By superimposing a 20-kOe external magnetic field, which decreased the magnitude of the hfs splitting, it was demonstrated that the direction of H_{eff} is opposite that of m_S . The latter was also demonstrated for cobalt^[138]. The case of Dy^{161} nuclei at room temperatures was also investigated and it was found that $H_{\text{eff}} \sim 2 \times 10^6$ Oe^[139,127d]. In Table X,

*Wei, Cheng, and Beck^[166] recently measured the nuclear magnetic specific heat (5.39) from 1.6° to 4.2°K in two ferromagnetic alloys of one structure (body centered cubic lattice): $\text{Co}_{0.3}\text{Fe}_{0.7}$ and $\text{V}_{0.33}\text{Fe}_{0.67}$, and have found that in the former alloy the Co nucleus is acted on by a field $H_{\text{eff}} \sim 312$ kOe, while the V nucleus in the second alloy is in a field ~ 61 kOe. Following^[137a], the authors of^[166] attribute this difference in H_{eff} to the fact that the Co^{59} nucleus is acted upon by a field H_{eff} which arises principally because of the magnetization of the s electrons of their own ionic core (i.e., Co), produced by their (s-d) exchange coupling with the 3d electrons of the same core, which have an uncompensated magnetic moment. In the case of the vanadium ion, on the other hand, its core apparently does not have the uncompensated 3d-electron moment, and therefore the contribution to H_{eff} is made by the same magnetization of the s electrons of the core of this vanadium ion, which in this case arises as a result of the weaker (s-d) exchange coupling with the neighboring iron ions.

Table X. Effective field H_{eff} acting on the nuclei in ferromagnets and antiferromagnets [169]

Nuclei	Substance	$H_{\text{eff}} \cdot 10^4 \text{Oe}$	Method of determination	Temperature of experiment, degrees K	Literature
^{57}Fe	Fe	-3.42	M	0	137
	Co	3.30	NMR	295	171
	Ni	3.12 ± 0.05	M	0	146
	CoPd	3.3	»	88	137, 172
$^{57}\text{Fe}^{3+}$ (tetra)	YIG	3.92 ± 0.05	»	Room	173
		3.90	»	»	174
		3.9	NMR	»	176
		3.90 ± 0.07	M	»	176
		4.6	»	Liquid air	174
$^{57}\text{Fe}^{3+}$ (oct)	YIG	4.74 ± 0.06	»	Room	173
		4.85	»	»	174
		4.7	NMR	»	175
		4.90 ± 0.07	M	»	176
		5.4	»	Liquid air	174
$^{57}\text{Fe}^{3+}$ (tetra)	DyIG	3.90	»	Room	174
		4.6	»	Liquid air	174
$^{57}\text{Fe}^{3+}$ (oct)	DyIG	4.85	»	Room	174
		5.4	»	Liquid air	174
$^{57}\text{Fe}^{3+}$	GdIG	4.0 and 4.9	NMR	Room	175
^{57}Fe	Fe_3O_4	5	M	»	146
		4.70 ± 0.20	»	»	176
		4.50 ± 0.20	»	»	176
		5.0 ± 0.20	»	»	177
		4.5 ± 0.20	»	»	177
		5.1 ± 0.20	»	»	177
		(tetra)	»	»	177
$^{57}\text{Fe}^{3+}$	$\text{NiO} \cdot \text{Fe}_2\text{O}_3$	4.5 ± 0.20 (oct)	»	85	177
		5.1	»	Room	146
$^{57}\text{Fe}^{3+}$	$\alpha\text{-Fe}_2\text{O}_3$ $\gamma\text{-Fe}_2\text{O}_3$	5.1 ± 0.20	»	»	177
		5.15	»	»	178
		5.0 ± 0.1	»	»	179
		5.05 ± 0.20	»	300	177
$^{57}\text{Fe}^{3+}$	$\text{Mg} \cdot \text{O}$	5.15 ± 0.20	»	85	177
		5.50	EPR	1.3	180
$^{57}\text{Fe}^{3+}$	FeF_2	3.40	M	0	145
^{59}Co	Co (fcc) Co (hcp) Fe Ni Fe $\text{Co}_{0.83}\text{Fe}_{2.17}\text{O}_4$	2.134	NMR	Room	168
		2.28	»	0	171
		2.20	C_{nuc}	0	131, 132
		3.20	»	0	131, 132
		0.80	»	0	131, 132
		3.0 ± 0.2	M	4.5	181
		4.10 ± 1.0	C_{nuc}	0	182
		1.70	NMR	Room	183
		-1.70	M	»	184
^{119}Sn	Fe Co Ni Mn_2Sn Mn_4Sn	-0.81 ± 0.04	»	100	142, 185
		-0.205 ± 0.015	»	100	142, 185
		$+0.185 \pm 0.01$	»	100	142, 185
		-0.45	»	0	188
		+2.00	»	0	186
^{198}Au	Fe	7.5	NP	0.015	127
^{114}In	Fe	1.8	NP	0.015	127
^{122}Sb	Fe	2.0	NP	0.015	127

M—Mössbauer effect, NMR—nuclear magnetic resonance, EPR—electron paramagnetic resonance, NP—nuclear polarization. If the symmetry of the radioactive nucleus site is indicated in the reference, it is listed also in the table. The plus or minus signs of the field are indicated clearly if known; if the fields are not indicated, this means that they are unknown.

taken from [169], is given a summary of the experimental data on the measurement of the fields H_{eff} acting on nuclei in various substances. The table also shows the temperature of the experiment, the method of measuring H_{eff} , the symmetry of the arrangement of the crystal lattice site occupied by the investigated ion (if that symmetry was reported in the corresponding source), and also the sign of the field relative to the magnetization of the electron system. Table X indicates also all the literature sources.

It must be emphasized that the fields H_{eff} , if correctly interpreted, can yield very valuable information

on the distribution of the "magnetic" electrons in the crystal, and also help clarify the physical nature of the magnetic properties of the transition metals (the genesis of the exchange coupling etc.). Watson and Freeman recently published a detailed investigation [169], in which they attempt to explain the origin of the effective fields in magnetic materials. Their analysis is based on the assumption that the main cause of these fields are effects of exchange polarization of the internal s electrons of the ionic cores of the crystal lattice, due to their exchange coupling with the uncompensated magnetic moments of the 3d or 4f electrons of the same

cores. The direct action on the nuclei is exerted by the Fermi contact mechanism^[140,141]. The Hamiltonian of this interaction between one nucleus and one electron is

$$\hat{\mathcal{H}} = -g g_{\text{nuc}} \mu_B \mu_{\text{nuc}} \left\{ \frac{8\pi}{3} \delta(\mathbf{r}) \mathbf{I} \mathbf{S} + r^{-3} \mathbf{I} (\mathbf{L} - \mathbf{S}) + 3r^{-5} (\mathbf{I} \mathbf{r}) (\mathbf{S} \mathbf{r}) \right\}, \quad (5.40)$$

where \mathbf{L} , \mathbf{S} , and \mathbf{I} are respectively the operators of electrons, orbital, spin, and nuclear spin moments; g and g_{nuc} are the electron and nuclear spectroscopic splitting factors. The term with the δ -function in (5.40) is called the Fermi contact interaction; it differs from zero only for s electrons whose wave function has no nodes on the nucleus. To the contrary, for s electrons the two last dipole terms in (5.40) vanish. Thus, the Fermi contact interaction can be set in correspondence with an effective magnetic field equal to

$$H_c = \frac{8\pi}{3} g \mu_B \mathbf{S} |\psi(0)|^2, \quad (5.41)$$

where $\rho(0) = |\psi(0)|^2$ is the density of the s electrons in the nucleus. Experiment shows that in many magnetic substances the sign of H_{eff} is negative with respect to the electron magnetization of the crystal. An analysis of the data on the measurement of H_{eff} for 3d metals, ferrites, rare earth ferrites with garnet structure, and also many salts have made it possible for Watson and Freeman^[169] to state, in contradiction to the previous pronouncements, for example in the well-known paper by Marshall^[129], that the main contribution to H_{eff} is made practically always by exchange polarization of the s electrons of the ionic cores of the crystal lattice with the spin density of the unpaired d or f electrons. As was first pointed out by Marshall^[129], in addition to the contribution of H_c from (5.41), the effective field includes also a local component H_l , which consists of the external field, the demagnetizing field of the specimen surface, and the Lorentz field $4M/3$, as well as the corrections to it for the case of noncubic crystals (and amounting to not more than 10^{-3} of the Lorentz field). In addition to this field, one must also take into account 1) the field due to the contact interaction with the conduction electrons that are polarized by their exchange coupling with the d or f electrons, 2) the field due to the contact interaction with the conduction electrons that are partially hybridized with the d electrons, 3) the field due to the magnetic dipole interaction of the d electrons, 4) the field due to the unquenched part of the orbital momenta of the d or f electrons.

Other factors can contribute to H_{eff} (see Sec. 5 in^[169]). We consider by way of an example the fields acting on the nuclei in metallic iron. The main negative contribution can be produced here by the magnetized 2s and 3s layers of the ionic core (~ 400 kOe). A positive contribution (100 kOe) is made by the magnetized conduction electrons, as was suggested by Marshall^[129]. At the same time, however, as shown by

Anderson and Clogston^[170], a negative effective field may arise, due to the covalent bond between the conduction electrons and the unfilled 3d group.

As can be seen from Table X, by measuring the Mössbauer effect the hfs of Fe^{57} was determined also in the anti-ferromagnetic compound FeF_2 ^[148]. It was found there (by extrapolation to 0°K) that $H_{\text{eff}} = 3.40 \times 10^5$ Oe. It was also found that the Fe^{57} nucleus in Co is acted upon by a field $H_{\text{eff}} = -312$ kOe, whereas in nickel $H_{\text{eff}} = -280$ kOe.^[146] A few oxides of transition metals and ferrites were also investigated (see Table X), in which H_{eff} for Fe^{3+} turned out to be of the order of 500 kOe. In the case of yttrium-iron garnet, the hfs was investigated separately for the tetrahedral and octahedral interstices.^[146] Experiments were also made to determine the magnitude and direction of H_{eff} of the rare earth ions of samarium, gadolinium, dysprosium, europium, and terbium in rare earth iron garnets.^[147] Investigations with the aid of nuclear magnetic resonance made it possible to determine the magnitude and the sign of the polarization of the conduction electrons in rare earth intermetallic compounds. An interpretation of these experiments makes it possible to assume that the s - f exchange interaction between localized 4f electrons of the rare earth iron and s electrons is negative and amounts to ~ 0.1 eV^[148]. Measurements of the Mössbauer effect for the determination of atomic magnetic moments in ferromagnetic and antiferromagnetic metals and alloys (see, for example,^[149]) is also very important. Finally, an interesting attempt was made^[143] to determine H_{eff} in iron, cobalt, and nickel with the aid of the Mössbauer effect on a nucleus of a diamagnetic atom. For this purpose specimens were prepared of strongly dilute alloys of radioactive tin (Sn^{119}) in these metals. The measurements have shown^[143] that $H_{\text{eff}} = -0.81 \times 10^5$ Oe in iron, $H_{\text{eff}} = -0.205 \times 10^5$ Oe in cobalt, and $H_{\text{eff}} = +0.185 \times 10^5$ Oe in nickel. The authors of^[143] have proposed still another mechanism for explaining the results obtained on the measurements of H_{eff} , acting on the nucleus of a diamagnetic atom in a ferromagnet. In their opinion, the wave function of the 4s electrons of the tin atom overlaps the functions of the 3d electrons of the Fe, Co, and Ni atoms which are nearest neighbors of the Sn ion, and the exchange coupling between these 4s and 3d electrons leads to a strong "magnetization" of the former. In the region of the Sn nucleus the prevailing spins will be those of 4s electrons that are anti-parallel to the magnetic moment of the 3d electrons, which in the case of iron and cobalt produces a negative field H_{eff} . Freeman and Watson^[144] (see also^[43]) have shown with the aid of Hartree-Fock calculations (with account of spin exchange polarization) that the field H_c is very sensitive to the form of the 3d-electron distribution near the lattice site (see Fig. 2 in^[144]). They consequently warn against introducing various hypothetical "mechanisms" of exchange polarization (for ex-

ample the mechanisms of [143] or the one mentioned by Goodings and Heine [142] and others). Thus, in determining H_{eff} great difficulties arise in the interpretation, inasmuch as this field is the result of a superposition of many different effects.

f) To conclude this chapter, which is devoted to an exposition of elementary theoretical treatments of the transition metals, let us dwell once more on a comparison of two basic microscopic models referred to above.

As will become particularly clear in the second part of the review, an advantage of the (s-d) metal is that it makes it possible to describe correctly the spin-wave branch of the energy spectrum of ferromagnets and antiferromagnets, it gives a good qualitative explanation of the scattering of conduction electrons and neutrons by magnetic inhomogeneities, explains one of the reasons for the fractional atomic magnetic moments, and can be used successfully to explain the internal magnetic fields acting on the atomic nuclei in transition metals with atomic magnetic order [see item e)].

At the same time, a shortcoming of the (s-d) exchange model, like that of the band model, is the sharp autonomization of the s and d electrons. A specific shortcoming of this approximation is the assumption of complete conservation of the "atomic" state of the d or f shells in the metal. It follows therefore that it is impossible to explain the fractional nature of the

average atomic magnetic moments (above the fractional contribution to the magnetized conduction electrons). Furthermore, this model eliminates completely the participation of the d electrons in the transport of the electric charge in the metal.

In spite of all the foregoing shortcomings, the (s-d) exchange model is undoubtedly useful in the treatment of the properties of f metals, dilute d alloys in solvents with low state density at the Fermi surface, and also certain d metals (such as iron). This model can be used with even greater justification to explain the properties of ferromagnetic and anti-ferromagnetic compounds of nonmetallic (semiconductor) type.

It can thus be stated that the s-d model, in leaning on the localization of the atomic magnetic moments in the crystal, greatly underestimates the degree of participation of the d electrons in the collective electronic properties of the Fermi system, connected primarily with the transport of electric charge in the crystal, with the formation of the Fermi surface in the crystal, in the electronic specific heat, in Pauli paramagnetism, etc.

Everything stated above concerning the main contents of the two basic model treatments of transition metals with atomic magnetic order can be summarized for the sake of clarity as follows:

Properties	Band model	s-d model
s states	$\psi_s(\mathbf{k}_s, \mathbf{r}) \sim e^{i\mathbf{k}_s \mathbf{r}}; u_s(\mathbf{k}_s, \mathbf{r}) \sim \text{const}$	$\psi_s(\mathbf{k}_s, \mathbf{r}) \sim e^{i\mathbf{k}_s \mathbf{r}}; u_s(\mathbf{k}_s, \mathbf{r}) \sim \text{const}$
s energy	$\epsilon_s(\mathbf{k}, \sigma_s) = \epsilon_s(\mathbf{k}_s) + A_s(\mathbf{k}_s) m_z \sigma_s$	$\epsilon_s(\mathbf{k}_s, \sigma_s) = \epsilon_s(\mathbf{k}_s) + A_s(\mathbf{k}_s) m_z \sigma_s$
d states	$\psi_d(\mathbf{k}_d, \mathbf{r}) \sim e^{i\mathbf{k}_d \mathbf{r}}; u_d(\mathbf{k}_d, \mathbf{r}) \sim \text{const}$	$\psi_d(\mathbf{k}_d, \mathbf{r}) \sim \varphi(\mathbf{r} - \mathbf{r}_n); u_d(\mathbf{k}_d, \mathbf{r}) = \delta(\mathbf{k}_d) \varphi(\mathbf{r} - \mathbf{r}_n)$
d energy	$\epsilon_d(\mathbf{k}_d, \sigma_d) = \epsilon_d(\mathbf{k}_d) + A_d(\mathbf{k}_d) m_z \sigma_d$	$\epsilon_d(\mathbf{k}_d, \sigma_d) = E_d - \text{Atomic level}$
Ratio of s and d states (Δ - band width)	$\Delta_d/\Delta_s \ll 1, m_d^*/m_s^* \gg 1$	$\Delta_d/\Delta_s = 0, m_d^*/m_s^* \rightarrow \infty$
Spin density	Smearred over the crystal, average atomic moment can be arbitrary and fractional	Completely localized at the crystal sites; the average atomic moment is a multiple of μ_B , and the spin coincides with its value for the isolated atom

Properties	Band model	s-d model
Advantages of model	Explains the anomalies of the electronic specific heat, paramagnetic susceptibility, fractional values of the atomic magnetic moments and carriers, qualitative description of x-ray spectra	Gives good agreement with the measured neutron and x-ray form factors, admits of simple spin-wave treatment, offers an explanation of the indirect exchange and scattering of neutrons and electrons by the magnetic inhomogeneities, a description of the magnetization of the s electrons and its influence on the static and kinetic electron properties of the crystals, and an explanation of the origin of the effective magnetic fields on the nuclei.
Difficulties	Ignores the spatial inhomogeneity of the electron density, and does not permit an explanation of the observed form factors and effects of scattering on magnetic inhomogeneities	The postulation of two autonomous s and d electron subsystems; the impossibility of explaining several causes of the fractional nature of the average atomic magnetic moments and carriers; the collectivization of d electrons is ignored
Field of applications	d metals and alloys (with high density of the solvent-metal states at the Fermi surface)	f metals, alloys, ferromagnetic and antiferromagnetic semiconductors (metal-solvents in alloys with low density of states at the Fermi surface)

Comparing once more the band and (s-d) exchange models, we can state that they represent two sides of one and the same coin, two different asymptotic approximations in the theory of transition metals with atomic magnetic order. The problem of further development of the theory consists in bringing together these two approximate treatments and freeing them simultaneously of the particular model approximations (see also Ch. V).

¹N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys*, Oxford, 1936.

²F. Seitz, *The Modern Theory of Solids*, N. Y., McGraw-Hill, 1940.

³A. H. Wilson, *The Theory of Metals*, 2 ed., Cambridge, 1954.

⁴a) H. Fröhlich, *Elektronentheorie der Metalle*, Berlin, 1936. b) R. E. Peierls, *Quantum Theory of Solids*, Oxford, Clarendon Press, 1955.

⁵G. V. Rayner, *Repts. Progr. Phys. (London)* **15**, 173 (1952).

⁶J. Callaway, *Solid State Physics (New York)*, **7**, 100 (1958).

⁷N. F. Mott, *Progr. Metal. Phys. (London)* **3**, 76 (1952).

⁸W. Hume-Rothery and B. R. Coles, *Advances Phys.* **3**, 149 (1954).

⁹L. D. Landau and E. M. Lifshitz, *Quantum Theory*, Pergamon, 1958.

¹⁰F. Hund, *Linienpektren und periodisches System der Elemente (Berlin)*, 1927; see also J. Slater, *Phys. Rev.* **28**, 291 (1926); G. Herzberg, *Atomic Spectra and Atomic Structure*, Prentice-Hall, N.Y., 1937.

¹¹A. S. Kompaneets, *Teoreticheskaya fizika (Theoretical Physics)*, 2d. ed., Gostekhizdat, 1957.

¹²P. Gombas, *Die statistische Theorie des Atoms und ihre Anwendungen*, Springer-Wien, 1949.

¹³J. Slater, *Phys. Rev.* **36**, 57 (1930).

¹⁴E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*, Cambridge, 1944.

¹⁵S. V. Vonsovskii and Ya. S. Shur, *Ferromagnetism (Ferromagnetism)*, Gostekhizdat, 1948.

¹⁶S. V. Vonsovskii, *Sovremennoe uchenie o magnetizme (Modern Theory of Magnetism)*, Gostekhizdat, 1953.

¹⁷Ya. G. Dorfman, *Magnitnye svoïstva i stroenie veshchestva (Magnetic Properties and Structure of Matter)*, Gostekhizdat, 1955.

¹⁸a) P. Selwood, *Magnetochemistry (Russ. Transl.)* 2d ed. IL, 1958. b) J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford, 1932.

¹⁹M. A. Él'yashevich, *Spektry redkikh zemel' (Spectra of Rare Earths)*, Gostekhizdat, 1953.

²⁰Spedding, Legvold, Daane, and Jennings, *Progress in Low Temperature Physics*, Vol. 2, Amsterdam, 1957; Chapt. XII, p. 368.

²¹D. H. Parkinson, *Repts. Progr. Phys. (London)* **21**, 226 (1958).

²²C. G. Shull and M. K. Wilkinson, *Revs. Modern Phys.* **25**, 100 (1953); *Phys. Rev.* **97**, 304 (1955).

²³I. Nakagawa, *J. Phys. Soc. Japan* **11**, 855 (1956).

²⁴C. J. Kriessman and H. B. Callen, *Phys. Rev.* **94**, 837 (1954).

²⁵J. Smit and H. P. J. Wijn, *Ferrites*, New York, 1959.

- ²⁶ Owen, Browne, Knight, and Kittel, *Phys. Rev.* **102**, 1501 (1956); Owen, Browne, Arp, and Kip, *J. Phys. Chem. Solids* **2**, 85 (1957); Sato, Arrott, and Kikuchi, *J. Appl. Phys.* **30**, 94 (1959).
- ²⁷ J. G. Daunt, *Progr. Low Temper. Phys.*, Vol. I, Amsterdam, 1955, p. 202.
- ²⁸ W. Marshall, *Phys. Rev.* **110**, 1280 (1958).
- ²⁹ a) L. D. Landau, *JETP* **30**, 1058 (1956), *Soviet Phys. JETP* **3**, 920 (1956). b) A. A. Abrikosov and I. M. Khalatnikov, *UFN* **66**, 177 (1958), *Soviet Phys. Uspekhi* **1**, 68 (1959).
- ³⁰ J. M. Luttinger, *Phys. Rev.* **119**, 1153 (1960).
- ³¹ a) Cheng, Wei, and Beck, *Phys. Rev.* **120**, 426 (1960). b) C. T. Wei and C. H. Cheng, *Phys. Rev.* **124**, 722 (1961).
- ³² D. Pines, *Solid State Phys. (New York)* **1**, 368 (1955).
- ³³ M. A. Blokhin, *Fizika rentgenovskikh lucheĭ (X-ray Physics)*, Gostekhizdat, 1953.
- ³⁴ É. E. Vainshteĭn, *Rentgenovskie spektry atomov v molekulakh khimicheskikh soedineniĭ i v splavakh (X-ray Spectra of Atoms in Molecules of Chemical Compounds and Alloys)*, AN SSSR, 1950.
- ³⁵ H. W. B. Skinner, *Repts. Progr. Phys. (London)* **5**, 257 (1939).
- ³⁶ a) S. A. Nemnonov and L. D. Finkel'shteĭn, *Izv. AN SSSR ser. fiz.* **25**, (1961) [sic]. b) Y. Cauchois and C. Bounelle, *Compt. rend.* **245**, 1230 (1957).
- ³⁷ R. E. Watson and A. J. Freeman, *Acta Cryst.* **14**, 27 (1961).
- ³⁸ R. J. Weiss and J. J. de Marco, *Revs. Modern Phys.* **30**, 59 (1958); *Phys. Rev. Lett.* **2**, 148 (1959).
- ³⁹ a) B. W. Batterman, *Phys. Rev. Lett.* **2**, 47 (1959); *Phys. Rev.* **115**, 81 (1959). b) Komura, Tomiie, and Nathans, *Phys. Rev. Lett.* **3**, 268 (1959); *J. Phys. Soc. Japan* **15**, 1434 (1960). c) Batterman, Chipman, and de Marco, *Phys. Rev.* **122**, 68 (1961).
- ⁴⁰ C. Herring, *J. Appl. Phys.* **31**, 3S (1960).
- ⁴¹ R. J. Weiss and A. J. Freeman, *J. Phys. Chem. Solids* **10**, 147 (1959).
- ⁴² Nathans, Shull, Shirane, and Andersen, *J. Phys. Chem. Solids* **10**, 138 (1959).
- ⁴³ R. E. Watson and A. J. Freeman, *Phys. Rev.* **120**, 1125, 1134 (1960).
- ⁴⁴ J. H. Wood, *Phys. Rev.* **117**, 714 (1960).
- ⁴⁵ F. Stern, *Phys. Rev.* **116**, 1399 (1959); *Bull. Amer. Phys. Soc.* **5**, 456 (1960).
- ⁴⁶ James, Legvold, and Spedding, *Phys. Rev.* **88**, 1092 (1952).
- ⁴⁷ a) Colvin, Legvold, and Spedding, *Phys. Rev.* **120**, 741 (1960). b) Alstand, Legvold, and Spedding, *Phys. Rev.* **121**, 1637 (1961). c) Green, Legvold, and Spedding, *Phys. Rev.* **122**, 827 (1961). d) Curry, Legvold, and Spedding, *Phys. Rev.* **117**, 953 (1960).
- ⁴⁸ a) H. H. Potter, *Proc. Phys. Soc.* **49**, 671 (1937); **53**, 695 (1941). b) P. R. Pallister, *J. Iron and Steel Inst.* **161**, 87 (1949). c) A. N. Gerritsen, *Physica* **19**, 61 (1953). d) A. N. Gerritsen, *Handb. d. Phys.* **19**, 187 (1956).
- ⁴⁹ B. R. Coles, *Advances. Phys.* **7**, 40 (1958).
- ⁵⁰ N. V. Volkenshteĭn and G. V. Fedorov, *Izv. AN SSSR ser. fiz.* **25**, 1379 (1961), *Columbia Tech. Transl.* p. 1391.
- ⁵¹ Kondorskii, Galkina, and Chernikova, *Izv. AN SSSR ser. fiz.* **21**, 1123 (1957), *Columbia Tech. Transl.* p. 1109; *JETP* **34**, 1070 (1958), *Soviet Phys. JETP* **7**, 741 (1958).
- ⁵² A. A. Sudovtsev and E. E. Semenenko, *JETP* **31**, 525 (1956), *Soviet Phys. JETP* **4**, 592 (1957).
- ⁵³ G. K. White and S. B. Woods, *Canad. J. Phys.* **35**, 346 (1957).
- ⁵⁴ a) A. P. Komar and V. V. Klyushin, *Izv. AN SSSR, ser. fiz.* **18**, 400 (1954), *Columbia Tech. Transl.* p. 96; Belov, Popova, and Talalaeva, *Kristallogr.* **3**, 733 (1958), *Soviet Phys. Crystallography* **3**, 738 (1959); J. Folger, *Coll. Poluprovodnikovye materialy (Semiconductor Materials)*, IL, 1954, p. 215; A. I. Suchkov, *FMM* **7**, 317 (1959). b) E. Uchida et al., *J. Phys. Soc. Japan* **11**, 27 (1956), I. G. Fakidov and A. Ya. Afanas'ev, *FMM* **6**, 176 (1958). Y. Shimomura and I. J. Tsubokawa, *J. Phys. Soc. Japan* **9**, 19 (1954).
- ⁵⁵ C. Zener, *Phys. Rev.* **81**, 440 (1951).
- ⁵⁶ S. V. Vonsovskii and Yu. A. Izyumov, *FMM* **10**, 321 (1960).
- ⁵⁷ R. L. White and J. P. Andelin, Jr., *Phys. Rev.* **115**, 1435 (1959).
- ⁵⁸ W. Low, *Paramagnetic Resonance in Solids, Solid State Physics, Suppl. 2*, New York, 1960.
- ⁵⁹ E. O. Wollan, *Phys. Rev.* **117**, 387 (1960).
- ⁶⁰ J. B. Goodenough, *Phys. Rev.* **120**, 67 (1960).
- ⁶¹ J. I. Frenkel, *Z. Physik.* **49**, 31 (1928).
- ⁶² F. Bloch, *Zs. Phys.* **57**, 545 (1929).
- ⁶³ A. Sommerfeld and H. Bethe, *Electron Theory of Metals*, (Russ. Transl.) ONTI, 1937.
- ⁶⁴ E. Wigner, a) *Phys. Rev.* **46**, 1002 (1934); b) *Trans. Farad. Soc.* **34**, 678 (1938).
- ⁶⁵ J. C. Slater, *Phys. Rev.* **49**, 537, 931 (1936).
- ⁶⁶ E. C. Stoner, *Proc. Roy. Soc.* **A154**, 656 (1936); **165**, 372 (1938); **169**, 339 (1939); *Repts. Prog. Phys. (London)* **11**, 43 (1948); *J. Phys. et Radium* **12**, 372 (1951).
- ⁶⁷ H. M. Krutter, *Phys. Rev.* **48**, 664 (1935).
- ⁶⁸ N. F. Mott, *Proc. Phys. Soc.* **47**, 571 (1935).
- ⁶⁹ E. P. Wohlfarth, *Proc. Leeds Philos. Lit. Soc.* **5**, 89 (1948); *Proc. Roy. Soc.* **A195**, 434 (1949); *Philos. Mag.* **52**, 374 (1951); *Revs. Modern Phys.* **25**, 211 (1953).
- ⁷⁰ G. C. Fletcher, *Proc. Phys. Soc.* **A65**, 192 (1952); G. C. Fletcher and E. P. Wohlfarth, *Philos. Mag.* **42**, 106 (1951).
- ⁷¹ a) J. Callaway, *Phys. Rev.* **115**, 346 (1959); **120**, 731 (1960); **121**, 1351 (1961). b) M. A. Asdente and J. Friedel, *Phys. Rev.* **124**, 384 (1961).
- ⁷² J. Callaway and D. M. Edwards, *Phys. Rev.* **118**, 923 (1960).

- ⁷³H. Jones and N. F. Mott, Proc. Roy. Soc. A157, 490 (1937).
- ⁷⁴E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933); 46, 509 (1934).
- ⁷⁵D. I. Blokhintsev, Osnovy kvantovoi mekhaniki (Principles of Quantum Mechanics), Gostekhizdat, 1949.
- ⁷⁶D. R. Hartree and W. Hartree, Proc. Roy. Soc. A157, 490 (1936).
- ⁷⁷J. H. Van Vleck, Magnetic Properties of Metals and Alloys, Seminar in Cleveland, Oct. 25-26, 1958; Chapt. I.
- ⁷⁸H. Bethe, Ann. d. Phys. 3, 133 (1929); J. H. Van Vleck, Phys. Rev. 41, 208 (1932); W. G. Penney and R. Schlapp, Phys. Rev. 41, 194 (1932); J. D. Dunitz and L. E. Orgel, J. Phys. Chem. Solids 3, 20 (1957).
- ⁷⁹I. D. Howarth, Proc. Roy. Soc. A220, 513 (1953).
- ⁸⁰L. D. Landau, Z. Physik 64, 639 (1930).
- ⁸¹Friedel, Leman, and Olszewski, a) 6th Conf. Magnetism and Magnetic Materials (New York, Nov. 14-17, 1960); b) J. Appl. Phys. 32, 325S (1961).
- ⁸²M. Shimizu, J. Phys. Soc. Japan 15, 376 (1960).
- ⁸³D. Bohm and D. Pines, Phys. Rev. 82, 625 (1951); 85, 338 (1952); 92, 609 (1953); D. Pines, Phys. Rev. 92, 626 (1952).
- ⁸⁴a) C. Herring and Ch. Kittel, Phys. Rev. 81, 869 (1951). b) C. Herring, Phys. Rev. 85, 1003; 87, 60 (1952).
- ⁸⁵T. Izujama, Progr. Theor. Phys. 23, 969 (1960).
- ⁸⁶A. A. Abrikosov and I. E. Dzyaloshinskiĭ, JETP 35, 771 (1958), Soviet Phys. JETP 8, 535 (1959).
- ⁸⁷S. V. Vonsovskii and L. Ya. Kobelev, FMM 11, 820 (1961).
- ⁸⁸L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Gostekhizdat, 1951.
- ⁸⁹S. V. Vonsovskii and E. A. Turov, J. Appl. Phys. 30, 9 (1959); S. V. Vonsovskii, J. phys. radium 20, 264 (1959); E. A. Turov and V. G. Shavrov, Trudy, Inst. of Metal Physics Acad. Sci. U.S.S.R., No. 20, 101 (1958); E. A. Turov and Yu. P. Irkhin, FMM 9, 488 (1960). see also collection "Ferrity" (Ferrites), Minsk, AN BSSR, 1961, p. 7.
- ⁹⁰S. P. Shubin and S. V. Vonsovskii, Sow. Phys. 7, 292 (1935).
- ⁹¹S. V. Vonsovskii, JETP 16, 981 (1946).
- ⁹²S. V. Vonsovskii and E. A. Turov, JETP 24, 419 (1953).
- ⁹³I. M. Lifshitz and M. I. Kaganov, UFN 69, 419 (1959), Soviet Phys. Uspekhi 2, 831 (1960).
- ⁹⁴Vonsovskii, Vlasov, and Turov, JETP 29, 37 (1955), Soviet Phys. JETP 2, 26 (1956). E. A. Turov, DAN SSSR 98, 949 (1954).
- ⁹⁵K. P. Rodionov and V. G. Shavrov, FMM 4, 385 (1957).
- ⁹⁶S. V. Vonsovskii and K. B. Vlasov, JETP 25, 327 (1953).
- ⁹⁷W. Gerlach, Ann. d. Phys. 8, 649 (1931); 12, 849 (1932).
- ⁹⁸T. Kasuya, Progr. Theor. Phys. 16, 45, 58 (1956).
- ⁹⁹J. Friedel and P. G. de Gennes, J. Phys. Chem. Solids 4, 71 (1958); R. J. Weiss and A. S. Marotta, J. Phys. Chem. Solids 9, 302 (1959).
- ¹⁰⁰F. N. Mott, Proc. Roy. Soc. A153, 699; A156, 368 (1936); Canad. J. Phys. 34, 1356 (1956).
- ¹⁰¹G. W. Pratt, Phys. Rev. 81, 440 (1957).
- ¹⁰²N. F. Mott and K. W. Stevens, Philos. Mag. 2, 1304 (1957).
- ¹⁰³W. Lomer and W. Marshall, Philos. Mag. 3, 185 (1958); W. Marshall and R. Weiss, J. Appl. Phys. 30, 220S (1959).
- ¹⁰⁴S. V. Vonsovskii and A. V. Sokolov, JETP 19, 615 (1949).
- ¹⁰⁵S. V. Vonsovskii and A. V. Sokolov, JETP 19, 703 (1949).
- ¹⁰⁶S. V. Vonsovskii and A. V. Sokolov, DAN SSSR 76, 197 (1959). Vonsovskii, Sokolov, and Veksler, UFN 56, 477 (1955); A. Z. Veksler, JETP 29, 261 (1955), Soviet Phys. JETP 2, 326 (1956).
- ¹⁰⁷A. V. Sokolov and A. Z. Veksler, JETP 25, 215 (1953).
- ¹⁰⁸A. I. Rezanov, Izv. AN SSSR, ser. fiz. 16, 581 (1952); DAN SSSR 82, 885 (1952). Memorial Volume to A. F. Ioffe, AN SSSR, 1950, p. 474.
- ¹⁰⁹A. V. Sokolov, JETP 28, 326 (1955), Soviet Phys. JETP 1, 333 (1966); Yu. P. Irkhin, FMM 11, 10 (1961). I. M. Shepeleva and Yu. P. Irkhin, FMM 11, 313 (1961).
- ¹¹⁰K. B. Vlasov and S. V. Vonsovskii, FMM 2, 413 (1956).
- ¹¹¹Yu. P. Irkhin and E. A. Turov, FMM 4, 9 (1957).
- ¹¹²E. A. Turov and Yu. P. Irkhin, FMM 9, 488 (1960).
- ¹¹³Yu. P. Irkhin, FMM 7, 3 (1959).
- ¹¹⁴M. Sh. Giterman and Yu. P. Irkhin, FTT 2, 144 (1960), Soviet Phys. Solid State 2, 134 (1960).
- ¹¹⁵A. A. Smirnov, DAN UkrSSR No. 1, 67 (1955); JETP 17, 730 (1947). M. A. Krivoglaz and A. A. Smirnov, Teoriya uporyadochivayushchikhsya splavov (Theory of Ordered Alloys), M., Fizmatgiz, 1958; A. A. Smirnov, Teoriya elektrosoprotivleniya splavov (Theory of Electric Resistivity of Alloys), Kiev, AN UkrSSR, 1960.
- ¹¹⁶Yu. P. Irkhin, FMM 6, 214 and 586 (1958).
- ¹¹⁷S. V. Vonsovskii, Izv. AN SSSR, ser. fiz. 11, 617 (1947).
- ¹¹⁸S. V. Vonsovskii, JETP 18, 219 (1948).
- ¹¹⁹A. I. Rezanov, DAN SSSR 82, 885 (1952); A. I. Rezanov and V. I. Cherepanov, DAN SSSR 93, 441 (1953).
- ¹²⁰E. A. Turov, Izv. AN SSSR, ser. fiz. 19, 474 (1958), Columbia Tech. Transl. p. 426.
- ¹²¹E. A. Turov, FMM 6, 203 (1958).
- ¹²²E. A. Turov and Sh. Sh. Abel'skiĭ, FMM 10, 801 (1960).
- ¹²³N. Kurti, J. phys. et radium 20, 141 (1959); J. Appl. Phys. 30, 215S (1959).
- ¹²⁴G. R. Khutsishvili, a) JETP 29, 894 (1955), Soviet Phys. JETP 2, 744 (1956), b) Trudy, Phys. Inst. Georgian Acad. Sci. 4, 3 (1956).

- ¹²⁵ N. E. Alekseevskii and I. F. Shchegolev, *Otchet (Report)*, Inst. of Physics Problems, Acad. Sci. U.S.S.R., 1954.
- ¹²⁶ Grace, Johnson, Kurti, Scurleck, and Taylor, *Comm. Conf. Basses Temper.*, Paris, 1955, p. 263.
- ¹²⁷ Samoïlov, Sklyarevskii, and Stepanov, *JETP* **36**, 644 and 1366 (1959) and **38**, 359 (1960), *Soviet Phys. JETP* **9**, 448 and 972 (1959) and **11**, 261 (1960). Samoïlov, Sklyarevskii, Gorobchenko, and Stepanov, *JETP* **40**, 1871 (1961), *Soviet Phys. JETP* **13**, 1314 (1961). Samoïlov, Sklyarevskii, and Gorobchenko, *JETP* **41**, 1783 (1961), *Soviet Phys. JETP* **14**, 1267 (1962).
- ¹²⁸ H. A. Tefheck and J. A. M. Cox, *Physica* **19**, 101, 673 (1953).
- ¹²⁹ W. Marshall, *Phys. Rev.* **110**, 1280 (1958).
- ¹³⁰ C. V. Heer and R. A. Erickson, *Bull. Amer. Phys. Soc. Ser. II*, **1**, 217 (1956).
- ¹³¹ C. V. Heer and R. A. Erickson, *Phys. Rev.* **108**, 896 (1957).
- ¹³² a) Arp, Kurti, and Petersen, *Bull. Amer. Phys. Soc.* **2**, 388 (1957). b) Arp, Edmunds, and Petersen, *Phys. Rev. Lett.* **3**, 212 (1959).
- ¹³³ N. Kurti and R. S. Safrata, *Phil. Mag.* **3**, 780 (1958).
- ¹³⁴ J. M. Baker and B. Bleaney, *Proc. Phys. Soc. A68*, 267 (1955).
- ¹³⁵ R. L. Mössbauer, *Z. Phys.* **151**, 124 (1958).
- ¹³⁶ R. L. Mössbauer, *UFN* **72**, 657 (1960), *Soviet Phys. Uspekhi* **3**, 866 (1961); F. L. Shapiro, *UFN* **72**, 685 (1960), *Soviet Phys. Uspekhi* **3**, 881 (1961).
- ¹³⁷ a) Hanna, Heberle, Littlejohn, Perlow, Preston, and Vincent, *Phys. Rev. Lett.* **4**, 177 (1960); Heberle, Hanna, Perlow, Preston, and Vincent, *Phys. Rev. Lett.* **4**, 513 (1960). b) Nagle, Frankenfelder, Taylor, Cochran, and Matthias, *Phys. Rev. Lett.* **5**, 364 (1960).
- ¹³⁸ J. G. Dash, *Conf. Resonance Absorption Without Recoil*, Urbana, U.S.A., July 1960.
- ¹³⁹ Ofer, Avivi, Bauminger, Marinov, and Cohen, *Phys. Rev.* **120**, 406 (1960).
- ¹⁴⁰ E. Fermi, *Z. Phys.* **60**, 320 (1930); E. Fermi and E. Segrè, *Rend. reale accad. Lincei* **4**, 18 (1933); *Z. Phys.* **82**, 729 (1933).
- ¹⁴¹ G. R. Khutsishvili, *UFN* **71**, 9 (1960), *Soviet Phys. Uspekhi* **3**, 285 (1961).
- ¹⁴² D. A. Goodings and V. Heine, *Phys. Rev. Lett.* **5**, 370 (1960).
- ¹⁴³ Boyle, Bunbury, and Edwards, *Phys. Rev. Lett.* **5**, 533 (1960).
- ¹⁴⁴ A. J. Freeman and R. E. Watson, *Phys. Rev. Lett.* **5**, 498 (1961); R. E. Watson and A. J. Freeman, *Phys. Rev. Lett.* **6**, 277 (1961).
- ¹⁴⁵ G. K. Wertheim, *Phys. Rev.* **121**, 63 (1961).
- ¹⁴⁶ G. K. Wertheim, *J. Appl. Phys.* **32**, 110 S (1960); *Phys. Rev. Lett.* **4**, 403 (1960).
- ¹⁴⁷ a) Caspari, Frankel, Ray, and Wood, *Phys. Rev. Lett.* **6**, 345 (1961). b) Caspari, Frankel, and Gilleo, *J. Appl. Phys.* **31**, 320 S (1960).
- ¹⁴⁸ V. Jaccarino, *J. Appl. Phys.* **32**, 110 (1961).
- ¹⁴⁹ Johnson, Ridout, Cranshaw, and Madsen, *Phys. Rev. Lett.* **6**, 450 (1961).
- ¹⁵⁰ W. Henry, *Phys. Rev.* **117**, 89 (1960).
- ¹⁵¹ J. C. Slater, *Phys. Rev.* **82**, 538 (1951).
- ¹⁵² A. B. Lidiard, a) *Proc. Phys. Soc. A66*, 1188 (1953); b) *Proc. Roy. Soc. A224*, 161 (1954), B. E. W. Elcock, *Proc. Roy. Soc. A67*, 295 (1954).
- ¹⁵³ Goodenough, Wold, and Arnott, *Phys. Rev.* **124**, 373 (1961).
- ¹⁵⁴ E. O. Wollan, *Phys. Rev.* **122**, 1710 (1961).
- ¹⁵⁵ Svenson, *Ann. d. Phys.* **14**, 699 (1932).
- ¹⁵⁶ D. M. Edwards, *Preprint, Proc. Roy. Soc.* (1962).
- ¹⁵⁷ A. B. Pippard, *Repts. Progr. Phys.* **23**, 176 (1960).
- ¹⁵⁸ Bozorth, Wolff, Davis, Compton, and Wernick, *Phys. Rev.* **122**, 1157 (1961).
- ¹⁵⁹ P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).
- ¹⁶⁰ P. A. Wolff, *Phys. Rev.* **124**, 1030 (1961).
- ¹⁶¹ Clogston, Matthias, Peter, Wolliams, Corenzwit, and Sherwood, *Phys. Rev.* **125**, 541 (1962).
- ¹⁶² A. M. Clogston, *Phys. Rev.* **125**, 439 (1962).
- ¹⁶³ W. M. Lomer, *British J. Appl. Phys.* **12**, 535 (1961).
- ¹⁶⁴ F. E. Hoare and J. C. Matthews, *Proc. Roy. Soc. A212*, 137 (1952).
- ¹⁶⁵ J. P. Burger and M. A. Taylor, *Phys. Rev. Lett.* **6**, 185 (1961).
- ¹⁶⁶ Wei, Cheng, and Beck, *Phys. Rev.* **122**, 1129 (1961).
- ¹⁶⁷ J. S. Van Wieringen, *Disc. Faraday Soc.* **19**, 118 (1955).
- ¹⁶⁸ A. C. Gossard and A. M. Portis, *J. Appl. Phys.* **31**, 205 (1960).
- ¹⁶⁹ R. E. Watson and A. J. Freeman, *Phys. Rev.* **123**, 2027 (1961).
- ¹⁷⁰ P. W. Anderson and A. M. Clogston, *Bull. Amer. Phys. Soc.* **6**, 124 (1961).
- ¹⁷¹ Gossard, Portis, and Sandle, *J. Phys. Chem. Solids*; C. Robert and J. M. Winter, *Compt. rend.* **250**, 3831 (1960); Budnick, Brunner, Blume, and Boyd, *J. Appl. Phys.* **32**, 120 (1961).
- ¹⁷² Taylor, Nagle, Frauenfelder, and Cochran, in press, see [¹⁶⁹] Table IX.
- ¹⁷³ C. Alf and G. K. Wertheim, *Bull. Amer. Phys. Soc.* **5**, 428 (1960).
- ¹⁷⁴ Bauminger, Cohen, Marinov, and Ofer, *Phys. Rev.* in press.
- ¹⁷⁵ Boyd, Brunner, Budnick, and Blume, *Bull. Amer. Phys. Soc.* **6**, 159 (1961).
- ¹⁷⁶ I. Solomon, *Compt. rend.* **251**, 2675 (1960).
- ¹⁷⁷ Bauminger, Cohen, Marinov, Ofer, and Segal, *Phys. Rev.*
- ¹⁷⁸ O. C. Kistner and A. Sunyar, *Phys. Rev. Lett.* **4**, 412 (1960).
- ¹⁷⁹ Kelly, Hass, Schreiner, and Beard, *Bull. Amer. Phys. Soc.* **6**, 135 (1961).
- ¹⁸⁰ E. S. Rosenvasser and L. Feher, *Bull. Amer. Phys. Soc.* **6**, 117 (1960).
- ¹⁸¹ Dash, Taylor, Nagle, Craig, and Visscher, *Bull. Amer. Phys. Soc.* **6**, 136 (1961).

- ¹⁸²S. R. Pollack, Bull. Amer. Phys. Soc. **6**, 169 (1961).
¹⁸³Brunner, Budnick, and Blume, Phys. Rev. **121**, 83 (1961).
¹⁸⁴H. F. Wegener and F. E. Obenshain, Phys. Rev. in press.
¹⁸⁵Boyle, Bunbury, Edwards, and Hall, Proc. Phys. Soc. **77**, 129 (1961).
¹⁸⁶Meyer-Schützmeister, Preston, and Hanna, Phys. Rev. in press.
- ¹⁸⁷V. G. Shavrov, FMM **13**, 663 (1962).
¹⁸⁸K. P. Belov and A. V. Ped'ko, JETP **42**, 87 (1962), Soviet Phys. Uspekhi **15**, 62 (1962).
¹⁸⁹R. G. Barnes and T. P. Graham, Phys. Rev. Lett. **8**, 248 (1962).

Translated by J. G. Adashko