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538.2

MAGNETIC IMPURITIES IN NONMAGNETIC METALS*

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AT first glance, the scope of this review seems quite narrow. However, the number of papers devoted to various problems pertaining thereto has been exceedingly large in recent years, and insofar as I can judge, the flow continues to increase. This is connected primarily with the fact that there are still many puzzling and not fully explained phenomena in this region (as stated by P. Anderson, "Mount Everest is right here"). In addition, it is very surprising that a small impurity of transition-metal atoms in a magnetic metal can lead to a large change, independent of the impurity concentration, in the properties of the metal, for example to a several-fold increase of the electronic specific heat at low temperatures, or to an increase of the thermoelectric power by several orders of magnitude. These experimental facts have been explained only most recently. I repeat, however, there is still many unanswered questions.

I. LOCALIZED SPINS

Presently there is no more any doubt that all the singularities of the substances under consideration are connected with the fact that the atoms of the transition metals, which have in the isolated state unfilled d or f shells and a nonzero electron spin, can retain this property in many cases when imbedded in a nonmagnetic metal. The question of the possible presence of such localized spins in metals has been the subject of an extensive literature. The main ideas in this field belong to J. Friedel and P. Anderson.[1] I am unable to discuss this question fully, but a few words are essential. In the main, the matter reduces to the following. When a magnetic atom is placed in a metal, we can no longer speak of individual energy levels. We can speak instead of an increased density of states in some energy interval in the conduction band. It should be noted that this takes place, of course, only when the impurity-atom energy level lies in the conduction band. But since the conduction band is very broad, this takes place quite frequently. However, these states themselves are still quite close to the former orbital states of the electrons in the isolated atom; in these states, consequently, the electrons spend an appreciable part of the time near one another, and there is strong interaction between them. In the isolated atom, the Coulomb interaction of the electron leads to the known Hund rules, according to which, in particular, the unfilled shell should have a maximum spin. Since, as already noted, considerable Coulomb interaction still remains when the impurity atoms are placed in the metal, the Hund rules hold here, too. Of course, all depends on the time that the electrons stay near the impurity. Quantitatively, the possibility of occurrence of a localized spin is determined by the ratio of the Coulomb interaction of the electrons in the d or f shells and by the probability of their transition to the valence band. The latter is represented by the extent of spreading of the former discrete energy level.

How does all this occur and to what changes in the properties of the conduction electrons in the metals does the presence of such quasibound states lead? This was demonstrated by P. Anderson using a very simple model as an example.[1] We write out the following Hamiltonian

$$\mathcal{H} = \sum_{p\alpha} \varepsilon_p n_{p\alpha} + \sum_{\alpha} \varepsilon_d n_{d\alpha} + \frac{1}{2} \sum U n_{d\alpha} n_{d-\alpha} + \sum_{p\alpha} (V a^+_{p\alpha} d_\alpha + V^* d^+_\alpha a_{p\alpha}); \quad (1)$$

here $a_{p\alpha}$ is the annihilation operator of a conduction electron with quasimomentum p and spin projection α, d_α is the annihilation operator of a d electron with spin projection α, $n_{p\alpha} = a^+_{p\alpha} a_{p\alpha}$ and $n_{d\alpha} = d^+_\alpha d_\alpha$ are the occupation numbers, the energies ϵ_p and ϵ_d are reckoned from the Fermi boundary, and the impurity level ϵ_d is assumed to be nondegenerate, with $\epsilon_d < 0$. The term with U is the part of the electron Coulomb interaction ensuring satisfaction of the Hund rule (see below), and the last term corresponds to mixing between the ϵ_d level and the conduction electrons. According to Anderson's estimate, U ~ 10 eV and V ~ 2 eV. Therefore, in the zeroth approximation, we can neglect the last term. The d electrons are then not bound with the conduction electrons. According to the Pauli principle, if one electron with upward spin is located at the ϵ_d level, then the next electron can have only a downward spin. But in this case its energy will be $\epsilon_d + U$. If this is a positive quantity, then the energy of such an electron lies above the Fermi level, and the state is not filled. Naturally, this reasoning is valid also when one electron with downward spin is located at the ϵ_d level. Thus, the term with U causes the ϵ_d level to correspond to a localized spin ½ (with projection +½ or −½). Of course, allowance for the term with V complicates the situation, and a limited region of values of V and U, in which localized spins are possible, is produced.

We shall not go into the details in this question, and consider instead, with the aid of the Hamiltonian (1), the scattering, with spin flip, of an s electron by an impurity. Assume that one electron with spin ½ is located at the level ϵ_d and a conduction electron with momentum p and spin −½ is scattered. Such a scattering can proceed in two ways: a) The electron (p, −½) is transformed into d, −½ and then the electron (d, ½) is transformed into (p′, ½). This corresponds to a transition amplitude

$$-\frac{|V|^2}{\varepsilon_p - \varepsilon_d - U}.$$

b) The electron (d, ½) is transformed into (p′, ½) and then the electron (p, −½) is transformed into (d, −½). In this case we have

$$-\frac{|V|^2}{\varepsilon_d - \varepsilon_{p'}}.$$

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If we assume that the scattering is elastic and the metal is isotropic, then $\epsilon_p = \epsilon_{p'}$, and the net result is

$$\frac{|V|^2 U}{(U+\varepsilon_d-\varepsilon_p)(\varepsilon_p-\varepsilon_d)}.$$

Usually only the electrons near the Fermi boundary itself are significant, so that $\epsilon_p \approx 0$. We then have a matrix element independent of p and equal to

$$\frac{|V|^2 U}{(U+\varepsilon_d)(-\varepsilon_d)}.$$

This is a positive quantity, since the existence of a localized spin in such a model requires in any case $\epsilon_d < 0$ and $U + \epsilon_d > 0$.

Three factors should be noted. First, the result is equivalent to "exchange" interaction of the electron spin with the impurity spin, in the form

$$-\frac{J}{2N}\sum_{p,p',\alpha,\alpha',\beta,\beta'} a^+_{p\alpha}\sigma^i_{\alpha\alpha'}a_{p'\alpha'}d^+_\beta\sigma^i_{\beta\beta'}d_{\beta'},$$

where

$$\frac{J}{2N} = -\frac{|V|^2 U}{(U+\varepsilon_d)(-\varepsilon_d)};$$

Here N is the density of the host-metal atoms, introduced for normalization purposes, and σ^i are Pauli matrices. Second, it follows from the foregoing conclusion that $J < 0$, i.e., the interaction has an antiferromagnetic character. Finally, ϵ_d or $U + \epsilon_d$ can be close to the Fermi boundary, and then J is not a small quantity. This is important, for usually spin interactions of the type $\sigma_1\sigma_2$ have a true exchange origin, and the corresponding energies are smaller by several times than the Fermi energy. Such an interaction, of course, is also present, so that the resultant interaction is determined by two mechanisms. The remark made above concerning the sign is always valid if the mechanism described above is the principal one, i.e., in any case when J is not small. However, in cases of rare-earth impurities (i.e., unfilled f shells), the true exchange interaction of the f or s electrons can sometimes play a more important role, and the sign of J may be positive.

This equivalence of the Anderson Hamiltonian and the exchange interaction was first demonstrated by Kondo,[2] in a manner approximately similar to that described above, and then Schrieffer and Wolff obtained this result rigorously by a canonical transformation of the Anderson Hamiltonian.[3] Of course, the Anderson Hamiltonian is the simplest model, but even if it is assumed that the ϵ_d level is degenerate, corresponding to an orbital angular momentum l, the Hamiltonian (1) can still be transformed into the exchange type. To be sure, the interaction energy $\mathcal{H}(\mathbf{p}, \mathbf{p}')$ then begins to depend strongly on the quasimomenta p and p'. According to Kondo,[2] it is proportional to the Legendre polynomial $P_l(\cos\theta_{pp'})$. According to calculations by Bernard Karolyi (oral communication), this circumstance is important in a numerical comparison of the theory with experiment, since the different quantities contain different angular integrals of J. Since we are more interested in the fundamentals of the problem, we shall assume J = const throughout.

I now proceed to different phenomena due to impurities with localized spins. There are very many such phenomena, and it is difficult to cover them all. But I shall attempt to report those that seem most important to me. This group of problems can be represented in the form of the symmetrical matrix shown in Fig. 1, where O denotes ordering, S superconductivity, and K the Kondo effect.

II. ORDERING (O)

Thus, we consider the interaction between the localized spins and conduction electrons in the form

$$\mathcal{H}_{\text{int}} = -\frac{J}{N}\sum_{R_n}\psi^+_\alpha(\mathbf{R}_n)\,\sigma_{\alpha\alpha'}\mathbf{S}_n\psi_{\alpha'}(\mathbf{R}_n); \qquad (2)$$

here σ—Pauli matrices and **S**—impurity spin operators (for $S = \frac{1}{2}$, $\mathbf{S} = \sigma/2$); the summation is over all the impurity atoms. The interaction (2) leads, as can be readily seen, to interaction of the localized spins with one another: one spin polarizes the conduction electrons, and these in turn polarize another spin. If we assume that $|J| \ll \epsilon_F$ (ϵ_F—Fermi energy), then we can confine ourselves to the lowest order in perturbation theory, i.e., to the second order. It is easy to see that the process of interaction of two impurity spins via electrons can be described by the picture shown in Fig. 2. The impurity spin produces a pair—an electron and a hole—which is then annihilated by interacting with the other impurity spin.

Figure 2 not only illustrates the transfer of the spin polarization by the electrons, but also is a Feynmann diagram, with the aid of which it is possible to obtain a quantitative measure of the effect; as a result we obtain the well known Ruderman-Kittel-Kasuya-Yosida (RKKY) formula[4]

$$H_{S_1S_2} = -\left(\frac{J}{N}\right)^2 \nu(\varepsilon_F) f(|\mathbf{R}_1-\mathbf{R}_2|)\,\mathbf{S}_1\mathbf{S}_2, \qquad (3)$$

where $\nu(\epsilon_F) = p_0 m/2\pi^2$ is the density of the states of the electron on the Fermi boundary, and

$$f(R) = \frac{1}{4\pi}\left(\frac{\sin 2p_0R}{2p_0R^4} - \frac{\cos 2p_0R}{R^3}\right), \qquad (4)$$

p_0 is the limiting Fermi momentum (for simplicity we use throughout units in which $\hbar = 1$). The Fourier transform of the function f(R), which we denote by $\chi(q)$, is

$$\chi(q) = \frac{1}{2} - \frac{4p_0^2-q^2}{8p_0q}\ln\left|\frac{2p_0+q}{2p_0-q}\right|. \qquad (5)$$

Thus, the interaction decreases in absolute magnitude like $1/R^3$, and at the same time oscillates rapidly with a period $1/2p_0$ of the order of the interatomic distances. Since the impurities are randomly disposed, this interaction is ferromagnetic for certain pairs, i.e., it tends to make their spins parallel, and antiferromag-

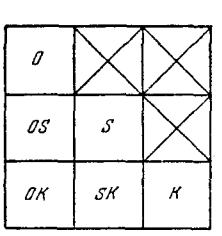

FIG. 1

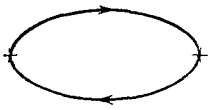

FIG. 2

netic for others. What kind of ordered states can occur under the influence of such an interaction? There are two different approaches. Although each point of view has its adherents, the question still remains unclear.

One approach is connected with the names Blandin, Friedel,[5] and Marshall.[6] The idea consists in the following. The oscillating and decreasing interaction cannot establish a long-range order in the metal. Therefore a state is produced in which the spins are oriented more or less randomly. Such a configuration is rigid at sufficiently low temperature, but its symmetry does not differ from the paramagnetic phase. There is therefore no exact phase transition, and all the singularities of the thermodynamic characteristics, such as specific heat or magnetic susceptibility, will have the form of maxima that are smeared out somehow. Each spin can be regarded as situated in a certain effective exchange field, i.e., having an energy $-\mathbf{S}\cdot\mathbf{Q}$ (the quantity $\mathbf{Q}$ is equivalent to $\mu_0\mathbf{H}$, where $\mathbf{H}$ is a certain magnetic field; $\mu_0\mathbf{S}$ is the magnetic moment of the impurity). We introduce a field-distribution function, which naturally depends only on the absolute value of Q; it is designated p (Q). It is then assumed that all the spins can be regarded separately, and the obtained characteristics must simply be averaged over Q with a distribution p (Q).

Of course, to obtain numerical characteristics it is necessary to know the function p (Q). No one has succeeded in calculating this function. However Klein and Brout[7] performed a calculation for a somewhat different interaction—the so-called Ising model, where $\mathbf{S}_1\cdot\mathbf{S}_2$ is replaced by $S_{1Z}S_{2Z}$ and it is assumed that each of the spins is equal to $\frac{1}{2}$. This substitution, of course, is a major shortcoming of such a calculation.

There is, however, a more general dimensional consideration, advanced by Blandin, to which there are fewer objections. At large distances, the amplitude of RKKY interaction decreases like $1/R^3$. With increasing concentration c, the average distance between the impurities varies in proportion to $c^{-1/3}$. Consequently, it can be assumed that the function p (Q) is such that all the average quantities with the dimension of energy, i.e., for example, $\sqrt{\overline{Q^2}}$, or the characteristic values of the temperature, are proportional to $1/\overline{R}^3$ or c. To this end, the function p (Q) must be of the form

$$p(Q, T)=\frac{1}{c}f\left(\frac{Q}{c}, \frac{T}{c}\right). \tag{6}$$

Even this leads immediately to many consequences. For example, if p (0, 0) ≠ 0, then at low temperatures the impurity part of the specific heat and of the magnetic susceptibility have the following form

$$\Delta C=\frac{1}{2}\frac{\pi^2}{3}Ncp(0, 0)\frac{4S^2}{2S+1}T, \tag{7}$$

$$\Delta\chi=2p(0, 0)\mu^2Nc, \tag{8}$$

where μ is the magnetic moment of the impurity, c the concentration, and N the density of the atoms of the host metal. According to (6), p (0, 0) ~ 1/c. Consequently, ΔC and $\Delta\chi$ do not depend on the impurity concentration. Since ΔC depends linearly on the temperature this term creates the impression that the linear electronic specific heat increases by a factor of several times, and does not depend on the impurity concentration. The same pertains to the magnetic susceptibility. Of course, the concentration determines the "Curie temperature," i.e., the characteristic temperature Θ beyond which this "ordering" is not felt. According to (6), $\Theta \sim c$, i.e., the temperature region where an increment of the type (7) and (8) exists, decreases with increasing concentration.

Further, dividing (7) by (8), we obtain

$$\frac{\Delta C}{\Delta\chi}=\frac{\pi^2}{3}\frac{S^2}{\mu^2(2S+1)}. \tag{9}$$

Consequently, p (0, 0) drops out. If we assume that $\mu \approx 2\mu_B S$, i.e., if we assume that the gyromagnetic ratio is close to 2 (μ_B—Bohr magneton), then we can attempt to determine the impurity spin and compare it with the measurements in the high temperature region $T \gg \Theta$, where paramagnetism obviously obtains and the paramagnetic susceptibility is given by

$$\Delta\chi\approx\frac{4\mu_B^2S(S+1)}{3T}.$$

The results obtained in Grenoble for Au + Fe and Cu + Mn are in splendid agreement with these considerations.[8] The Grenoble physicists have also made many measurements to check two consequences of formula (6), and on the whole agreement is obtained in all cases.

Favoring this model is also the smearing of all the transitions (broad maxima of C and χ instead of sharp singularities), and the large coercive force following magnetization. The latter is due to the fact that some spin orientation is established in a strong magnetic field, i.e., a function p (Q) is obtained. In this case it is no longer anisotropic. This function exhibits stiffness, i.e., it does not follow the variations of the external field.

However, there are two fundamental objections. First, since Q is a vector with a random orientation, its distribution function should strictly speaking be equal to $p(Q)dQ = p_1(Q)Q^2dQ$. And even if $p_1(0) \neq 0$, still p (0) = 0, and this completely upsets the entire concept. The second objection will be discussed later. There is also experimental evidence against this concept. This will also be discussed later.

We shall now discuss the second approach. This is the Overhauser idea of the so-called spin density wave.[9] We imagine that the conduction electrons have become aligned in such a way that a periodic spin density distribution has been established (in particular, this distribution can be homogeneous, i.e., ferromagnetism). This, of course, means an increase in the electron energy. But if the Hamiltonian (2) is averaged over this electron distribution, then we obtain again $-\sum_n \mathbf{Q}(\mathbf{R}_n)\mathbf{S}_n$, where

$$\mathbf{Q}(\mathbf{R}_n)=\frac{J}{N}\langle\psi_\alpha^+(\mathbf{R}_n)\sigma_{\alpha\alpha'}\psi_{\alpha'}(\mathbf{R}_n)\rangle$$

($\langle\ldots\rangle$ denotes averaging over the electrons). Although the field Q has different directions at different points, the impurity spin is always oriented as required, and the result is a decrease of the energy, which can compensate for the increase of the electron energy. It can be shown that this occurs below the Curie point, which is proportional to the impurity concentration and is of the order of $\Theta \sim cJ^2/\epsilon_F$ (ϵ_F—Fermi energy). In this case the transition should be abrupt. The experimentally observed smoothness of the transition can be attributed to inhomogeneity of the impurity concentration.

What kind of spin density wave is actually established? Obviously, this is determined by the energy minimum. Let us assume that the wave has the form of a helicon (i.e., the end of the vector **Q** describes a helix) with a wave vector **q**. In this case the change of energy per unit volume turns out to be

$$\Delta E = -(cJ)^2 \nu(\varepsilon_F) S^2 \chi(q), \tag{10}$$

where the function $\chi(\mathbf{q})$ is determined by formula (5). It is assumed here that the metal is homogeneous and the impurities are perfectly randomly oriented. The function $\chi(\mathbf{q})$ is monotonic, and its maximum value corresponds to q = 0. This means that a ferromagnetic configuration is preferred in such a model.

In fact, in the derivation of (10) we did not take into account the fact that the impurity atoms occupy definite places in the crystal cells, and therefore the averaging can be carried out only over the cells and not over the positions in the cells. As a result we obtain

$$\Delta E = -(cJ)^2 \nu(\varepsilon_F) S^2 \frac{1}{N} \sum_{\mathbf{R}_n \neq 0} f(\mathbf{R}_n) \cos(\mathbf{q}\mathbf{R}_n) \varphi(\mathbf{R}_n), \tag{11}$$

where the summation is carried out over the entire crystal lattice, and the function $\varphi(\mathbf{R}_n)$ takes into account the correlation of the cells in which the impurity atoms may be located. The importance of taking this function into account is connected with the fact that the most significant in the sum over $\mathbf{R}_n$ are short distances, on the order of the interatomic dimensions, where the function $\varphi(\mathbf{R}_n)$ can differ greatly from unity, since the correlation existing in the liquid state undoubtedly is retained after the alloy is cooled.* However, since little can be said concerning this function, it is usually assumed equal to unity. The sum over $\mathbf{R}_n$ is then

$$\lim_{P\to\infty}\left[\sum_{|\mathbf{K}|<P} \chi(\mathbf{q}+\mathbf{K}) + \frac{1}{N}\int_{|\mathbf{K}|<P} \frac{d^3\mathbf{K}}{(2\pi)^3}\chi(\mathbf{K})\right],$$

where the summation is over the periods of the reciprocal lattice. It is convenient to subtract from this the expression for the ferromagnetic case, i.e., with q = 0. It is then possible to go to the limit as $P \to \infty$. As a result we get

$$\Delta E - \Delta E_{\text{ferr}} = -(cJ)^2 \nu(\varepsilon_F) S^2 \sum_{\mathbf{K}} [\chi(\mathbf{q}+\mathbf{K}) - \chi(\mathbf{K})]. \tag{11'}$$

Concrete calculations for different types of lattices show that this sum frequently has a maximum at $q \to 0$. Moreover, no attention was paid here to the anisotropy energy, which, obviously, will tend to relate the period of the wave to the period of the crystal lattice. It is therefore perfectly probable that what is actually realized is not the **q** that corresponds to the minimum of the function (11'), but another value, corresponding for example to the nearest K.[10] The foregoing example is a very simple one. Other types of spin-density wave are not excluded.

Insofar as I know, the physical properties of this model have not yet been sufficiently investigated. If the effective field varies in magnitude (for example, a plane wave $Q_x = A\cos(\mathbf{q}, \mathbf{R})$, $Q_y = Q_z = 0$), then in principle there is no difference between this and the preceding approach, for a certain distribution p (Q) is also obtained, and it can be shown that its gauge properties (formula (6)) are conserved. This is possibly the only real way of obtaining $p(0) \sim 0$. However, if ferromagnetism or a helicoid is present, the effective field can change only in direction but not in magnitude. In this case $p(Q) \sim \delta(Q - Q_0)$. In light of the foregoing reasoning, it may turn out that this contradicts the experiment. Actually, the impurity part of the specific heat depends in this case exponentially on the temperature ($\Delta C \sim e^{-Q/T}$). Nonetheless, there is actually no contradiction even in this case.

Kondo was the first to note that the energy spectrum of the electrons changes in the presence of impurities.[11] Namely, in the vicinity of the Fermi energy, in a region of the order of $\Theta \sim cJ^2/\epsilon_F$, the effective mass of the electrons (Fig. 3) increases. Kondo introduced an effective field, and his expression for $\Delta m/m$ was proportional to c/Q. Since $\overline{Q}$ is itself proportional to c, the change of the effective mass was independent of the concentration and was of the order of unity. In an experiment, this should be manifest in the form of an increase of the coefficient in the linear electronic specific heat. This means that the experimentally observed fact can be attributed not to the impurity part of the specific heat, but to the electronic part. However, as indicated by Klein,[12] if the expression for the Kondo electronic specific heat is distributed over the distribution p (Q), then it will contain

$$\int \frac{p(Q)}{Q}\, dQ,$$

and if $p(0) \neq 0$, then the integral diverges logarithmically. The resultant correction to the specific is proportional not to T but to $T \ln(\Theta/T)$, something not observed in the experiment. This is the second argument against the conception of Blandin, Friedel, and Marshall.

In fact, Kondo's calculations must be refined.* The correction considered by him is actually the first of an infinite series. In the presence of long-range order, these corrections are none other than the interaction of the electrons with the spin waves,† and the change of the effective mass has the same origin as that occurring in the interaction between the electrons and the phonons. In the case of ferromagnetic ordering, the correction to the specific heat is proportional to $T \ln(\Theta/T)$, which apparently is evidence against ferromagnetism. In the case of any antiferromagnetic structure, a correction propor-

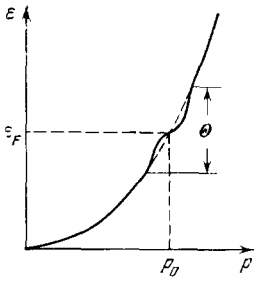

FIG. 3

*This remark is due to I. E. Dzyaloshinskiĭ.

*Unpublished results by the author of this review

†The absence of a large contribution to the specific heat from the spin waves themselves can be attributed to the anisotropy energy.

tional to T is obtained. In all cases, this correction is independent of the concentration. The case of a random effective field was not considered, but apparently Kondo's result remains qualitatively unchanged, i.e., the argument against the conception of Friedel, Blandin, and Marshall remain.

Finally, let me report experiments on the determination of the magnetic field at a nucleus with the aid of the Mossbauer effect. The results of Violet and Borg,[13] who determined the field at the nuclei of a small Fe impurity in Au, offer evidence, first, that the iron atoms occupy definite positions in the cell (this is seen from the distinct character of the quadrupole splitting of the lines at temperatures $T \gg \Theta$). Second, at low temperature the result indicates that each atom is acted upon by a field of definite magnitude. The line width is independent of the concentration. To be sure, the dependence of the transition temperature on the concentration has the form $\Theta \sim c^{\alpha}$, where $\alpha < 1$ (with different values in different investigations), and this may indicate an inaccuracy of this approach (for example, the correlation of the impurity positions may come into play). The results on Cu + Fe show that the p (Q) dependence is not δ-like in this case. This can be interpreted as favoring the conception of Blandin-Friedel-Marshall or may indicate that the spin-wave density has a different form.

On the whole it can be stated that the first concept is more fully developed than the second, so that it is too early to draw final conclusions. I personally, however, am more impressed by the spin-density wave concept, which so far has encountered no real contradictions (the nonlinear dependence of Θ on the concentration in Au + Fe contradicts both concepts, but it seems to me that if this effect is real it would be easier to explain within the framework of the second concept).

This is all I have to say about ordering at the moment, although I shall return to it in connection with superconductivity and with the Kondo effect.

III. SUPERCONDUCTIVITY (S)

In this section I shall report only phenomena not connected with ordering. The measurements by Matthias and others on lanthanum with small admixture of rare earths[14] have shown that superconductivity is very sensitive to the presence of localized spins. The critical temperature (T_c) decreases rapidly with increasing magnetic-impurity concentration, and one per cent suffices to eliminate the superconductivity. The first explanation of this effect is due to Herring, Matthias, and Suhl.[15] They explained the change of T_c at low impurity concentrations. Subsequently, L. P. Gor'kov and the present author,[16] using the method of temperature Green's functions, constructed a theory suitable for all concentrations (in the absence of ordering).

Physically, the action of magnetic impurities is based on the possibility of electron scattering with spin flip, which was already mentioned at the beginning of this review. As is well known (see, for example, [17]), in a superconductor the electrons combine into the so-called Cooper pairs with opposite spins. The pair dimension, in other words the correlation length in the pure metal, is of the order of $\hbar v_F/T_c$ (v_f—velocity on the Fermi boundary), i.e., usually 10^{-4}—10^{-5} cm. After being scattered by the impurity, the electron of the pair can reverse its spin. In such a state, the pair is unstable. It is clear that the effective scattering with spin flip should suppress the superconductivity. This is actually the case. The change of the critical temperature is described by the formula

$$\ln\left(\frac{T_{c0}}{T_c}\right) = \psi\left(\frac{1}{2}+\frac{\rho}{2}\right) - \psi\left(\frac{1}{2}\right), \qquad (12)$$

where $\psi(x) = [\ln \Gamma(x)]'$, Γ is the Gamma function,

$$\rho = \frac{1}{\pi\tau_s T_c}, \quad \frac{1}{\tau_s} = \frac{1}{6}\nu(\varepsilon_F)\frac{J^2}{N}cS(S+1),$$

and τ_s is time of electron travel without spin flip. At small concentrations we have

$$T_c \approx T_{c0} - \frac{\pi}{4\tau_s}. \qquad (13)$$

At a concentration c_{cr} such that

$$\tau_{s\,cr} = \frac{1.1}{T_{c0}}, \qquad (14)$$

T_c vanishes.

Abrikosov and Gor'kov[16] observed also the possibility of "gapless" superconductivity. The gap in the energy spectrum vanished at a concentration of approximately $0.9\,c_0$. This means that even at T = 0 such a superconductor can absorb quanta of arbitrary energy, and its specific heat will depend linearly on the temperature. However, the absence of resistance to a small electric current is still retained. This is connected with the fact that the so-called ordering parameter, which characterizes the number of Cooper pairs in the Bose condensate (see [17]), must be proportional to the energy gap, as is the case for a pure superconductor. It can be stated that just as not all the particles enter the condensate in a non-ideal Bose gas at T = 0, in a superconductor with magnetic impurities not all the Cooper electron pairs are at the level with lowest energy. The remaining pairs are distributed somehow among the higher levels, and under certain conditions reach the level corresponding to the decay of the pair into individual electrons. I shall note here that, following our prediction, it has turned out that gapless superconductivity is not a rarity and is encountered under a variety of situations.

Subsequently Reif and Woolf,[18] using the tunnel-contact method, verified the state density obtained in such a theory. Apparently, in the case when the impurity has really a localized spin (for example Pb with Gd impurity), the agreement turns out to be good. To be sure, according to these measurements, the gapless superconductivity sets in at concentrations lower than called for the theory of Abrikosov and Gor'kov. However, as shown by Fulde and Maki,[19] this is apparently attributed to the influence of ordering.

Many calculations were made of various properties of superconductors with magnetic impurities, for example the thermal conductivity or the absorption of sound. I shall not discuss them in detail, however.

IV. SUPERCONDUCTIVITY AND ORDERING (SO)

From the formulas presented above for the change of the critical temperature it follows that T_c changes appreciably in the region of concentrations such that

$1/\tau_S \sim T_{C0}$. But the order of magnitude of $1/\tau_S$ is cJ^2/ϵ_F, i.e., precisely the ordering temperature Θ. In view of this, the intersection of the $T_C(c)$ and $\Theta(c)$ curves has the form shown in Fig. 4a. This raises the question of how the curves will behave subsequently, and in particular whether a phase that is simultaneously ordered and superconducting can exist. This problem was solved so far only for the case when the ordering corresponds to ferromagnetism (F).[20]

L. P. Gor'kov and A. I. Rusinov[21] have shown that the coexistence of superconductivity and ferromagnetism is possible. If at the same time the spin-orbit interaction (which leads to the appearance of a term proportional to $\sigma \cdot p \times p'$ in the scattering amplitude) is sufficiently large in the metal, then, in accordance with the prediction of [21], T_C and Θ do not change in the region of the intersection of the curves, and the entire region below this point is occupied by the SF phase. This prediction was refined by Bennemann,[22] who called attention to the need for taking into account the change of the time τ_S and the polarization of the spin by the exchange field. Since this suppresses the scattering with spin flip (the total spin of the electron and the impurity is conserved, and the spin of the impurity is quenched by the effective field), the real curve of T_C might even go above the curve for the disordered case (N) after the intersection (Fig. 4b). This refinement agrees with experiment.[2

Fulde and Maki[19] calculated the critical temperature and the main properties in ferromagnetic ordering and in the presence of an external field, and reached the conclusion that the problem reduces to replacement of $1/\tau_S$, which enters in the theory of Abrikosov and Gor'kov, by the combination

$$\frac{1}{\tau_s} + \frac{\tau_{tr}c_L^2e^2H^2}{3} + \frac{J^2\tau_{SO}}{2}; \qquad (15)$$

Here the second term is the consequence of the twisting of the Cooper-pair orbits by the external magnetic field (τ_{tr} is the usual transit time which enters the conductivity of the normal metal, v_F is the velocity of the Fermi boundary). The last term is the consequence of the ordering. Here $I = NcJ\bar{S}_z$, and τ_{SO} is the characteristic transit time connected with the spin-orbit interaction. The decrease of τ_{SO} reduces the effect of spin ordering. The calculation of Fulde and Maki pertains to the case when $1/\tau_{SO} \gg T_{C0}$. It is curious that there is a region of concentrations where the critical field depends nonmonotonically on the temperature. This is connected with the fact that the moment I itself depends on the field. Instead of the ordinary monotonically decreasing curve, a curve with a maximum is obtained. This is observed in the experiments of Crow, Guerstin, and Parks.[24] On the other hand, if the effects of the spin-orbit scattering are small, then the region of coexistence of superconductivity and ferromagnetism is much smaller, and there is a region of first-order phase transitions (Fig. 4c). This case is analyzed in detail by Sarma, de Gennes, and Cyrot.[25] Here, too, a nonmonotonic dependence of the critical field on the temperature is possible. There are many interesting details, which I am omitting. Instead, I wish to stop and discuss two particularly unusual aspects.

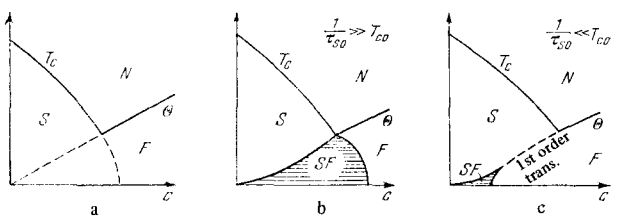

FIG. 4

First, the question of pairing with nonzero momentum. Fulde and Ferrel, and independently of them Larkin and Ovchinnikov,[26] advanced the following idea. If we consider a system of electrons magnetized, say, with the aid of impurity ferromagnetism, and disregard scattering with spin flip, then at $T = 0$ a first-order phase transition will take place into a purely superconducting phase at $I = \Delta_0/\sqrt{2}$, where $I = NcJS$ and Δ_0 is the superconducting gap. It turns out, however, that at large values of $I = 0.755\Delta_0$, a possibility appears of transition into a special superconducting phase in which the Cooper pairs have a nonzero momentum and Δ depends on the coordinate with a characteristic period $q_0^{-1} = (2.4\,I/v_F)^{-1}$. Such a phase has many interesting peculiarities; for example, when $T \ll \Delta_0$, the specific heat depends on the temperature like $1/\ln^3(\Delta_0/T)$.

Unfortunately, apparently, this phase is not realized in practice, at any rate if the electrons are polarized by magnetic impurities. For this phase to be realized it is necessary that the ordinary mean free path be larger than the period of the structure. This is impossible to realize even if the substance contains no impurities other than the magnetic atoms, for as a rule the energy of the potential interaction of the electron with the impurities is of the order of the Fermi energy and the energy J is several times smaller. Although in the case of rare-earth impurity in lanthanum the potential interaction is small, the spin-orbit interaction is to the contrary large, and this greatly interferes with the effect.

I shall now describe one more hypothesis. The preceding hypothesis pertained to the case of a small gap Δ and of developed magnetism. Another hypothesis, belonging to Anderson and Suhl,[27] pertains to the opposite case, that of strong superconductivity and weak magnetism, in other words to the concentration region where $\Theta \ll T_C$. In this case we can assume the superconducting characteristics to be the same as for the pure metal. Anderson and Suhl calculated the function $\chi(q)$ which determines, as already mentioned, the energy of the ordered state with a helical spin-density wave with wave vector q. It turned out that when $q < \Delta_0/v_F$, the function $\chi(q)$ decreases in this case and becomes equal to zero when $q \to 0$. This means that even in the homogeneous model $\chi(q)$ is maximal not at $q = 0$ but at a finite value of q, which turns out to be of the order of $(p_0^2\Delta_0/v_F)^{13} \sim (50\,\text{Å})^{-1}$. This means that in this case we can expect appearance of a spin-density wave with a period of the order of 50 Å. This phenomenon was called by the authors "cryptoferromagnetism." Since the pair turns out to be much larger than the interatomic distances, we can expect the inhomogeneities of the impurity concentration to have less effect on the smearing of the transition point, and the transition to become sharper than without superconductivity. This is apparently indeed observed in the experiments.

V. THE KONDO EFFECT (K)

I now proceed to the most difficult cell of the matrix —the Kondo effect. It was observed, as far back as in the thirties, that in noble metals the resistance frequently has a minimum as a function of the temperature (see [28]); this means that there exists a scattering mechanism, whose efficiency increases with decreasing temperature. In many cases a maximum was observed below the minimum. It was ascertained subsequently that this new mechanism of resistance is connected with the magnetic impurities. The experiments were performed with different combinations of the host metal and the impurity, for example: AgMn, CuFe, AuFe, MgMn, CuMn, ZnMn, AuV, AuMo, etc. The minimum was observed only at sufficiently small magnetic-impurity concentrations, as a rule 0.1% and below. In 1956, N. E. Alekseevskiĭ and Yu. P. Gaĭdukov [29] performed measurements on gold with an exceptionally small iron impurity, and found that the resistance, in a large temperature interval, satisfies the law

$$\rho = \rho_1 + \rho_2 \ln\left(\frac{1}{T}\right), \tag{16}$$

and then approaches a certain finite limit at lower temperatures. There are therefore no more reasons for calling this phenomenon the Kondo effect than there are for calling ferromagnetism a Heisenberg or a Weiss effect. But this has already been established in the literature, and I shall therefore also use this term.

There were many incorrect attempts to explain this phenomenon, but only in 1964 did Kondo [30] present a correct interpretation. The point is that usually the part of the resistance connected with the presence of the $J\sigma \cdot S$ interaction is calculated in the Born approximation. This was justified by the smallness of J (as I have already noted, J need by no means be small). This yielded a constant which was added to the ordinary residual resistance. Kondo calculated the next higher approximation for the scattering amplitude, and found that the correction is of the order of $J/\epsilon_F \ln(\epsilon_F/\epsilon)$, where ϵ is the electron energy reckoned from the Fermi boundary. If $J < 0$, the correction to the resistance has a positive sign.

The appearance of the logarithm is important in what follows, and I shall therefore present a simple derivation. Let us consider the amplitude for the scattering of the electron by the impurity. In the initial state, the quasimomentum of the electron is p, the spin projection is α, and the impurity spin is M; in the final state we have respectively p′, α', and M′.

In the first Born approximation we have

$$A^{(1)\mathbf{p}'\alpha' M'}_{\mathbf{p}\alpha M} = -\frac{J}{N}\left\langle OM'\left| a_{p'\alpha'} \sum_{p_1 p_1' \alpha_1 \alpha_1'} a^+_{p_1\alpha_1}\sigma_{\alpha_1\alpha_1'}\mathbf{S}a_{p_1'\alpha_1'}a^+_{p\alpha}\right| OM\right\rangle,$$

where $|OM\rangle$ denotes the equilibrium state of the electrons and the impurity atom with spin projection M. This expression is equal to

$$A^{(1)\mathbf{p}'\alpha' M'}_{\mathbf{p}\alpha M} = -\frac{J}{N}(1-n_{p'})(1-n_p)(\sigma\mathbf{S})^{\alpha' M'}_{\alpha M}. \tag{17}$$

The factors $1 - n_p$ express the fact that the initial and final states should be free.

In the second approximation we have

$$A^{(2)\mathbf{p}'\alpha' M'}_{\mathbf{p}\alpha M} = \left(\frac{J}{N}\right)^2\left\langle OM'\left| a_{p'\alpha'} \sum_{p_1 p_1' \alpha_1 \alpha_1'} a^+_{p_1\alpha_1}\sigma_{\alpha_1\alpha_1'}\mathbf{S}a_{p_1'\alpha_1'}(E_{\text{нач}} - H_0 + i\delta)^{-1}\right.\right.$$

$$\times \sum_{p_2 p_2' \alpha_2 \alpha_2'} a^+_{p_2\alpha_2}\sigma_{\alpha_2\alpha_2'}\mathbf{S}a_{p_2'\alpha_2'}a^+_{p\alpha}\left|\right. OM\rangle.$$

Simple calculation yields

$$A^{(2)\mathbf{p}'\alpha' M'}_{\mathbf{p}\alpha M} = \left(\frac{J}{N}\right)^2 (1-n_{p'})(1-n_p)\left[\sum_{p_1}\frac{1-n_{p_1}}{\varepsilon_p - \varepsilon_{p_1} + i\delta}(\sigma\mathbf{S}\cdot\sigma\mathbf{S})^{\alpha' M'}_{\alpha M}\right.$$

$$\left. - \sum_{p_1}\frac{n_{p_1}}{-\varepsilon_{p'} + \varepsilon_{p_1} + i\delta}\sum_{ik}(\sigma_i\sigma_k S_k S_i)^{\alpha' M'}_{\alpha M}\right].$$

Since $\epsilon_{p'} = \epsilon_p$, it follows therefore that in the case of ordinary potential scattering the number n_{p_1} would not appear at all under the sign of the integral with respect to p_1, but in this case, since the spin operators S_i are not commutative, we have

$$\begin{aligned}(\sigma\mathbf{S})(\sigma\mathbf{S}) &= S(S+1) - \sigma\mathbf{S},\\ \sum_{ik}\sigma_i\sigma_k S_k S_i &= S(S+1) + \sigma\mathbf{S}.\end{aligned} \tag{18}$$

When integrating with respect to p_1 we recall that all the energies are reckoned from the Fermi surface, we assume the limits to be symmetrical, and we put $|\epsilon_p| \ll \epsilon_F$. We then obtain

$$A^{(2)\mathbf{p}'\alpha' M'}_{\mathbf{p}\alpha M} = \left(\frac{J}{N}\right)^2 (1-n_{p'})(1-n_p)\left[-S(S+1)\delta_{\alpha\alpha'}\delta_{MM'}\nu(\varepsilon_F)i\pi(1-2n_p)\right.$$

$$\left. - (\sigma\mathbf{S})^{\alpha' M'}_{\alpha M}\sum_{p_1}{}'\frac{1-2n_{p_1}}{\varepsilon_p - \varepsilon_{p_1}} + (\sigma\mathbf{S})^{\alpha' M'}_{\alpha M}\nu(\varepsilon_F)i\pi\right] \tag{19}$$

(all the sums over p_1 are transformed into integrals, $\sum \to \frac{1}{(2\pi)^3}\int d^3p_1$; $\sum'$ denotes the principal value of the integral).

The second term in this expression yields the logarithm. (The remaining terms will be discussed later). Confining ourselves to logarithmic accuracy, we obtain

$$A^{(2)\mathbf{p}'\alpha' M'}_{\mathbf{p}\alpha M} \approx 2\left(\frac{J}{N}\right)^2 \nu(\varepsilon_F)(1-n_{p'})(1-n_p)(\gamma\mathbf{S})^{\alpha' M'}_{\alpha M}\ln\frac{\varepsilon_F}{\max\{|\varepsilon_p|, T\}}. \tag{20}$$

Thus, the result in this approximation reduces to the substitution

$$\frac{J}{N} \to \frac{J}{N}\left(1 - 2\frac{J}{N}\nu(\varepsilon_F)\ln\frac{\varepsilon_F}{\max\{|\varepsilon_p|, T\}}\right). \tag{21}$$

The scattering amplitude begins to depend logarithmically on the energy of the electrons. Since the electrons taking part in the electric conductivity have an energy on the order of T, it follows that the exchange part of the resistance has in this approximation the form

$$\rho_{\text{exch}} \approx \rho_{\text{exch},0}\left(1 - 4\frac{J}{N}\nu(\varepsilon_F)\ln\frac{\varepsilon_F}{T}\right), \tag{22}$$

where $\rho_{\text{exch},0}$ is the constant Born value. This is the result obtained by Kondo. In the temperature region where the correction is small, formula (22) agrees well with experiment.* I shall now comment on the result. In the Born approximation, the resistance is independent of the sign of J, but here it begins to depend on the sign, becoming larger if $J < 0$, i.e., if the interaction has the antiferromagnetic sign. A simple explanation for this fact was proposed by Anderson. The next higher approximations following the Born approximation take into account the correlations in the positions of the electron and of the impurity. If $J < 0$, then the electron tends to

*With logarithmic accuracy, the exchange and potential scattering do not interfere. Therefore the total resistance is $\rho_{\text{exch}} + \rho_{\text{pot}}$, where ρ_{exch} is determined by formula (22).

approach the impurity with an opposite spin orientation. But when the spin orientation is opposite, scattering with spin flip becomes possible, i.e., there is a reaction channel which does not exist in the case when the spins of the electron and of the impurity are oriented in parallel. This means that when $J < 0$ the scattering amplitude is larger than $J > 0$.

Further, from the manner in which this result is obtained, it follows that two circumstances are significant here. First, the sharpness of the edge of the Fermi surface. This is precisely why, the scattering amplitude ceases to depend on the electron energy as soon as $|\epsilon_p| \ll T$. A second important circumstance is the noncommutativity of the spin operators. This takes place if the spins are not polarized by an external or an internal magnetic field. If such a polarization does take place, then the change of the spin orientation is connected with the change of the energy. As a result, a term $\pm Q$ appears in the denominator of the sum that yields the logarithm. This means that if $Q \gg T$, then the logarithmic integral will be cut off from below at Q. In this case the resistance will also contain $\ln(\epsilon_F/Q)$. In other words, the logarithmic term and the resistance can increase with decreasing temperature in any case only so long as $Q \ll T$. The role of Q can be played either by the effective field introduced above (it has the same order as the Curie temperature Θ), or else by $\mu_0 H$, where H is the external magnetic field and $\mu_0 S$ is the magnetic moment of the impurity. We shall assume for the time being that there is no external field, and the concentration is so small that $\Theta \sim cJ^2/\epsilon_F$ is much lower than the temperature at which the logarithmic correction, which is of the order of $J/\epsilon_F \ln(\epsilon_F/T)$, becomes of the order of unity.

Before I proceed, let me discuss the question of the so-called giant thermal emf. Let me remind you what this is all about. If an electric field and a temperature gradient exist in the metal, then the electric current is given by

$$j = \sigma E + \beta \nabla T.$$

If the circuit is opened, then $j = 0$ and $E = -(\beta/\sigma)\nabla T$. Introducing the potential $E = \nabla\varphi$, we obtain $d\varphi/dT = -\beta/\sigma$, i.e., the potential difference per degree is $-\beta/\sigma$. With the aid of the kinetic equation with a specified travel time, we obtain (see [31])

$$\frac{d\varphi}{dT} = -\frac{\beta}{\sigma} = -\frac{\int \tau(\varepsilon) v^2 \nu \frac{\partial n}{\partial \varepsilon} \nu(\varepsilon)\, d\varepsilon}{eT \int \tau(\varepsilon) v^2 \frac{\partial n}{\partial \varepsilon} \nu(\varepsilon)\, d\varepsilon}, \qquad (23)$$

where $\tau(\epsilon) = 1/w(s)$ is the time between the collisions or their reciprocal scattering probability, v is the electron velocity, ν is the density of states, and n is the distribution function (the energies are reckoned from ϵ_F). The function $\partial n/\partial\epsilon$ is close to $-\delta(\epsilon)$. The integrals with this function are evaluated in accordance with the rule

$$\int F(\varepsilon) \frac{\partial n}{\partial \varepsilon} d\varepsilon = -F(0) - \frac{\pi^2 T^2}{6} \left(\frac{\partial^2 F}{\partial \varepsilon^2}\right)_0 - \ldots$$

if the function F varies slowly in the vicinity of $\epsilon = 0$. As applied to formula (23), this rule yields

$$\frac{d\varphi}{dT} = \frac{\pi^2 T}{3e} \frac{\partial}{\partial \varepsilon} [\ln v^2 \tau \nu]\Big|_{\varepsilon = 0}. \qquad (24)$$

With this, $d\varphi/dT$ is of the order of $T/e\epsilon_F$, or of the order of 10^{-8} V/deg at a temperature of the order of 1° K. Such values are actually observed in pure metals.

However, if the scattering probability contains a term proportional to $2n(\epsilon) - 1$, which varies rapidly in the vicinity of $\epsilon \approx 0$, then this rule no longer holds. Moreover, the quantity $2n(\epsilon) - 1$ is odd in ϵ, and consequently the integrand in the numerator of (23) becomes a function that is even in ϵ in the zeroth approximation. This changes the result radically. The derivative $\frac{\partial}{\partial\epsilon}(2n(\epsilon) - 1)$ is of the order of $1/T$. If we substitute this in (24), we see that the thermal emf is not dependent on the temperature. The terms with $2n(\epsilon) - 1$ are the result of the circling around the poles during the integration of the intermediate states, as was the case, for example, in the derivation of (19). It is much more difficult to retain this dependence in the scattering probability. Kondo has shown that such terms appear in the scattering probability as a result of interference between the potential and exchange scattering. If both are assumed to be isotropic, then the resultant expression is

$$\frac{d\varphi}{dT} = \frac{4\pi^2}{e} \nu(\varepsilon_F) JU \frac{\rho_{exch}}{\rho}, \qquad (25)$$

where $\rho_{exch}/\rho = J^2S(S+1)/[U^2 + J^2S(S+1)]$ is the ratio of the "exchange" part of the resistance to the total resistance, U is the amplitude of the potential scattering. It is assumed here that $J \ll U$. The order of magnitude of this expression is $J^3/eU\epsilon_F^2$. If we assume that $U \sim \epsilon_F$ and $J \sim 0.2\,\epsilon_F$, then we obtain 10^6 V/deg. The value obtained in the experiment on AuFu was 10^{-6}–10^{-5} V/deg. Unlike in pure metals, in accordance with (25) $d\varphi/dT$ does not depend on the temperature. The same is observed experimentally down to very low temperatures, where the thermal emf decreases in absolute magnitude. This may be connected either with the ordering or with the formation of a quasibound state, which will be discussed later. The sign of $d\varphi/dT$ is determined by the ratio of the signs of J and U. For most alloys with a Kondo effect the sign is negative. On the high-temperature side, the effect begins to decrease when the total scattering begins to increase as a result of the phonons.

Let me remark that prior to Kondo's explanation, the giant thermal emf was attributed to the interference scattering upon ordering. The latter explanation is in all probability incorrect, since giant thermal emfs occur also above the ordering temperature.

Let us return now to expressions (21) and (22). If the concentration is sufficiently low, then we can arrive at a situation wherein the correction becomes of the order of unity even before reaching the Curie temperature $\Theta \sim CJ^2/\epsilon_F$. What will occur in this case? The first to sum the principal terms were Suhl[33] and the present author.[34]

In the logarithmic approximation, the result (for $T = 0$) is,

$$\frac{J}{N} \to \frac{J}{N}\left(1 + 2\frac{J}{N}\nu(\varepsilon_F)\ln\frac{\varepsilon_F}{|\varepsilon|}\right)^{-1}. \qquad (26)$$

If $J > 0$, then this expression can always be used. If, however, $J < 0$, then this expression becomes infinite at some energy. The same pertains to the resistance. At some temperature

$$T_K = a\varepsilon_F e^{-\frac{N}{2|J|\nu(\varepsilon_F)}}, \quad (27)$$

where a is a constant of the order of unity, we get $\rho \to \infty$. This is the Kondo temperature. It does not depend on the concentration. It is clear that the logarithmic approximation is insufficient at temperatures on the order of or lower than T_K. Two ideas were proposed for solving this problem.

One method belongs to Suhl and Wong.[35] Maleev and Ginzburg[36] in Leningrad follow the same trend and have formulated the method most clearly. It is assumed that the scattering amplitude, as a function of the energy regarded as a complex variable, is analytic in the entire complex plane, in which a cut is drawn along the positive axis from zero to infinity. The unitarity condition is then used for the scattering matrix

$$i(T^+ - T) = T^+T. \quad (28)$$

If we write this operator equation in matrix form, then we get on the right side a sum over the intermediate states, which contain in addition to one electron also an arbitrary number of electron-hole pairs. It is assumed that these many-particle states make no essential contribution. Under this assumption, the unitarity condition is transformed into an equation for the scattering matrix T. The solution is obtained with allowance for the aforementioned analytic properties and the requirement that the result must go over into the formula (26) obtained from perturbation theory at high energies or temperatures.

The shortcomings of this approach are as follows:

a) A certain doubt with regard to the limitation of the intermediate states. The point is that, as can be readily shown, perturbation theory can yield equations having sufficient accuracy, but it is impossible to show that they coincide with the equations of Suhl and Maleev with better than logarithmic accuracy.

b) The assumption concerning the analytic properties of the scattering amplitude is not unique.

The results of this approach (I shall call it the unitary approach) are as follows: At T = 0 and $\sigma \to 0$, the effective electron-impurity scattering cross section reaches the "unitary" limit

$$\sigma = \frac{4\pi}{k^2}(2l+1), \quad (29)$$

where the factor $(2l + 1)$ takes into account the fact that the "Kondo effect" can appear in each partial amplitude separately, and the most important amplitude is naturally the one in which it appears the earliest.

With decreasing temperature, the $\rho(T)$ curve gradually approaches the corresponding value, with

$$\rho(0) - \rho(T) \sim \begin{cases} \dfrac{1}{\ln \dfrac{T_K}{T}}, & l \neq 0, \\ \dfrac{1}{\ln^2 \dfrac{T_K}{T}}, & l = 0. \end{cases} \quad (30)$$

There is an additional specific heat proportional to the impurity concentration. It has a maximum at some temperature on the order of the Kondo temperature, and decreases like $1/\ln^3(T_K/T)$ when $T \to 0$. The thermal-conductivity coefficient satisfies the Wiedemann-Franz law, i.e., it can be obtained from the electric conductivity. Ther thermal emf was determined, but I shall not stop to discuss it here. The magnetic moment of the impurity was not calculated. The predictions agree with experiment qualitatively, but the logarithmic law for $\rho(0) - \rho(T)$ has apparently not been confirmed quantitatively.

Another idea was advanced first by Nagaoka,[37] although at present this idea is being developed not by him but by Yosida[38] and by myself.[39] (Kondo[40] and Anderson[41] are also doing related work.)

The idea is based on the fact that the behavior of the scattering amplitude at $J < 0$ is very similar to the behavior of electron-electron scattering amplitude in the case when the electrons are attracted to one another. As is well known, this is a symptom of the instability of the ground state, and corresponds to the superconducting transition (see [17]). It is natural to assume in this case, too, the formation of a certain "quasibound" state of the electron with localized spin, of the type of Cooper pairs in a superconductor. We are actually dealing here with a collective effect, which is manifest by the appearance of a certain electron-impurity correlation. Just as in superconductors, however, the situation is similar in many respects to the situation when true bound states appear.

I shall not report all the investigations in this field. Those based on perturbation theory, as a rule, do not take into account all the necessary diagrams. In particular, this pertains to work by Nagaoka himself for the spin $\frac{1}{2}$.[37] In view of this, I consider attempts (for example by Hamann[42]) at solving these equations more accurately than by Nagaoka himself in his first papers to be meaningless. On the other hand, there are investigations based on a variational approach.[40,41] However, as always, the accuracy of the results of such an approach is difficult to check. What are the results of the "bound state" idea? I find it difficult here to resist the temptation of presenting my own result.[39]

The calculation technique is based on representing the spin operator with the aid of creation and annihilation operators for fictitious fermions:[34]

$$\hat{S}^i = \sum_{\beta\beta'} a^+_\beta S^i_{\beta\beta'} a_{\beta'}, \quad (31)$$

where $S^i_{\beta'\beta}$ are the matrices of the corresponding spin, say the Pauli matrices for $S = \frac{1}{2}$, and the term on the right side is simply a notation for the sum (for example, for $S = \frac{1}{2}$ we have $S_z = \frac{1}{2}(a^+_{1/2}a_{1/2} - a^+_{-1/2}a_{-1/2})$. Although the introduction of such fermions means the introduction of unphysical states (physical states are those in which one of the occupation numbers n_β is equal to unity and the remainder are equal to zero), but we can get rid of them when necessary. The introduction of quasifermions makes it possible to go over to the usual field-theory technique (see [43]). In particular, the scattering amplitude is obtained by summing a two-dimensional sequence of Feynmann diagrams, which we call a "parquet." Examples are shown in Figs. 5a and 5d, while Fig. 5e shows a diagram not pertaining to this sequence. The dashed lines correspond here to fictitious fermions a_β, and the solid lines to electrons. This is precisely how expression (26) was obtained in [34]. The diagrams of the "parquet," following a slight modification of the dashed lines and of the "bare" vertices,

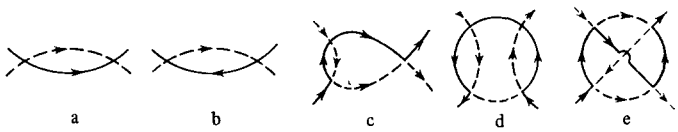

FIG. 5

actually yield the scattering amplitude with required accuracy, and not only with logarithmic accuracy. Since I did not succeed in proving that the corresponding equations go over into the Suhl-Maleev equation,[35,36] the latter circumstance causes me to be doubtful.

The formation of quasibound states is taken into account by introducing "mean values" of the type $\langle \psi_\alpha a_\beta \rangle$. Their total number is four, since ψ and a can be replaced by ψ^+ and a^+. At first glance, such quantities are not equivalent, since they do not conserve the number of electrons. In fact, however, such a matrix element denotes simply a transition of the electron into the quasibound state. In exactly the same manner quantities of this type denote in superconductivity the transition of free electrons into a Cooper pair. Here, however, the situation is somewhat different, since the "parquet" is a much more complicated sequence than the superconducting "ladder." The results are as follows: when T = 0 it can be shown that the bound state can be produced only when $J < 0$ with total spin $S - \frac{1}{2}$. The binding energy is equal to

$$\varepsilon_b = K\varepsilon_F \left(\frac{N}{\nu(\varepsilon_F)|J|}\right)^{S-1} \exp\left(-\frac{N}{2\nu(\varepsilon_F)|J|}\right), \qquad (32)$$

where $K \sim 1$. Unfortunately, the problem can be solved only in the logarithmic approximation, and there is no complete assurance that $K \neq 0$. This is precisely what prevents us from obtaining the thermodynamic characteristics at $T \neq 0$ for an arbitrary spin. However, for S = 1 there is an important mitigation. In this case a ladder is obtained in place of the parquet at a total spin $S - \frac{1}{2}$. As a result (subject to some additional assumptions), the problem does not differ greatly in complexity from superconductivity. The results for this case are as follows: there is a transition temperature T_c, connected with the binding energy at T = 0 by the relation

$$\varepsilon_b = \frac{8}{3\gamma} T_c, \qquad (33)$$

where $\gamma = 1.78$. The bound state is destroyed by the magnetic field H_c, which has the following asymptotic values:

$$\begin{aligned} g\mu_B H_c &\approx \Lambda\left\{1 - \left[2\nu^2(\varepsilon_F)\left(\frac{J}{N}\right)^2 \ln\left(\frac{T_c}{T}\right)\right]^{-1}\right\}, \quad T \to 0, \\ g\mu_B H_c &\approx \pi\sqrt{\frac{6}{7}\zeta(3)\,T_c(T_c - T)}, \quad T \to T_c, \end{aligned} \qquad (34)$$

where Λ is of the order of the Fermi energy (it is connected with T_c by the relation $T_c = (2\Lambda\gamma/\pi) \times \exp[-N/2\nu(\epsilon_F)|J|)]$, meaning that it is practically impossible to destroy this state with a magnetic field at low temperatures.

The specific heat is given by

$$\begin{aligned} \Delta C &= cN \cdot 3.16 \frac{T}{T_c}, \quad T \to 0, \\ \Delta C &= cN\left(1{,}08 + 0.34\,\frac{T - T_c}{T_c}\right), \quad T \to T_c. \end{aligned} \qquad (35)$$

The linear specific heat at low temperatures is evidence that there is no energy gap. One can speak more readily of the appearance of a maximum in the density of the states at the Fermi boundary itself. The width of this maximum is of the order of T_c, and the maximum gradually smoothes out as $T \to T_c$. The jump at $T = T_c$ is apparently not real.

The magnetic moment is given by

$$\left.\begin{aligned} \Delta M &= \frac{2}{3} cN \frac{(g\mu_B)^2 H}{T}, \quad T > T_c, \ \mu_B H \ll T, \\ \Delta M &= \frac{2}{27} cN \frac{(g\mu_B)^2 H}{T}, \quad T \ll T_c, \ \mu_B H \ll T, \\ \Delta M &= cN\left[\frac{3}{7} g\mu_B + \frac{16\gamma}{7\pi^2} \frac{(g\mu_B)^2 H}{T_c}\left(\ln\frac{3\pi T_c}{2\gamma g\mu_B H} + \frac{1}{2}\right)\right], \\ & T \ll \mu_B H \ll T_c. \end{aligned}\right\} \qquad (36)$$

In measurements of the susceptibility in a weak field, the situation corresponds to an apparent decrease of the magnetic moment of the impurity by a factor of 3, but not to a vanishing of this moment.

For the spin $S = \frac{1}{2}$, owing to the parquet situation, it is impossible to obtain similar expressions, but the magnetic moment can be expressed in terms of the value of the "ordering parameter" R, which should be close to T_c:

$$\Delta M = cN \frac{(g\mu_B)^2 H}{R}, \quad T \to 0 \qquad (37)$$

(the relation between H and T is arbitrary). A similar result was obtained by Ishii and Yosida.[44] It follows therefore that at $S = \frac{1}{2}$ there is only the polarizability of the complex, and no moment is left at all.

With respect to the electric resistance at S = 1, it can be stated that it approaches the unitary limit in accordance with the law (the "exchange part!)

$$\rho_{exch} = \rho_{об\text{м}}(0)\left[1 - \alpha\left(\frac{T}{T_c}\right)^2\right], \quad \alpha \sim 1, \ T \ll T_c. \qquad (38)$$

The constant α cannot be determined exactly. Let me remark that the results on the specific heat and on the resistance agree qualitatively with the first papers of Nagaoka. Although the presented results agree in many respects with the experimental data, nonetheless they do not seem to be undisputable. Without going into technical details, I shall confine myself here only to this remark.

Let me report also results by others. Anderson,[41] using a variational procedure, obtained the law $\Delta\chi \sim T^{-1/2}$ and $\Delta C \sim T^{1/2}$ for the case $S = \frac{1}{2}$, while Hamann and Bloomfield[42] obtained $\Delta C \sim T^{0.57}$ from an exact solution of the Nagaoka equation for $S = \frac{1}{2}$. From this same result, Murate and Wilkins[45] obtained a variation like $1/\ln^2(T_c/T)$ for the approach of the resistance to the unitary limit as $T \to 0$. I have already mentioned my own objections to these approaches.

Further, there is a prevalent opinion, although not proved rigorously by anyone, that the ground quasibound state must be spinless at any impurity spin S, i.e., the electron cloud must compensate for the impurity spin. I have some doubts with this respect, since I was unable to observe any logarithmic singularities in the diagrams with two electron lines for S = 1. However, even total screening of the localized spin by the conduction electrons at $S = \frac{1}{2}$, let alone such a possibility for any spin, raises again the question of the correctness of the very concept of the localized spin and of the validity of the $J\sigma \cdot S$ interaction. This has induced many authors, particularly Dworin[46] and Suhl,[47] to start

not from the "exchange interaction" of the spins, but from more fundamental models. The most promising is the new approach by Suhl,[47] who considers the interaction of the electrons with the impurity atom and of the electrons with one another. It is stipulated as a condition that the amplitude of the mutual scattering of the electrons in the triplet state must have a pole.

The solution of the coupled equations for the Green's function of the electrons and for the electron-electron vertex yields, after making some simplifying assumptions, the following results. At high temperatures, the resistance increases logarithmically with decreasing T, while the magnetic susceptibility follows the Curie law with localized spin $S = \frac{1}{2}$. At low temperatures, the resistance approaches the unitary limit in accordance with a quadratic law, and the magnetic susceptibility attends to a constant on the order of (37). Thus, the results of the "quasibound" approach for the spin $\frac{1}{2}$ are confirmed. However, in addition, Suhl's new method is valuable because in principle it makes it possible to clarify the question of the screening of the spin when $S > \frac{1}{2}$. This apparently will be done in the near future.

What is the experimental situation? Measurements of the resistance by Daybell and Steyert[48] in CuFe and CuCr show that as $T \to 0$ the value of $\rho(T)$ ceases to increase and approaches a finite limit quadratically. The limiting value of the effective cross section for Cr was 2.4 times larger than for Fe, and if it is to believed that this is the unitary limit (as is obtained from all the theories), then it is clear that the Kondo effect takes place not only for s-scattering.

The measurements of the magnetic susceptibility in the same experiments show that the magnetic moment decreases when the temperature is decreased, but it is difficult to say whether it vanishes. Anderson assumes that these results agree well with his $\Delta\chi \sim T^{-1/2}$ law, but in my opinion they likewise do not contradict my formulas,[39] although, of course, the latter pertain only to the spin S = 1 and cannot claim to be universal. From the formula for the Kondo temperature it follows that if $|J| < \epsilon_F$, then $T_K \ll \epsilon_F$. However, as I have already noted, J need not necessarily be small. This, too, is confirmed by experiments by Kume[49] in gold with vanadium as an impurity, where T_K turns out to be in the vicinity of 300° K. Incidentally, in these experiments, since a wide temperature interval can be investigated, it is possible to confirm well the quadratic decrease of the resistance. As to the magnetic susceptibility, it behaves more readily like $T^{-0.2}$. Incidentally, all the theoretical calculations pertain actually only to the case $|J| \ll \epsilon_F$, and it is therefore possible that a comparison of the results of Kume with the existing theory is not always meaningful. But a quadratic law for the resistance, if it does exist, should be very general, since it is not connected with the Fermi statistics. Furthermore, the fact that it holds in the case of AuV offers additional evidence against the unitary results.

One more interesting experimental result was obtained by Frankel and co-workers[50] with the aid of the Mossbauer effect. They measured the field at the iron nucleus in a dilute CuFe solution. It turned out that although this field saturates when the temperature is decreased, in accordance with the law

$$H_{hf} = H_{sat} B_J \frac{g\mu_B H_0}{T},$$

where H_0 is the external field, B_J is the Brillouin function, and the saturation field H_{sat} itself depends on the applied field up to very strong fields. The authors conclude therefore that the bound state at low temperatures is not destroyed up to $\mu_B g H_0 > (4-5)\,T_C$. This corresponds to the result (34) presented above concerning the critical field at low temperatures.

I have purposely listed the main concept, since none of them can still be regarded as final. Let me note one more interesting idea by Schrieffer,[51] namely that all the impurities of the transition metals in nonmagnetic fields have a localized spin, but for some of them the Kondo temperature lies above the melting point, and at lower temperatures the electron cloud screens the impurity spin completely. This recalls the proverb: "All men are bald, but some have their baldspot overgrown with hair."

In conclusion, let me report one more result having a bearing on the Kondo effect. I have in mind the tunnel characteristics at small potential differences. If two metals are separated by a layer of insulator of thickness of only several interatomic distances, then an electric current may flow between the metals as a result of the so-called tunnel effect. Usually the insulator is a film of oxide on the surface of the metal. This device is called a tunnel contact. Such a contact, at not too large voltages, has a linear characteristic, i.e., a constant resistance. However, more detailed experiments have shown that in many cases the effective resistance depends on the potential difference and has a maximum at V = 0. Applebaum and Anderson[52] and Zawadowski and Solyom[53] attributed this to the presence of magnetic impurities in an insulating layer between the metals. In this case, a $\sigma \cdot S$ term appears also in the tunnel Hamiltonian, interferes with the exchange scattering without tunneling, and produces the same Kondo effect. At low temperatures, the logarithmic integral is cut off from below at eV, giving for the effective resistance a dependence on the potential difference in the form $\ln(\epsilon_F/eV)$ all the way to $eV \sim T$. These considerations are well confirmed by experiments of Wyatt, Rowell,[54] and others. In particular, Mezei[55] has purposely introduced chromium into an aluminum tunnel contact and confirmed finally that the maximum is connected with the magnetic impurities.

VI. THE KONDO EFFECT AND ORDERING (KO),[56] NEGATIVE MAGNETORESISTANCE

As already noted in the preceding chapter, an external or internal field, by ordering the spin, leads to a suppression of the Kondo effect. This means that below a temperature $T < Q$, where Q is any internal effective field of the order of Θ or $\mu_B g H$, the logarithm takes the form $\ln(\epsilon_F/\Theta)$ or $\ln(\epsilon_F/\mu_B g H)$, and ceases to increase with decreasing temperature.

However, the role of the spin polarization is not limited to this. The scattering amplitude $\sigma \cdot S$ leads to an effective scattering cross section proportional to $S(S+1)$. But in the case when the impurity spins are polarized,

all that is left of $\sigma \cdot S$ is $\sigma_z S$. Therefore $S(S+1)$ in the scattering probability is replaced by S^2. Alternately, we can say with respect to this effect that scattering with spin flip becomes forbidden. Thus, besides the fact that the logarithm becomes a constant, the coefficient in the resistance component connected with the $\sigma \cdot S$ interaction also decreases.

If the ordering is ferromagnetic or occurs under the influence of an external field, then there is one more effect, namely interference between the potential scattering and the $\sigma \cdot S$ interaction. Indeed, for an electron with a spin projection along the field, we obtain a scattering amplitude $U - JS$, as for an electron with a spin against the field we get $U + JS$ (of course, if $T \ll Q$; U is the potential-scattering amplitude). The corresponding scattering probabilities are proportional to $U^2 \pm 2JSU + (JS)^2$. The probability must be averaged over all the impurities. If the ordering has an antiferromagnetic or random character, then the interference term vanishes following such an averaging. But if ferromagnetism or polarization by an external field takes place, then it remains. For the corresponding times we obtain

$$\tau_{\pm} \sim \frac{1}{U^2} \pm \frac{2JS}{U^3} + \frac{4(JS)^2}{U^4} - \frac{(JS)^2}{U^4}$$

(it is assumed here that $J \ll U$). The next to the last term arises here as a result of interference. Since the conductivities is due to "plots" and "minus" electrons add up, the total conductivity will be proportional to

$$\frac{\tau_+ + \tau_-}{2} \sim \frac{1}{U^2} + \frac{3(JS)^2}{U^4},$$

and to corresponding resistivity is

$$\rho \sim U^2 - 3(JS)^2.$$

In the absence of interference we will have

$$\rho \sim U^2 + (JS)^2.$$

We have not taken the Kondo effect into account here. If $Q \gg T_K$, then we get for $T \ll Q$

$$\rho \sim U^2 + (JS)^2 \left[1 + \frac{2J}{N} \nu(\varepsilon_F) \ln \frac{\varepsilon_F}{Q}\right]^{-2} - 4(JS)^2. \qquad (39)$$

Thus, when $T \sim Q$, the growth of the logarithm in the second term stops, and $S(S+1)$ is replaced by S^2. In addition, a third negative term appears. The result of all this is that the ordering causes not simply the cessation of the growth of the resistance with decreasing temperature, but also the appearance of a maximum on the plot of the resistance against the temperature at $T_{max} \sim Q$. I emphasize once more that the maximum is due to two causes, and can therefore occur also in the case of antiferromagnetic ordering. Of course, to this end it is necessary that the corresponding temperature be lower than T_{min}, at which the total resistance has a minimum. If Q is connected with ordering, then $T_{max} \sim \Theta$, i.e., it is proportional to the concentration. On the other hand, if it is due to the external field, then T_{max} is proportional to H.

In addition, it should be noted that an external field, by polarizing the spins, must cause the resistance to be decreased by the $\sigma \cdot S$ interaction. This decrease can be larger than the increase of the resistance due to the twisting of the electron orbits, and the net result may be negative magnetoresistance.

All these phenomena, namely the maxima, their positions, and the negative magnetoresistance, were observed in the experiments and agree well with the foregoing considerations (see [28]). I shall not present the rather complicated formulas, which furthermore can be claimed to be rigorous only if the orientation of the spins is connected with the external field, since, as already mentioned, the question of the type of ordering has not yet been clarified. I note only that when $\mu_B g H \ll T$, the correction to the resistance will obviously be proportional to $-(\mu_B g H)^2/T^2$ or $\rho(H) - \rho(0) \sim -(\Delta M)^2$, where ΔM is the impurity part of the magnetic moment.[57]

Of course, in the case when the Kondo effect actually leads to the formation of bound states with zero total spin, the question of ordering below the Kondo temperature becomes meaningless; however, if the spin is incompletely compensated, then the question of ordering at $\Theta < T_K$ still remains, but obviously it is meaningless to solve it so long as the question of spin compensation is unclear.

VII. KONDO EFFECT IN SUPERCONDUCTIVITY (SK)

There is a large number of papers in this field. Almost all deal with the case of small concentrations. Apparently, a result most worthy of confidence was obtained by Fowler and Maki[58] with the aid of a certain modification of Suhl's theory. I obtained the same result[59] for S = 1 with the aid of the method I already mentioned. According to these results, the bound state cannot occur if T_K is lower than the superconducting-transition temperature of the pure sample. On the other hand, if T_K if higher than this temperature, then T_c decreases, and in accordance with my calculations

$$\frac{\delta T_c}{T_{c0}} \sim -\frac{c\varepsilon_F}{T_c}. \qquad (40)$$

For comparison I remaind you that if $T_{c0} \gg T_K$, then the change of the critical temperature with changing impurity concentration at low concentrations is of the order

$$\frac{\delta T_c}{T_{c0}} \sim -\frac{cJ^2}{\varepsilon_F T_{c0}}. \qquad (41)$$

Thus, according to these results, the critical temperature drops noticeably in the presence of the Kondo effect. However, the results of a result by Ginzburg,[60] based on the unitary approach, according to which T_c is increased by the presence of magnetic impurities if $T_c \ll T_K$. For physical reasons, I consider this result to be very doubtful.

In concluding this section, let me say that if $T_{c0} \gg T_K$, the Kondo corrections will nevertheless apparently have an effect on the properties of superconductors. In any case, allowance for these corrections in τ_s, which determines the properties of the superconductors with magnetic impurities, will improve the agreement between theory and experiment.[61]

This concludes the present review. Of course, as stated at the beginning I could not touch upon all the problems connected with magnetic impurities. For ex-

ample, the question of magnetic impurities in so-called almost-ferromagnetic metals such as palladium[62] was completely left out. There are many interesting aspects to that question, too, for example giant magnetic moments, a ferromagnetic transition under the influence of a small magnetic impurity, and many others. But these questions, in my opinion, call for a separate review no smaller in size that a present one, based on a detailed exposition and development of Landau's conception of the Fermi liquid.

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