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MAGNETIC FIRST ORDER PHASE TRANSITIONS

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1. INTRODUCTION

MAGNETIC transformations of ferromagnets at the Curie point or of antiferromagnets at the Neel point are usually, from the thermodynamic point of view, second order phase transitions. In the last 5–6 years, however, much experimental material has been accumulated, indicating that there exist also magnetic systems in which these transitions are of first order. Such systems include many compounds and alloys, and also a large group of rare-earth metals. In spite of the great variety of magnetic systems in which these transitions have been observed, and also in spite of the different character of the transformations themselves, a common feature of all the first order magnetic phase transitions is that the principal role in the transformation is played by the change of the magnetic (exchange) interactions, whereas the changes of the volume and of the symmetry of the crystal lattice are only concomitant phenomena.

All magnetic first-order phase transitions can be conditionally subdivided into two groups: order-disorder transitions and order-order transitions. The order-disorder transitions are called transitions with inversion of the exchange interaction. This term was used by Kittel in a theoretical analysis of magnetic transformations connected with the change of the character of the spin ordering and arising in ferromagnetism-antiferromagnetism transitions, and also in transitions of substance with complicated helical magnetic structures into the ferromagnetic or antiferromagnetic state. Transitions of the order-disorder type are due to destruction of the spin order and are observed in ferromagnetism-paramagnetism transformations, and also in antiferromagnetism-paramagnetism transformations. A theoretical analysis of this class of magnetic transitions was first performed by Bean and Rodbell.

According to the theory of Kittel[1], and also of Bean and Rodbell[2], the main cause of magnetic first-order phase transitions is the strong change of the exchange interactions as a function of the interatomic distances, and also the associated change in the elastic energy of the material. This magnetic-transformation mechanism is called the exchange-striction mechanism of magnetic phase transitions. One of the necessary conditions for realization of large volume changes of the exchange integrals is a sufficiently high compressibility of the material. In this connection, great interest attaches to investigations, at high hydrostatic pressures, of ferro- and antiferromagnets having the indicated properties to a lesser or greater degree. In this review we shall consider in greater detail these two quantitative treatments of magnetic phase transitions[1,2], in light of which we discuss the available experimental data concerning investigations of magnetic, electric, and elastic properties of various magnetic systems with different types of spin ordering. In addition, we consider data on the influence of high pressure and strong magnetic fields on the temperature of the magnetic transformations. In the conclusion we shall report on papers in which other model explanations, not connected with the exchange-striction mechanism, are proposed for the explanation of magnetic first-order phase transitions.

It must be noted that from the formal point of view one can classify as magnetic first-order transitions of the order-order type also the transformations of antiferromagnets at the Morin point, i.e., transitions due to the reorientation of the spins relative to the crystal axes (e.g., the low-temperature transition in α-Fe_2O_3). As shown by Dzyaloshinskiĭ[123], the existence of transitions of this type can be explained within the framework of the Landau theory (see[5]). This class of magnetic transformations is not connected with the inversion of the exchange and is not considered in the present review.

2. MAGNETIC FIRST-ORDER PHASE TRANSITIONS OF THE ORDER-DISORDER TYPE

1) Classification of Magnetic Phase Transitions

Historically, the first theoretical analysis of magnetic phase transitions of ferromagnets was the statistical-thermodynamic theory of Weiss. The temperature dependence of the magnetization calculated on the basis of this theory actually describes, in general outline, the experimentally observed character of this phenomenon, i.e., the continuous transition from the ordered to the disordered state of the spin system. After Ehrenfest introduced the classification of phase transitions, magnetic transformations at the Curie point of ferromagnets were classified as second-order phase transitions, in accordance with the entire set of the then available experimental data.

As is well known, according to Ehrenfest, a phase transition is characterized by the order of those derivatives of the thermodynamic potential Φ, which experience finite changes during the transformation. First-order phase transitions include those in which the first derivatives of the thermodynamic potential with respect to the temperature T and the pressure P change jumpwise, and therefore jumpwise changes occur in such quantities as the entropy S and the volume V:

$$S=-\frac{\partial\Phi}{\partial T},\quad V=\frac{\partial\Phi}{\partial P}.$$

Second-order phase transitions are those in which the first derivatives of Φ are continuous, but its second derivatives are discontinuous, namely the specific heat C_p, the compressibility κ, and the coefficient volume thermal expansion α:

$$C_P = -T\left(\frac{\partial^2\Phi}{\partial T^2}\right)_P, \quad \varkappa = -\frac{1}{V}\left(\frac{\partial^2\Phi}{\partial P^2}\right)_T, \quad \alpha = \frac{1}{V}\left(\frac{\partial^2\Phi}{\partial P\,\partial T}\right).$$

According to this definition, in the case of magnetic second-order phase transitions, besides the sharp changes of C_p, κ, and α, there should be discontinuities of the magnetic susceptibility, the volume magnetostriction, and of the magnetocaloric effect at the transformation point. With further development of both theoretical and experimental investigations connected with problems of ordering, remarks were made that the identification of magnetic transformations as second-order phase transitions calls for an additional and more detailed analysis. This concerned primarily the questions connected with character of the anomalies and with the finite nature of the "jumps" of different physical quantities in second-order phase transitions. Theoretical calculations of the spontaneous magnetization, based on theoretical calculations in accordance with the Ising scheme[3] (two-dimensional plane lattice of magnetic moments), have shown that in this case the temperature dependence of the magnetization has a very sharp drop at the Curie point, and the specific heat tends to infinity. Interest in the Ising model increased particularly in connection with the work by Onsager, who pointed out the possibility of a rigorous analytic analysis of the ordering phenomena for a two-dimensional lattice. Experimental investigations of magnetic phase transition have shown that in many cases (principally in magnetic transformations of antiferromagnets) the temperature dependence of the specific heat is in the form of a λ curve, thus indirectly confirming the infinite magnitude of the jump which, as already noted above, was predicted theoretically for the particular case of a flat lattice. At the same time, a finite jump of the specific heat was observed for most ferromagnets, and the magnitude of this jump, as shown by Belov and co-workers (see[4]), could be calculated on the basis of the thermodynamic theory of second-order phase transitions of Landau and Lifshitz[5], the application of which to magnetic phenomena was first considered by Vonsovskiĭ[6] and Ginzburg[7]. Several attempts were made to find a suitable theoretical scheme, within the framework of which one could identify with assurance the various phase transformations among the second-order transitions.* Thus, for example, Ginzburg[10] advanced arguments indicating that the singularities of different second-order transitions can be attributed to different ratios of the volume and correlation energies. Verification of the validity of these considerations calls for experimental investigations of exceedingly high precision. Taking into account the very limited accuracy of the available experimental data, it is impossible at present to discuss exhaustively the behavior of ferromagnets at the Curie point in light of the aforementioned theory, so that the identification of this phenomenon as a second-order phase transition is to some degree arbitrary.

The first to suggest that purely magnetic transformations can be of first order was Rice[11]. In an investigation of the general thermodynamic properties of a magnetic Ising lattice, Rice has shown that the magnetic transformation connected with the disordering of the spin system can be a first-order transition if the exchange interactions change with changing interatomic distance, and as a result of these changes the lattice becomes deformed. These questions were considered in greater detail by Bean and Rodbell[2,12], who determined the concrete conditions for the occurrence of magnetic first-order phase transitions and who predicted new phenomena connected with the influence of high pressure on the temperature of magnetic transformations.*

*Semenchenko [8], on the basis of further development of the Gibbs theory of thermodynamic stability, noted that second-order transitions are identical with critical phenomena; the magnetic transformations at the Curie point of ferromagnets were considered as transcritical transitions. Phase transitions in ferroelectrics were considered from a similar point of view by Tiza [9].

2) The Bean and Rodbell Theory of Magnetic Phase Transitions

In their theory, Bean and Rodbell[2] considered on the basis of the molecular field model the interaction between an assembly of magnetic dipoles, and the entire attention was focused on the change of the character of the phase transition in the presence of a strong volume dependence of the exchange interaction. It was shown that in substances having large compressibility and a strong shift of the Curie temperature, changes of pressure can realize conditions under which the magnetic transition connected with the destruction of the magnetic structure, i.e., an order-disorder type of transition, is a first-order phase transition. The physical picture of this phenomenon is as follows. If it is assumed that the exchange interaction changes strongly when the interatomic distance changes, then the decrease of the volume at a given temperature leads to a change of the spontaneous magnetization σ_s of the ferromagnet as a result of a change of the exchange forces. The change of σ_s will be accompanied by a change of the dimensions of the sample and by the occurrence of elastic stresses. In turn, taking into account the strong volume dependence of the exchange integral, striction changes of the sample lead in final analysis to a new equilibrium value of the Curie temperature (T_c). If this change of the effective temperature is sufficiently large, then a situation can arise wherein a spontaneous magnetization will be observed above the true Curie point (T_0) of the "rigid" system, i.e., a system in which the exchange interaction does not change with the volume, and there is no associated spontaneous lattice deformation. Inasmuch as the existence of spontaneous magnetization at $T_c > T_0$ is due to the deformation of the lattice, and is in a certain sense unstable, the change of the elastic stresses with increasing temperature can lead to a sharp decrease of the spontaneous magnetization, i.e., to a first-order phase transition. Whether the magnetic transformation will have in each concrete case the features of a first-order or a second-order phase transition depends on the ratio of the exchange to elastic energies, on the compressibility κ, and on the change of the exchange energy β upon compression.

Bean and Rodbell proposed that the dependence of the Curie temperature on the volume is of the form

$$T_C = T_0\left[1 + \beta\frac{(V - V_0)}{V}\right], \tag{2.1}$$

*Later, similar ideas were considered also by Farrell and Meijer [13].

where V_0 is the volume of the sample in the absence of exchange interaction; the parameter β can be either positive or negative. The free energy of the system G_V per unit volume contains five terms: the exchange energy, the elastic energy, the entropy, and the energies due to the external magnetic field and the pressure:

$$G_V = -NkT_C\frac{\sigma^2}{2} + \frac{1}{2\varkappa}\left(\frac{V-V_0}{V_0}\right)^2 - TNk\left[\ln 2 - \frac{1}{2}\ln(1-\sigma^2) - \frac{\sigma}{\operatorname{arcth}\sigma}\right] - H\sigma_s\sigma + \frac{P(V-V_0)}{V}; \quad (2.2)$$

here σ is the relative magnetization, i.e., the ratio of the specific magnetization at a given temperature to the magnetization at T = 0°K. Minimization of the free energy with respect to the volume makes it possible to determine the equilibrium value of the volume:

$$\frac{V-V_0}{V_0} = N\varkappa kT_0\beta\frac{\sigma^2}{2} - P\varkappa, \quad (2.3)$$

which shows that the volume changes are consequences of the influence of the pressure and the magnetization. Substitution of (2.3) in (2.2) and minimization of the energy with respect to the magnetization make it possible to determine (in implicit form) the temperature dependence of σ:

$$\frac{T}{T_0} = \frac{\sigma}{\operatorname{arcth}\sigma}\left(1 + \eta\frac{\sigma^2}{3} - P\varkappa\beta\right), \qquad \eta = \frac{3}{2}Nk\varkappa T_0\beta^2. \quad (2.4)$$

Relation (2.4) contains the parameter η, the absolute values of which determine the character of the magnetic phase transition in each concrete case. $\eta > 1$ for first-order transitions and $\eta < 1$ for second-order transitions. This can be verified by examining the $\sigma = f(T/T_0)$ dependence expressed by Eq. (2.4). Figure 1 shows the temperature dependence of the magnetization for different values of the parameter η. For the case $\eta = 0$ and P = 0, we have the usual functional dependence of σ on T/T_0, determined by the Brillouin function. When $\eta < 1$, as seen from the curves of Fig. 1, the transition is of second order, whereas when $\eta > 1$ the transition at the Curie point is of first order. The dashed $\sigma(T/T_0)$ curve for $\eta = 4$ shows the non-equilibrium states of the magnetic ordering, corresponding to the maximum of the free energy (states with such values of σ cannot be realized). The analysis of the dependence of the free energy on the magnetization is based on the expression

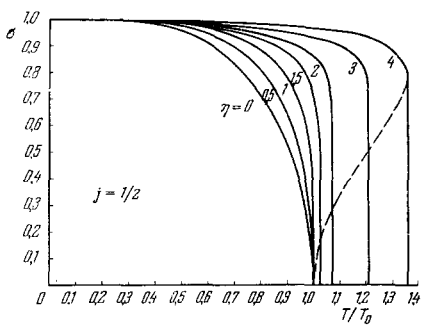

FIG. 1. Temperature dependence of the reduced spontaneous magnetization σ, calculated for different values of the parameters η in accordance with the theory of Bean and Rodbell [2].

$$\left(\frac{2G_V}{NkT_0}\right)_{\min} = -\frac{P\varkappa}{NkT_0} - \frac{2T}{T_0}\ln 2 - \frac{2H\sigma_s\sigma}{NkT_0} + \left(\frac{T}{T_0} - 1 + P\varkappa\beta\right)\sigma^2 + \frac{1}{\sigma}\left(\frac{T}{T_0} - \eta\right)\sigma^4 + \frac{T}{15T_0}\sigma^6 + \frac{T}{28}T_0\sigma^8 + \ldots, \quad (2.5)$$

which is the result of substituting (2.3) in (2.2) and replacing the expression for the entropy by a series in powers of σ. The subsequent grouping of the terms with equal powers of σ yields Eq. (2.5). Bean and Rodbell have shown that when $T/T_0 < 1$ and σ is small, the free energy is determined mainly by the term containing σ^2, which leads to a decrease of the free energy with increasing σ, since the coefficient of σ^2 is negative. With further increase of σ, the contribution of the terms containing σ^4 and σ^6 increases, and this leads to an increase of the free energy. Therefore the plots of G/NkT_0 against σ have minima at definite values of σ and T. At the Curie point, the coefficient of σ^2 vanishes, i.e.,

$$T_C = T_0(1 - P\varkappa\beta). \quad (2.6)$$

The character of the phase transition is determined by the sign of the coefficient of σ^4. The magnetic transformation will be a second-order phase transition if this coefficient is positive, i.e., if

$$\frac{T}{T_0} > \eta. \quad (2.7)$$

On the other hand, when $T/T_0 < \eta$, then at temperatures above T_C the negative contribution from the term containing σ^4 leads to a minimum of the free energy at $\sigma \neq 0$, and this, as already noted, causes a first-order transition. The foregoing is illustrated by plots of $(G_0 - G_\sigma)/G_0$ against σ, calculated for $\eta = 1.2$ at P = 0 and different values of T/T_0 (Fig. 2).

A more general criterion determining the character of the phase transition under conditions of compression of matter was derived on the basis of (2.6) and (2.7), namely

$$P\varkappa\beta > 1 - \eta. \quad (2.8)$$

The relation (2.8) indicates that an external pressure can change the character of the magnetic transformation. Whereas, for example, at atmospheric pressure (for the case $\beta > 0$) the magnetic transformation was a first-order transition, at high pressures the transformation can become a second-order transition.

In concluding this section, let us dwell on the qualitative analogy between the determination of the type of the magnetic phase transition by the theory of Bean and

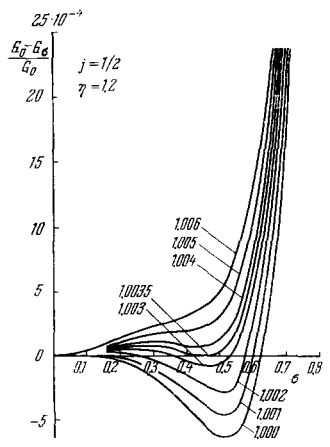

FIG. 2. Plots of the free energy against σ as calculated by Rodbell and Bean [2] for the case j = 1/2 and $\eta = 1.2$. The numbers at the curves correspond to the ratio T/T_0.

Rodbell and the general thermodynamic theory of phase transitions of Landau and Lifshitz[5]. This analogy was emphasized by Banerjee[14]. As is well known, the theory of Landau and Lifshitz is based on general thermodynamic relations with allowance for the symmetry properties of the crystal. It is assumed here that the thermodynamic potential $\Phi(T, P, \xi)$ can be expanded in a series about the transformation point, where the ordering parameter ξ is small*. Vonsovskiĭ[6] and Ginzburg[7] used this theory to study phase transitions at the Curie points of ferromagnets, using the magnetization of the material ($\xi = \sigma$) as the ordering parameter. When account is taken of the energy of the external magnetic field, the expansion of the thermodynamic potential is of the form

$$\Phi = \Phi_0 + a\sigma^2 + b\sigma^4 - \sigma H, \tag{2.9}$$

where a and b are coefficients that depend on P and T. At equilibrium, near the Curie point, $\partial\Phi/\partial\sigma = 0$; on this basis, Eq. (2.9) can be rewritten in the form

$$a\sigma + b\sigma^3 = H. \tag{2.10}$$

A thermodynamic analysis of the properties of the coefficients a and b indicates that at the Curie point a = 0 and b should always be positive for second-order phase transitions. Perfectly analogous conclusions can be drawn also on the basis of the theory of Bean and Rodbell. Indeed, Eq. (2.5), obtained in the theory of Bean and Rodbell, can be written in the form of (2.11), if the terms that do not depend on σ are denoted by A_0:

$$\frac{2G}{NkT_0} = -A_0 + A\sigma^2 + B\sigma^4 - H\sigma. \tag{2.11}$$

This equation corresponds to Eq. (2.9), and the condition $A = 0$, $B > 0$, which defines a second-order phase transition in the theory of Bean and Rodbell, is perfectly analogous to the condition for second-order phase transitions in the theory of Landau and Lifshitz ($a = 0$, $b > 0$). On this basis, Banerjee proposes[14] that the theory of Landau and Lifshitz can be generalized also to include the case of first-order phase transitions, the condition for which, in analogy with the theory of Bean and Rodbell, should be taken to be $a = 0$ and $b < 0$. For an experimental determination of the character of a magnetic phase transition, Banerjee proposes to use the method of "thermodynamic coefficients," developed by Belov[4] and widely used at present for a precision determination of the Curie point and of the spontaneous magnetization. In this case, according to Eq. (2.10), the quantities a and b can be obtained from the isotherm $H/\sigma = f(\sigma^2)$, the linear part of which is determined by the coefficient b. The sign of this coefficient, as already noted, should be negative for first-order phase transitions.

Thus, two independent criteria have been obtained for determining the character of the magnetic phase transition. One of them is the absolute magnitude of the parameter η, which is calculated from the experimental data on the compressibility and on the temperature shift of the magnetic transformation with changing pressure, starting from relation (2.4). The second criterion is the sign of the coefficient b, which is determined from magnetic measurements only, in accordance with Eq. (2.10). The available experimental data, which will be discussed later, offer evidence that the relation (2.4) is satisfactorily valid.

*As is well known, at the present time the question of the singularities of the thermodynamic potential and of its derivatives at a second-order phase transition point cannot be regarded as solved, so that the problem of the validity of expanding the thermodynamic potential at the second-order phase transition point should be regarded as open.

3) Investigation of Magnetic Transformations in Manganese Arsenide and Comparison of the Experimental Data with the Theory

The theory developed by Bean and Rodbell[2] was used by them, and also by Rodbell and de Blois[15] to explain the magnetic transformations in manganese arsenide. In spite of the many investigations of the magnetic transformations in MnAs, the nature of these transformations is not yet fully clear. The experimental investigations of Guillaud[16] and Serres[17] have shown that at temperatures 313 and 399°K the magnetic properties of MnAs experience a change. At low temperatures, MnAs has ferromagnetic properties; near 313°K a sharp drop of the magnetization takes place, accompanied by a change of the volume and by release of the latent heat of the transformation. In the temperature interval from $\Theta_1 = 313$ to $\Theta_2 = 399$°K, an increase of the susceptibility is observed with increasing temperature, and only above 399°K does MnAs become paramagnetic and its susceptibility obeys the Curie-Weiss law. These magnetic transformations are accompanied by changes of the crystal structure. In the ferromagnetic ($T < \Theta_1$) and paramagnetic ($T > \Theta_2$) states, MnAs has a lattice with hexagonal symmetry D_{6h}^4. The magnetic transformation Θ_1 causes an orthorhombic distortion of the crystal lattice, which vanishes at the temperature Θ_2[18]. In Guillaud's opinion, change of the magnetic properties of MnAs can be explained by assuming that at $\Theta_1 = 313$°K a transition takes place from the ferromagnetic into the antiferromagnetic state, and at $\Theta_2 = 399$°K the inverse transition takes place. This assumption was confirmed by Meyer and Taglang[19], who investigated the magnetocaloric effect of MnAs and observed a reversal of the sign of the effect at 310 and 390°K. From thermodynamic considerations, it could be assumed that the observed increase of the temperature under adiabatic demagnetization of the sample is connected with antiferromagnetic ordering of the spin magnetic moments of MnAs in the indicated temperature interval. However, a neutron diffraction investigated by Bacon and Street[20], and also investigations of the antiferromagnetic resonance, did not confirm the presence of antiferromagnetic ordering in this compound. This contradiction in the experimental data has led to various interpretations of the nature of the magnetic transformations in MnAs. In Kittel's theory[1], the transition at $\Theta_1 = 313$° is regarded as a magnetic transformation with inversion of the exchange interaction, resulting from simultaneous realization of exchanges of different types, differing from each other in magnitude and having different dependences on the interatomic distances. In the opinion of Bean and Rodbell[2], the transformation in MnAs at 313°K is a transition from the ferromagnetic to the paramagnetic state, and the maximum of the susceptibility at 399°K is due to the Jahn-Teller effect and is connected with the structural changes of the lattice. As already indica-

ted above, in this model one considers an exchange interaction that has one sign and varies isotropically with the volume.

Inasmuch as the main premise of the theoretical papers[1,2] was the strong dependence of the exchange-interaction integrals on the interatomic distances and the associated change of the elastic energy, the experimental investigations of the elastic properties and of the effects of the temperature shift of magnetic transformations with changing pressure are of fundamental importance for the verification of the validity of the conclusions of these theories. Let us consider these experimental results in greater detail.

The elastic properties of MnAs were investigated by Grazhdankina and Burkhanov[21]. Their purpose was to measure the elastic constants in a wide temperature interval that includes both the transition temperatures Θ_1 and Θ_2. The measurements were made by a resonance method using a composite vibrator and piezo-quartz excitation[22] at frequencies on the order of 60 kHz. Measurements of the Young's modulus E and of the shear modulus G on the same samples have made it possible to determine the Poisson coefficient and the compressibility $\kappa = 3(1 - 2\mu)/E$. In the indicated temperature interval, the thermal expansion and the magnetization of MnAs were also investigated.

Figure 3 shows the temperature dependences of the magnetization σ and of the reciprocal molar susceptibility $1/\chi_M$, measured[21] at H = 10 kOe. In accordance with data by others, a sharp drop of the magnetization takes place at T = 313°K, and at 392°K there is a peak of the function $1/\chi_M(T)$. Figure 4 shows plots of the Young's modulus E, the shear modulus G, the Poisson coefficient μ, and the compressibility κ as functions of the temperature. An anomalous growth of the moduli is observed only in the region of 400°K, i.e., in the temperature region Θ_2 where a peak of the temperature dependence of the susceptibility is observed. However, in the temperature region Θ_1 = 311°K, where a sharp decrease of the magnetization takes place, no anomalous changes of the moduli were observed. The magnitudes of the moduli at room temperatures are given in Table I.

Figure 5 shows the temperature dependences of the coefficient of thermal expansion α, according to which the magnetic transformation at Θ_1 = 311°K is accompanied by a jumplike change of the length of the sample, and the transformation in the region $\Theta_2 \sim 400$°K is accompanied by an abrupt change of α. These data are in

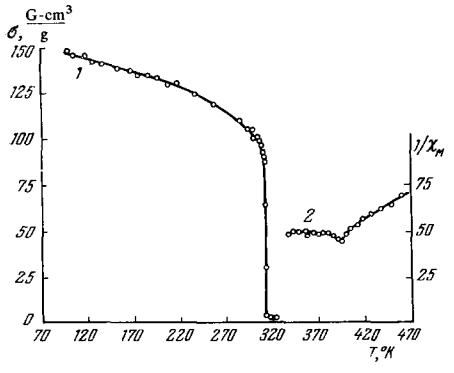

FIG. 3. Temperature dependences of the magnetization of MnAs (1) and of the reciprocal molar susceptibility (2), measured at H = 10 kOe.

Table I

E, dyne/cm^2	G, dyne/cm^2	μ	$\varkappa$, cm^2/dyne
$3.22 \cdot 10^{11}$	$1.29 \cdot 10^{11}$	0.27	$4.5 \cdot 10^{-12}$

qualitative agreement with the results of an x-ray diffraction investigation of the temperature variation of the parameters of the MnAs crystal lattice, obtained earlier by Willis and Rooksby[23].

A comparison of the measured values of the elastic moduli with the theoretically calculated ones[1,2] points to a good agreement between the experiment and the theory of Bean and Rodbell[2]. The compressibility calculated from formula (2.4) equals 2.2 $\times 10^{-11}$ cm^{2}dyne^{-1}, which differs only by a factor of 2 from the measured value $\kappa = 4.5 \times 10^{-11}$ cm^{2}dyne^{-1}, and the additional allowance for the thermal expansion of the lattice[15] in the theory of Bean and Rodbell leads to a striking agreement between the theoretical value $\kappa = 4.6 \times 10^{-12}$ cm^{2}dyne^{-1} with the experimental data. An estimate of E made by Kittel[1] using formula (3.8) gives a value of 4.2×10^{12} dyne/cm^2 for the Young's modulus, which is larger by one order of magnitude than the measured value of E. The fact that there is no quantitative agreement with the predictions of Kittel's theory is apparently not due only to the approximate character of the calculation. Serious difficulties arise also in the interpretation of the experimental data on the shift of the transition temperature Θ_1 with changing pressure. The sign of the effect $d\Theta_1/dP$ does not correspond to the change of Δa (the crystal-lattice parameter of MnAs) in the magnetic transformation. According to Kittel's theory, the ferromagnetism-antiferromagnetism (F → AF) transition should be accompanied by an expansion of the lattice, determined by Eq. (3.4), but actually a strong contraction of the parameter a takes place.

An investigation of the influence of hydrostatic compression on the temperature of the magnetic transforma-

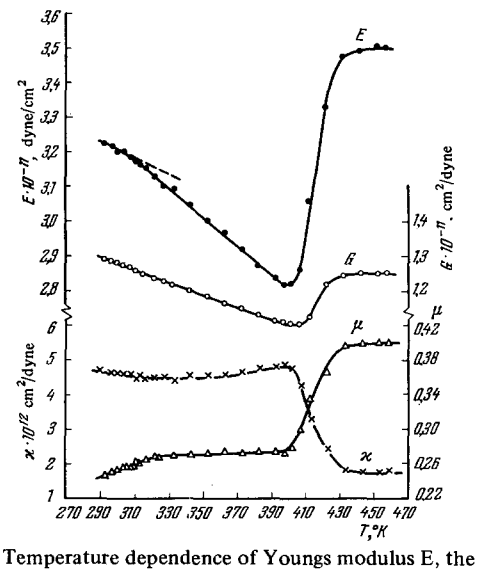

FIG. 4. Temperature dependence of Youngs modulus E, the shear modulus G, the Poisson coefficient μ, and the compressibility κ of MnAs [21].

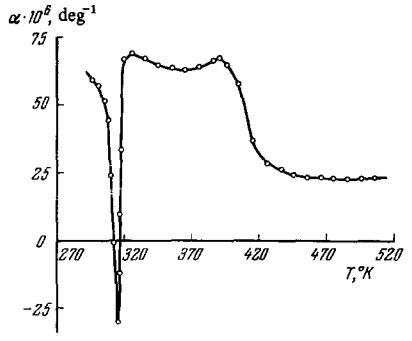

FIG. 5. Temperature dependence of the coefficient of thermal expansion of MnAs [21].

tion of MnAs has made it possible to verify further the theory of Bean and Rodbell. The shift of the magnetic-transition temperature Θ_1 with changing pressure was first determined by Rodbell and Wilson (see[24]) with the aid of magnetic measurements performed at room temperature and in a relatively narrow pressure interval (up to 1000 atm). The value of $d\Theta_1/dP$ was determined later on the basis of electric measurements up to 5000 atm[25]. The results obtained in these investigations had to be refined, since the values of $d\Theta_1/dP$ differed from each other. Further investigations at high pressures were made by Grozhdankina and Bersenev[26], who determined the temperature shift of the magnetic transformation of MnAs under compression with the aid of both magnetic and electric measurements in the temperature range from 77 to 400°K and at pressures up to 11 000 atm. These measurements have shown that the effect of the shift of Θ_1 with changing pressure should be determined only in the region of low pressures, up to 2500 atm. Higher pressures lead to a different phase transition, connected with the formation of a new modification of MnAs, which apparently has antiferromagnetic ordering at low temperatures. On the basis of these results, a P-T diagram of the magnetic transformations in MnAs was constructed and agreed in general outline with the theoretical predictions[12].

Figure 6 shows the temperatures determined by Grashdankina and Bersenev at various pressures with the aid of magnetic induction measurements[26]. It is seen from the plots that at atmospheric pressure Θ_1 = 314°K and decreases appreciably with increasing pressure. Measurements made with increasing and decreasing P do not give the same results: a hysteresis is observed, the width of which increases with increasing pressure. In all cases the inverse transition, i.e., the transformation observed when the sample is cooled, occurs at a lower temperature and has a more diffuse character. It is important that at low pressures (curves 1—3) hydrostatic compression of the sample leads only to a shift of the temperature dependence of the induction emf V(T) towards lower temperatures, without a change in the magnitude of the emf and in the form of its temperature dependence. At pressures above 2700 atm (curves 5 and 6), there is not only a shift of Θ_1, but also a sharp decrease of V, this being connected with the change of the character of the magnetic transformation itself, due to the transformation of a non-magnetic modification of MnAs. The occurrence under pressure of a new modification of MnAs at temperatures T_C is confirmed also by investigations of electric resistance. Figures 7 and 8 show R(P) plots obtained in the region of the temperatures Θ_1 and T_C. The different character of the variation of R(P) in the region of the indicated transitions indicates the presence of two different types of transformations. At low pressures (up to 2500 atm)

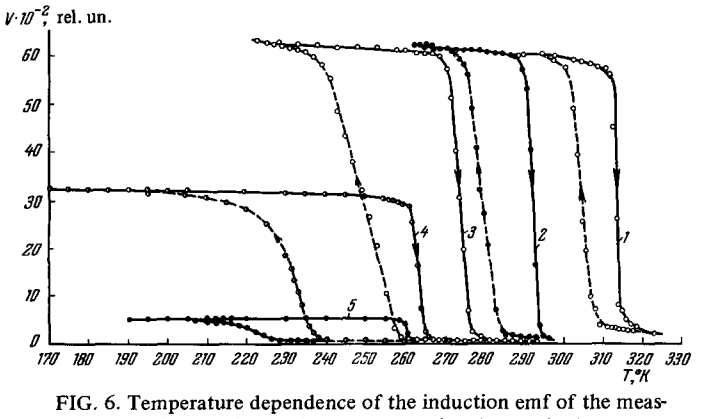

FIG. 6. Temperature dependence of the induction emf of the measuring coil (relative units) at various pressures. 1 – Atmospheric pressure, 2 – P = 1400 kg/cm², 3 – P = 2350 kg/cm², 4 – P = 2780 kg/cm², 5 – P = 2970 kg/cm². The solid curves were obtained while heating the sample, and the dashed ones while cooling [26].

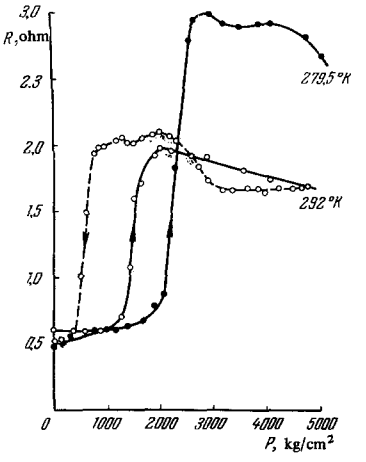

FIG. 7. Dependence of the electric resistance of MnAs on the pressure. Measurements in the region of the magnetic-transition temperature Θ_1 [26].

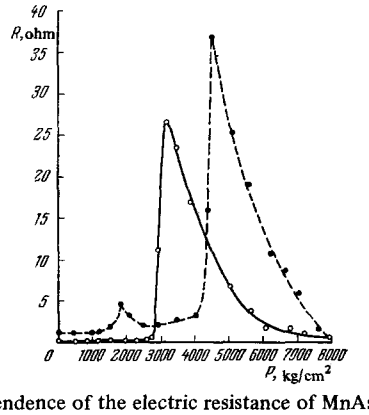

FIG. 8. Dependence of the electric resistance of MnAs on the pressure. Measurements in the region of the transition temperature T_C [26].

the main effect of hydrostatic compression is the shift of the temperature of the magnetic transformation $d\Theta_1/dP = -(16.0 \pm 0.3) \times 10^{-3}$ deg/atm (Fig. 9, curve 1). It can be assumed that in this region a strong decrease of the exchange interaction is not accompanied by a noticeable change of the spontaneous magnetization of MnAs. The transformation in the interval 2500–2700 atm is connected with the formation, under pressure, of a nonmagnetic modification of MnAs, and the temperature of this transformation decreases very strongly with increasing P, namely $dT_C/dP = -(34 \pm 7) \times 10^{-3}$ deg/atm (Fig. 9, curve 2). On the basis of magnetic measurements made at low temperatures and high pressures (from 4700 to 11 000 atm), a magnetic transformation was observed of the high-pressure phase of MnAs, due apparently to the occurrence of antiferromagnetic ordering; the change of the Neel temperature under pressure is in this case equal to $dT_N/dP = (2.22 \pm 0.7) \times 10^{-3}$ deg/atm (Fig. 9, curve 3).

In Rodbell's opinion[27], the above-described P-T diagram of magnetic phase transitions in MnAs (Fig. 9) is in qualitative agreement with the theoretical prediction[12]. In[12] Bean and Rodbell considered, on the basis of their model, the conditions for the equilibrium between the different magnetic states, for the four possible combinations of the signs of the parameters β and T_0. It was shown, as a particular case, that for ferromagnetic compounds consisting of two magnetic sublattices, transitions from the ferromagnetic to the antiferromagnetic and then to the paramagnetic state are possible when the pressure and temperature are changed. Figure 10a shows the equilibrium diagram taken from[12]. The diagram was constructed for the case $\eta = 2$ in coordinates $P^*k\beta$ and T/T_0, where $P^* \equiv P - \alpha T/\kappa$. The transition from P^* to P changes the initial slope of the phase-transition line, and rotation of the coordinate axes through 90° leads to a phase diagram that corresponds to that obtained experimentally (Figs. 10 b–c). However, this agreement should be regarded only as qualitative, since the model calculated by Bean and Rodbell is a rather crude approximation when applied to MnAs. The main defect of the calculation is that the anisotropic character of the exchange interactions existing in real crystals are ignored.* Attempts at a quantitative calculation of the concrete expressions for the functional dependence of the temperature of the transition on the external magnetic field intensity in the region of strong fields are likewise unsatisfactory[15]. The causes of the discrepancy between the values of $d\Theta_1/dH$ calculated on the basis of this model and the measured values in pulsed magnetic fields on the order of 120 kOe are not clear, but the different determinations of $d\Theta_1/dH$ in constant fields (up to 30 kOe) agree with one another[28,29]. Nonetheless, it can be stated on the whole that the Bean and Rodbell theory is a correct

*In a recent paper, Goodenough and Kafalas [125] present a new interpretation of the magnetic phase transition in manganese arsenide. It is proposed that besides the strong volume dependence of the exchange parameters, there is also a change of the magnetic moment of the Mn atoms with the changing volume of the MnAs. The magnetic transformation at the temperature Θ_1 is connected with electronic transitions due to the change of the width of the 3d-band and to the considerable exchange striction in the basal planes.

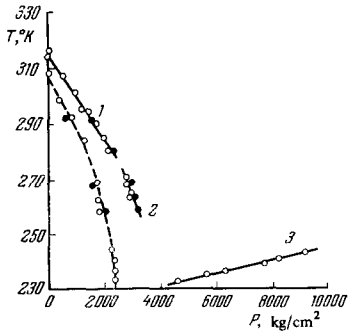

FIG. 9. Phase diagram of MnAs [26]. 1 – Pressure dependence of the temperature of the magnetic transformation Θ_1, 2 – changes of the transition temperature T_C, 3 – change of the Neel point of the high-pressure phase; the dashed curve was obtained while cooling the sample, ○ – obtained from magnetic measurements, ● – from electric measurements.

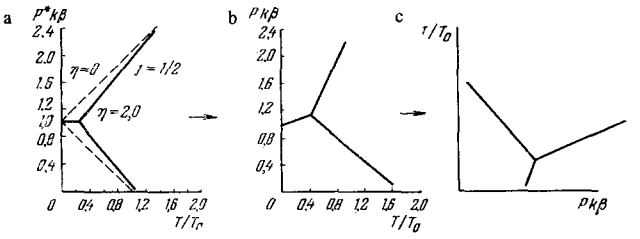

FIG. 10. Phase diagrams of magnetic transitions. a) Bean-Rodbell theory [12], b, c) experiment [26].

Table II. Experimental data on the compressibility κ and $d\Theta/dP$ effects in certain ferro- and antiferromagnetic compounds (the parameter η was calculated from formulas (2.1) and (2.4) of the Bean and Rodbell theory)

Compound	Θ, °K	dΘ/dP, 10³ deg/atm	κ, 10¹² cm²/dyne	β	η	Type of transition	Literature
MnAs	313	−16.0±0.3	4.5	12	1.82	F → P 1st ord.	21, 26
MnTe	310	2.3±0.3	2.3	−3.2	0.45	AF → P 2d ord.	30, 31
MnP	291	−1.2±0.05	1.5	4	0.35	F → P 2d ord.	32
CrTe	343	−6.2±0.4	2.2	8	0.34	F → P 2d ord.	32, 34

qualitative description of magnetic phase transformations, since the conditions for realization of first or second-order transitions agree with the theoretical criterion η defined by (2.4). This can be seen from Table II, which gives the values of the parameters β and η calculated from formulas (2.1) and (2.4) on the basis of the experimental data on $d\Theta/dP$ and the compressibility for certain ferro- and antiferromagnetic compounds.

It is seen from the presented data that $\eta > 1$ for first-order phase transitions and $\eta < 1$ for second-order transitions, in full agreement with the conclusions of the theory (see the summary Table III at the end of Sec. 8).

3. MAGNETIC FIRST-ORDER TRANSITIONS OF THE ORDER-ORDER TYPE

4) Kittel's Theory of Magnetic Transformations with Inversion of the Exchange Interaction

Investigation of the magnetic transformations with inversion of the exchange interaction is an interesting theoretical problem, since ordinary thermodynamic theories of phase transitions, using the model of the

molecular field with a temperature-independent exchange interaction, are unable to explain these transformations. Smart[35] has shown that for a relative magnetization σ_j in the sublattice j there exist $(N/n)(1+\sigma_j)$ spins oriented in one direction and $(N/n)(1-\sigma_j)$ spins oriented in the opposite direction; the entropy of such a system is

$$S = k \ln \prod_{j=1}^{n} \frac{(N/n)!}{\left[\frac{N}{n}(1+\sigma_j)\right]!\left[\frac{N}{n}(1-\sigma_j)\right]!}.$$

It is seen from this expressions that the entropy of the system does not change if the directions of all the spins of the given sublattices are reversed, since S is an even function of σ_j. Thus, if the directions of the magnetization in some of the sublattices are reversed during the transformation without a change of σ, such a transformation occurs without a change of entropy, and consequently is a second-order phase transition. Experiments, however, refute this conclusion. It has been established experimentally that magnetic transformations connected with the change of the type of spin ordering are not second-order transitions but first-order transitions. Smart was the first to point out that allowance for the dependence of the coefficients of the Weiss molecular field on the temperature makes it possible to explain magnetic transformations with inversion of the exchange, which is essentially equivalent to assuming that the exchange integrals depend on the interatomic distances. Neel[36], Pratt[37], and Liu[38] also attempted to explain these transitions. Among the shortcomings of the cited papers is that they did not reveal the cause of the change in the magnitudes of the exchange interactions with changing temperature.

Kittel[1] gives a physical justification for the change of the exchange integrals, and explains the main features of the phase transitions connected with the change of the type of magnetic ordering. The transition from the antiferromagnetic into the ferromagnetic state is considered by Kittel on the basis of a two-sublattice model. It is assumed that the change of the character of the magnetic ordering at the transition point is due to the fact that there exist in the substance simultaneously different types of exchange interactions, differing from one another in magnitude, sign, and in the different dependence on the interatomic distances. If, owing to the thermal expansion, the lattice parameter assumes a certain critical value a_c, at which the positive exchange-interaction integral reverses sign, then a transition takes place from one magnetic state to another. The free energy at atmospheric pressure is written in the form

$$F = \frac{1}{2} RV (a - a_T)^2 - \rho (a - a_c) V \mathbf{M}_A \mathbf{M}_B, \tag{3.1}$$

where the first term determines the change of the elastic energy, and the second the change of the exchange energy with changing lattice parameter a. Here $\mathbf{M}_A$ and $\mathbf{M}_B$ are the sublattice magnetizations, V is the volume, $\rho = \partial\alpha/\partial a$ is the rate of change of the exchange interaction as a function of the interatomic distance, R is the elastic constant divided by a^2, and a_T is the value of the lattice parameter when $\mathbf{M}_A \perp \mathbf{M}_B$, corresponding to zero exchange energy, since the second term of Eq. (3.1) vanishes in this case. For simplicity, Kittel does not take into account the dependence of the sublattice magnetization on the temperature and on the interatomic distances, i.e., he assumes $|\mathbf{M}_A| = |\mathbf{M}_B| = M$, and also that the exchange interactions vary linearly with a, i.e., only the first term is taken into account in the Taylor expansion of the exchange energy

$$E_{ex} = -\left[\rho (a - a_c) + \frac{1}{2}\rho' (a - a_c)^2\right] \mathbf{M}_A \mathbf{M}_B. \tag{3.2}$$

The equilibrium value of the lattice parameter is obtained by minimizing F with respect to a at the given temperature:

$$a = a_T + \left(\frac{\rho}{R}\right) \mathbf{M}_A \mathbf{M}_B, \tag{3.3}$$

from which we determine the change of the parameter a when the substance goes from one magnetic state to the other:

$$\Delta a = a_\Phi - a_{AF} = \frac{2\rho}{R} M^2. \tag{3.4}$$

It is seen from this expression that the sign of Δa is determined by the sign of ρ, i.e., by the sign of the effect of the change of the transition temperature T_s with changing pressure. Substituting (3.3) in (3.1) yields

$$\frac{F}{V} = -\left(\frac{\rho^2}{2R}\right) (\mathbf{M}_A \mathbf{M}_B) - \rho (a_T - a_c) \mathbf{M}_A \mathbf{M}_B. \tag{3.5}$$

When the sign of the exchange interaction changes, the sign of the first term in (3.5) remains unchanged; it is perfectly obvious that the effective sign of the exchange interaction is determined by the sign of the second term in (3.5). On the other hand, if the magnetic sublattices are oriented at an angle to each other, and φ is the angle between $\mathbf{M}_A$ and $\mathbf{M}_B$, then it is necessary to introduce in (3.5) a term containing $\cos^2\varphi$, which acts like a potential barrier separating the two magnetic states. This can lead to a hysteresis of the transition temperature T_s, determined by the relation $\Delta T_s = 2a\rho M^2/\gamma c_L$, where c_L is the lattice specific heat, and γ is the Gruneisen constant. The influence of the pressure and of the magnetic field on the transition temperature was determined from the Clausius-Clapeyron equation; this yielded

$$\left(\frac{dT_s}{dP}\right)_H = \frac{V\frac{\Delta a}{a}}{\Delta\left(\frac{\partial F}{\partial T}\right)} = \frac{1}{Ra\left(\frac{\partial a_T}{\partial T}\right)_P}, \tag{3.6}$$

$$\left(\frac{\partial T_s}{\partial H}\right) = \frac{\Delta\sigma}{\Delta s} = \frac{2MV}{\Delta\left(\frac{\partial F}{\partial T}\right)} = \frac{1}{\rho M}\left(\frac{\partial a_T}{\partial T}\right)_P. \tag{3.7}$$

Kittel's attempt to use the theory developed by him to explain the magnetic transformation in MnAs required an additional calculation, connected with the consideration of the possible exchange interactions realized in hexagonal crystals of the NiAs type. A formula was obtained for Young's modulus in terms of the pressure shift of the transformation temperature dT_s/dP and the thermal coefficient of linear expansion α:

$$E = \frac{2}{\alpha\left(\frac{\partial T_s}{\partial P}\right)}. \tag{3.8}$$

The value of E calculated by means of this formula for MnAs differed by one order of magnitude from the measured Young's modulus, and the sign of the effect dT_s/dP also disagreed with the conclusions of Kittel's theory. These questions were already considered by us in subsection 3, in the analysis of the experimental data on

MnAs, which indicate that the magnetic transformation in MnAs is apparently not connected with inversion of the exchange interaction, and is more likely due to destruction of the spin disorder.

Recently, much experimental material was obtained on magnetic transformations for which it has been demonstrated experimentally and without any doubt that they are magnetic transitions with exchange inversion. Such transitions were observed in substances with different (crystal and magnetic) structures (subsection 8, table III). We shall consider below only the most characteristic cases of such transitions ($Mn_{2-x}Cr_xSb$, FeRh, and Mn_3GaC), investigated most fully and most systematically.

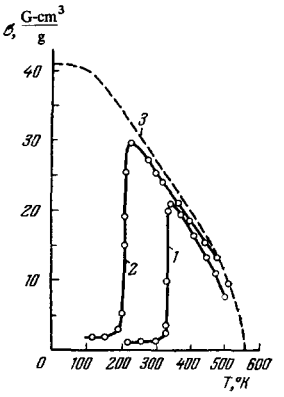

FIG. 11. Temperature dependences of the magnetization of the alloys $Mn_{2-x}Cr_xSb$. 1 – x = 0.13, 2 – x = 0.05, 3 – x = 0 (Mn_2Sb).

5) Comparison of Theory with Experiment. Magnetic Transformations in $Mn_{2-x}Cr_xSb$, FeRh, and Mn_3GaC

a) When Mn_2Sb is alloyed with chromium, solid solutions of the type $Mn_{2-x}Cr_xSb$ are produced. On the basis of neutron-diffraction[41,42] and magnetic measurements[43,44] it was established that, depending on the value of x, which determines the chromium concentration, these alloys have different spin ordering at low temperatures: ferromagnetic (x = 0), helical (x < 0.022), and antiferromagnetic (0.025 < x < 0.20). When the temperature is increased, a change takes place in the type of magnetic structure from antiferromagnetic (AF) or helical (H) ordering to a ferrimagnetic structure (F) of the Mn_2Sb type. In the concentration region 0.025 < x < 0.035 the magnetic structure changes twice: AF → H → F[45,46]. All the indicated transformations, which occur with increasing temperature, are first-order phase transitions, as is evidenced by the release of heat, by the jumplike change of the volume and magnetization, and also by the thermal hysteresis in the vicinity of the transition temperature T_S. The AF → F transitions are accompanied by a sharp change of kinetic effects such as electric conductivity, thermal emf, Hall effect, and change of the electric resistivity in the magnetic field[51]. Investigations of $Mn_{2-x}Cr_xSb$ alloys in strong pulsed magnetic fields[50,52] have shown that the antiferromagnetic state can be destroyed by a sufficiently strong magnetic field exceeding a certain threshold value H_S. The transition temperature T_S can also be altered by the action of high pressures.

The first to observe first-order magnetic phase transitions in $Mn_{2-x}Cr_xSb$ were Swoboda et al.[43], who initiated an extensive cycle of research on magnetic transformations with inversion of the exchange interaction. X-ray diffraction and magnetic measurements of $Mn_{2-x}Cr_xSb$ were made in[43] in the range of concentrations 0.025 ≤ x ≤ 0.20. Figure 11 shows the temperature dependences of the magnetization for some of the investigated alloys. The plots reveal a sharp increase of σ at the point T_S, connected with the occurrence of ferromagnetic order, which in turn is destroyed with further increase of temperature at the Curie point. X-ray diffraction studies have shown that the AF → F transition leads to a change of the magnetic structure only, and is not accompanied by a change of the crystallographic symmetry of the lattice. Both above and below T_S, the lattice has a tetragonal symmetry of the type P4/nmm. In the case of the magnetic transformation, a sharp change takes place in the lattice parameters: the c axis increases jumpwise, and the a axis decreases at the point T_S. It is seen from Fig. 12 that the transition temperature changes with the quantity x, but in different alloys the AF → F always occurs at the same value of the parameter 6.53 Å. On this basis, the hypothesis was advanced that the main cause of the AF → F transition in these compounds is the reversal of the sign of one of the exchange-interaction constants, owing to the strong dependence of the exchange integrals on the interatomic distances. In this connection, when the lattice parameter reaches as a result of thermal expansion a certain critical value, the AF → F transition takes place. It is assumed that addition of chromium to the Mn_2Sb leads only to a decrease of the lattice parameters, and causes no significant changes in the exchange or magnetic interactions, since the spontaneous magnetization, the Curie temperature, and the magnetic crystallographic anisotropy[47] of the $Mn_{2-x}Cr_xSb$ alloys change only insignificantly with changing x. In this connection, one might expect that the introduction into Mn_2Sb of not only chromium, but also of other elements with atomic radii smaller than those of Mn and Sb would lead to a compression of the lattice and cause its parameters to approach the critical dimensions, thereby resulting ultimately in an AF → F transition with increasing temperature. Indeed, addition of Cu, Va, Co, Zn, Ge, and As to the Mn_2Sb also led to AF → F transformations[43], thus demonstrating the validity of the indicated assumptions concerning the nature of the magnetic phase transitions in these alloys.

Neutron-diffraction investigations by Claud and Jarrett[41], and later by Austin et al.[42] have shown that the magnetic structure of $Mn_{2-x}Cr_xSb$ (in the ferrimagnetic state) is the same as that of Mn_2Sb (Fig. 13).

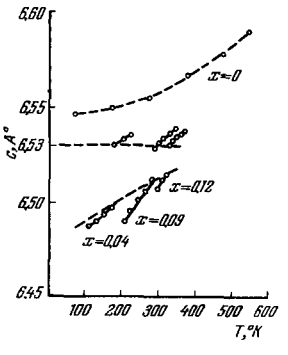

FIG. 12. Temperature dependences of the parameter c of the crystal lattice of the alloys $Mn_{2-x}Cr_xSb$.

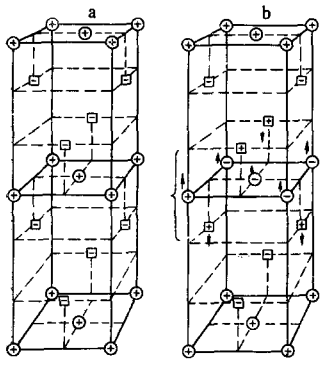

FIG. 13. Magnetic structures of the alloys $Mn_{2-x}Cr_xSb$ in the ferromagnetic (a) and antiferromagnetic (b) states. The circles denote Mn I, the squares Mn II. In the antiferromagnetic state, the magnetic moments of all the neighboring layers are antiparallel; in the ferromagnetic state, the Mn I layers are antiparallel to the Mn II layers. The arrows label the three-layer goups Mn II–Mn I–Mn II.

Substitution of Cr for Mn leads to a change in the values of the magnetic moments of Mn I and Mn II, which occupy different crystallographic positions. In the antiferromagnetic state, the magnetic moments of Mn I and Mn II are respectively 1.4 μ_B and 2.8 μ_B. Upon transition into the ferrimagnetic state ($T > T_S$), the magnetic moment of Mn I increases by 0.4 μ_B, and the magnetic moment of Mn II decreases by 0.5 μ_B. In order to explain the resultant value of the magnetic moment, namely $\sim 0.9\ \mu_B$, it was proposed in[48,49] to regard the magnetic structures of these compounds as three-layer groups Mn II–Mn I–Mn II, formed by the planes (001), having ferrimagnetic ordering above T_S and antiferromagnetic ordering at low temperatures (Figs. 13a and b). Within the limits of each of the indicated planes, there is a strong exchange interaction of the spin magnetic moments, and the exchange between different planes is much weaker. Starting from such a magnetic model, one could assume that these alloys are a very convenient system for an experimental verification of Kittel's theory. If it is assumed that the interplanar exchange interaction reverses sign at a certain critical value of the parameter c, then according to the Kittel theory this change should cause a first order AF → F phase transition accompanied by a jumplike change in the parameter $\Delta c = 2\rho M^2/R$. This conclusion of the theory, and also the relations (3.6) and (3.7), were confirmed experimentally[48-50]. It should be noted that this agreement must be regarded only as a qualitative verification of Kittel's theory. This is connected with the fact that it is impossible to measure the elastic modulus of the alloys $Mn_{2-x}Cr_xSb$. For the same reason, Jarrett's attempts[39] to estimate the different parameters of the AF → F transitions on the basis of the more exact theoretical relations derived by him are also of qualitative character. Nonetheless, as shown by numerous experimental investigations, the theory reflects correctly the main and most characteristic features of transitions with inversion of the exchange, and can be applied not only to layered uniaxial ferro- and antiferromagnets, but also in a number of cases to other magnetic structures, such as for example FeRh and Mn_3GaC.

b) Magnetic first-order phase transitions in FeRh alloys were first observed by Fallot[53] who noted that ferromagnetism is produced in the alloy at the transition point T_S with increasing temperature. Later, on the basis of magnetic[54,55], x-ray diffraction[56], and neutron-diffraction[57-60] investigations it was established that this transformation is connected with a change in the type of the magnetic structure and is a transition from the antiferromagnetic into the ferromagnetic state. The alloys have an ordered body-centered cubic structure of the CsCl type. In the antiferromagnetic state, each atom of iron is surrounded by six other atoms of iron with opposite spins; the magnetic moment of the iron is equal to 3.3 μ_B, and the magnetic moment of the rhodium atoms is zero. At temperatures above T_S, the orientation and magnitude of the magnetic moments change, i.e., the magnetic moments of the iron and rhodium in the ferromagnetic state are respectively 2.8 μ_B and 0.8 μ_B and are parallel to each other. The transition temperature is very sensitive to the chemical composition of this alloy[54,55]. Hofer and Cucka[61] and also Kouvel[62] have shown that a deviation of the composition of the FeRh from stoichiometric or the introduction of Pt, Pd, and Ir impurities leads to a strong change of T_S. This apparently explains the disparity between the values of the latent heat of the transition and the absolute values of T_S and dT_S/dH obtained by various authors[63-66]. It is perfectly obvious that for a reliable comparison of the experimental data with the theory comprehensive measurement of several physical quantities on the same samples are essential. This was done by Zakharov, Kadomtseva, et al.[66] who investigated the temperature dependences of the magnetization (Fig. 14), Young's modulus, and the crystal lattice parameter of the alloy FeRh; simultaneously they performed dilatometric investigations of this alloy (Fig. 15). They measured also the values of dT_S/dP and dT_S/dH. Analyzing the experimental data, the authors of the cited paper reached the conclusion that the AF → F interaction in FeRh can be explained on the basis of Kittel's theory. If we assume that the exchange interaction in a

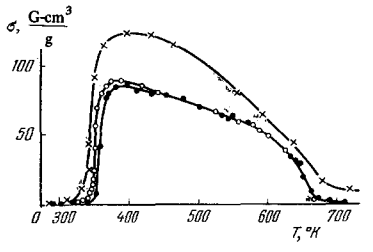

FIG. 14. Temperature dependence of the magnetization of the alloys FeRh at H = 1770 Oe (● – heating, O – cooling) and H = 14,500 Oe (X – heating) (from [66]).

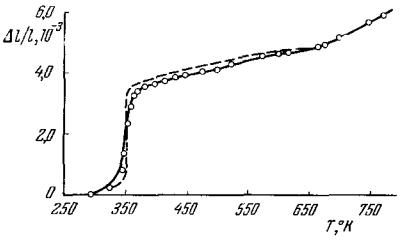

FIG. 15. Temperature dependence of the thermal expansion of the alloy FeRh. Solid – experimental data, dashed – calculated curve [66].

cubic crystal has an isotropic character and depends only on the volume, then expression (3.3) of Kittel's theory takes the form $V/V_T = 1 \pm \rho\kappa_T M^2$. The temperature dependence of the thermal expansion, calculated in accordance with this formula, agrees qualitatively with the experimental data (see Fig. 15).

c) As shown by Bouchaud and Fruchart[67,68], the compound Mn_3GaC experiences an AF → F transition at the point $T_S = 150°K$ with increasing temperature. X-ray diffraction and magnetic measurements have shown that this transformation, as well as the majority of transitions with exchange inversion, is not accompanied by a change in the crystallographic symmetry (perovskite-type lattice). The AF → F transition is a typical magnetic first-order phase transition, as can be clearly seen from the temperature and field dependences of the magnetization (Figs. 16 and 17). It was established that the transition temperature changes under the influence of an external magnetic field: $dT_S/dH = 0.33 \times 10^{-3}$ deg-Oe^{-1} and under the influence of high pressure: $dT_X/dP = -2.51 \times 10^{-3}$ deg/atm. From these data, on the basis of the Clausius-Clapeyron equations

$$Q_1 = \frac{\Delta V}{(1/T_s)(dT_s/dP)}$$

and

$$Q_2 = \frac{\Delta\sigma}{(1/T_s)(dH_s/dT)}$$

they calculated the heat of transition Q in the AF → F transformation. These two expressions give the closest values $Q_1 = 0.93$ and $Q_2 = 1.02$ cal/g. However, in spite of the fact that the signs of the dT_S/dP and dT_S/dH effects agree with the general thermodynamic relations given above, a difficulty arises in the interpretation of these effects on the basis of Kittel's theory.

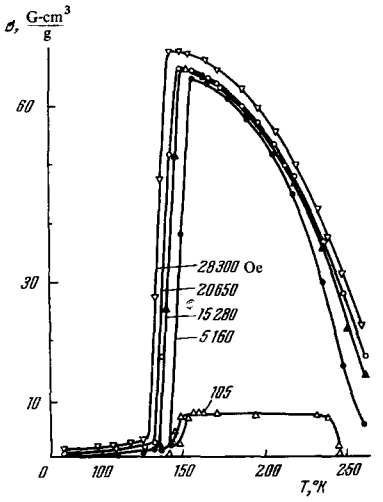

FIG. 16. Temperature dependences of the magnetizations of the alloy Mn_3GaC [68].

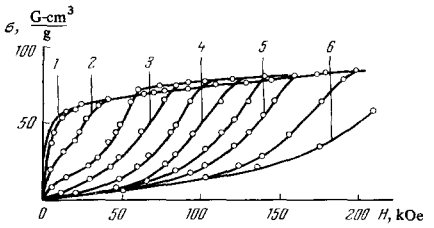

FIG. 17. Isotherms of magnetization of the alloy Mn_3GaC [68]: 1 – T = 146°K, 2 – T = 138°K, 3 – T = 134°K, 4 – T = 121°K, 5 – T = 111°K, 6 – T = 96°K.

The magnetic transformation in Mn_3GaC differs from the AF → F transitions in $Mn_{2-x}Cr_xSb$ and FeRh in the fact that the change of the spin ordering with increasing temperature at the point T_S in Mn_3GaC is not accompanied by an expansion of the lattice (as would be expected from Kittel's theory), but by a strong contraction. In this connection, the experimentally observed negative values of the dT_S/dP and dT_S/dH effects do not agree with Kittel's formulas (3.6) and (3.7). Pauthenet and Guillot[69] made an attempt to eliminate these contradictions. They also analyzed the AF → F transition on the basis of the exchange-inversion mechanism of magnetic transitions, but took additional account of the ferromagnetic and antiferromagnetic states of the spin entropy in the expression for the thermodynamic potentials, and also of the exchange interactions, both inside the sublattices and between the sublattices; this led to a qualitative agreement between theory and experiment.

4. MODELS OF MAGNETIC FIRST-ORDER TRANSITIONS NOT CONNECTED WITH THE EXCHANGE-STRICTION MECHANISM

So far we have considered investigations in which the magnetic first-order phase transitions were explained on the basis of the exchange-striction mechanism. There are, however, theoretical papers in which these transitions are explained with the aid of other model representations, not connected with the assumption of a strong dependence of the exchange-interaction integral on the volume of the crystal lattice. Thus, for example, Yosida and Miwa[70] explain magnetic transformations of the order-order type, i.e., transitions with inversion of the volume, occurring in rare-earth elements with helicoidal magnetic structure, on the basis of the complicated temperature dependence of the constants of the magnetic crystallographic anisotropy. According to Dzyaloshinskiĭ[71], the magnetic structure of rare-earth metals is determined to a considerable degree by the shape of the Fermi surface. Transitions between different structures are connected with changes of the electron energy spectrum, which become strong when the wave vector of the magnetic structure coincides with the extremal diameter of the Fermi surface. The source of all these changes is the temperature dependence of the parameter of the exchange interaction. In the case when the exchange parameter has smooth values at which conditions for the existence of the minimum of the thermodynamic potential are violated, jumplike changes can occur in the magnetic structure, i.e., a first-order phase transition.

Karpenko and Berdyshev[72] associate the inversion of the exchange interaction in antiferromagnetic semiconductors of the $Li_{0.1}Mn_{0.9}Se$ type with the change of the electric carrier density. In this case it is assumed that there are two competing types of exchange interactions: an antiferromagnetic interaction of the Kramers type (low temperatures) and a ferromagnetic interaction via the conduction electrons, the role of which increases with increasing temperature as the result of the strong

increase of the carrier density. Thus, the effective sign of the exchange is determined by the relative contributions of interactions with opposite signs. According to Blum[73], magnetic phase transitions of the order-disorder type can arise in many cases in connection with the special character of the splitting of the electronic energy levels, due to the crystal and the magnetic fields. The possibility of a first-order transition from the ferromagnetic into the paramagnetic state was indicated by Shimizu[90] on the basis of an analysis of the criterion of ferromagnetism in accordance with the band model. In the opinion of Mitsudo et al.[75], and also of Penn and Cohen[76], first-order transitions in the Neel point of antiferromagnetic metals (e.g., the magnetic transformation in Cr[77]) can be attributed to singularities of the electronic energy spectrum of these metals. The hypothesis were advanced that a large influence is exerted on the character of the magnetic phase transition by the biquadratic indirect exchange in certain antiferromagnetic compounds.[78]

In a recently published paper, Bulaevskiĭ and Khomskiĭ[74] considered, on the basis of the self-consistent field method, magnetic transitions in antiferromagnetic semiconductors (such as V_2O_3 and Ti_2O_3[120-122]) with allowance for the possible excitation of localized electrons in the conduction band. In view of the strong dependence of the energy gap of the electronic spectrum of the crystal on its magnetic structure, the magnetic transformation is accompanied by an appreciable change of the electric properties, namely, when the magnetic order vanishes the substance is transformed from a semiconductor into a metal. These transformations are first-order phase transitions if the gap in the paramagnetic state is sufficiently small.

The influence of the magnetic crystallographic anisotropy on the magnetic transitions with exchange inversion were considered in many papers, and were discussed in detail in the monograph of Belov, Belyanchikova, et al.[79], so that we shall not concern ourselves with these questions here. We shall dwell only on model representations of first-order magnetic transitions of the order-disorder type, which are not connected with the exchange-striction mechanism.

6) Biquadratic Indirect Exchange and Magnetic Transformations in Certain Antiferromagnetic Compounds

Neutron-diffraction investigations of the antiferromagnetic compounds NiO and MnO have shown that the change of the magnetization with temperature in the region of the Neel point does not follow the Brillouin function: the $\sigma(T)$ curve is steeper, and the magnetization jumps down to zero in the immediate vicinity of T_N. In this connection, it was proposed that the transition from the antiferromagnetic into the paramagnetic state in these compounds is a first-order phase transition. A characteristic and very significant feature of the described phase transitions is the sharp change of the elastic constants of the crystal in the absence of any volume changes in the region of the antiferromagnetic transformation. The effects of the shift of the transition temperature with changing pressure are relatively small in these compounds. An attempt to calculate the jump of the magnetization at the Neel point on the basis of theories in which account is taken of the volume dependence of the exchange interactions did not yield positive results. It was therefore assumed that the magnetic first-order phase transition in the indicated compounds is due not to the exchange-striction mechanism, but to some other causes.

Rodbell, Jacobs, et al.[78] have shown that if account is taken of the biquadratic term in the isotropic indirect exchange during the course of calculation of the temperature dependence of the magnetization in the approximation of the molecular-field theory, i.e., if it is assumed that the energy of the exchange interaction is of the form

$$I(\mathbf{s}^a\mathbf{s}^b) - j(\mathbf{s}^a\mathbf{s}^b)^2, \tag{6.1}$$

then it is possible to obtain satisfactory agreement between the calculated $\sigma(T)$ curve and the experimental data. Anderson[80] first pointed out the possible presence of a term biquadratic in the spins, $-j(\mathbf{s}^a\mathbf{s}^b)^2$, in the expression of the exchange energy, and estimated approximately the magnitude of this term. Later, on the basis of an experimental investigation of the paramagnetic resonance[81] and a calculation of the interaction of the paramagnetic ions in antiferromagnets[82] it was also concluded that a biquadratic term must be taken into account in the isotropic indirect exchange. It was shown there that the ratio j/I is of the order of 0.01–0.05. In[79], the temperature dependences of the magnetic moments of the sublattices of the antiferromagnetic compounds NiO and MnO were calculated on the basis of the theory of the molecular field; no account was taken of the change in the elastic properties during the magnetic transformation, and only the change of the exchange energy and of the entropy of the spin system were taken into account. Allowance for the biquadratic term in the exchange energy leads to a change in the form of the temperature dependence of the magnetization in accordance with the formula

$$\frac{T}{T_N} = F(\sigma)\left[1 + \frac{2s^2\sigma^2(2j_1+2j_2)}{I_2}\right], \tag{6.2}$$

where

$$F(\sigma) = \frac{3Nks\sigma}{(s+1)\frac{\partial S^*}{\partial\sigma}};$$

here S^* is the entropy of the spin system, j_1 and j_2 are the parameters of the biquadratic exchange with the first and second coordination spheres, respectively, and I_2 is the exchange parameter with the second coordination sphere in the bilinear term of the Hamiltonian $I(\mathbf{s}^a\mathbf{s}^b)$. Figure 18 shows the dependence of σ on T/T_N for NiO, calculated in accordance with formula (6.2) under the assumption that $I_1 = I_2 = I$ and $j_1 = j_2 = j$[79]. Agreement with the experimental data is obtained when $j/I = 0.015$ for NiO and $j/I = 0.02$ from MnO. From the plots of Fig. 18 we see that the magnetization in the region of the Neel point changes sharply when the temperature changes, and the character of this change corresponds to a first-order phase transition. In the case when $j = 0$, i.e., when no account is taken of the biquadratic indirect exchange, calculation in accordance with (6.2) leads to the usual dependence of the magnetization on the temperature, corresponding to the Brillouin function, and consequently to a second-order magnetic phase transition (dashed curve of Fig. 18).

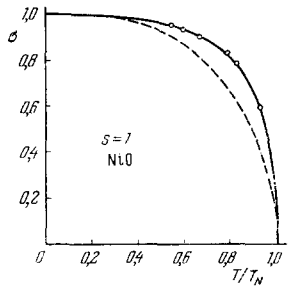

FIG. 18. Temperature dependence of the magnetization of the antiferromagnetic sublattices of NiO. The dashed curves were calculated on the basis of the classical molecular-field theory; the solid curves are calculated with allowances for the biquadratic exchange [78]; the points are the experimental data of neutron-diffraction investigations.

7) Blum's Theory of the Magnetic Transformation in Uranium Dioxide

According to Blum[73], magnetic first-order transitions can arise in many cases in connection with the special character of the splitting of the electronic energy levels, due to the crystal and magnetic fields. Figure 19 shows by way of an example the schematic picture of such a splitting. Under the influence of the electric field of the crystal, the degenerate level is first split into two sublevels, a singlet and a triplet. The energy difference between the low-lying nonmagnetic singlet and the higher triplet is Δ. The magnetic field causes an additional splitting of the triplet into two sublevels. The magnetic properties of the system, and also the character of the magnetic phase transition, are determined by the ratio of the splitting energies Δ and $g\mu_B H$, due to the action of the electric and magnetic fields. The calculation is performed in the approximation of the molecular-field theory, i.e., the magnetic field that splits the triplet is produced by the internal molecular field due to the presence of exchange interaction between the magnetoactive ions. The magnitude of this field is proportional to the magnetization $H = \lambda M$, where λ is a constant determined by the integral of the exchange interaction. If a magnetic field H is weak, i.e., weaker than $\Delta/g\mu_B$ (Fig. 19a), then the magnetization of the system in the ground state will be zero, since the lowest level is the nonmagnetic singlet, and the influence of all the higher energy states of the system can be neglected. On the other hand, if the magnetic field H is sufficiently large, then one of the components of the triplet will lie below the singlet and will make a contribution to the magnetization, so that at $T = 0°K$ the system has a resultant magnetic moment (see Fig. 19b). The decrease of the magnetization with increasing temperature, connected with the population of the excited states, leads to a decrease of the splitting of the triplet and consequently to a change of the energy position of the magnetic component of the triplet. Under certain conditions, it is a first-order phase transition. To determine the equilibrium properties of the system, and also the conditions that lead to the particular character of the magnetic transformations, Blum's theory makes use of a statistical method of investigating phase transitions. In this case, as is well known, it is necessary to know the distribution function Z. If the picture of the splitting of the energy levels corresponds to the case shown in Fig. 19, then the distribution function is of the form

$$Z = 1 + e^{-\Delta/kT}\left(1 + e^{g\mu_B H/kT} + e^{-g\mu_B H/kT}\right). \tag{7.1}$$

The magnetization of the system is given by

$$M = \left(\frac{\partial F}{\partial H}\right) = -kT\frac{\partial}{\partial H}\ln Z = g\mu_B\frac{e^{g\mu_B H/kT} - e^{-g\mu_B H/kT}}{e^{\Delta/kT} + 1 + e^{g\mu_B H/kT} + e^{-g\mu_B H/kT}}. \tag{7.2}$$

If only the internal magnetic field $H = \lambda M$ is taken into account, the equation for the magnetization takes the form

$$M = \frac{g\mu_B\left(e^x - e^{-x}\right)}{e^{\Delta/kT} + 1 - e^x - e^{-x}}, \tag{7.3}$$

$$x = g\mu_B\frac{\lambda M}{kT}, \quad M = \frac{kTx}{g\mu_B\lambda}. \tag{7.4}$$

The presence of the term $e^{\Delta/kt}$ in (7.3) complicates somewhat the solution of this equation. Here, as in the usual case, when the magnetization is determined by the Brillouin function, the solution for M is obtained graphically by plotting M against x and determining their intersection points. For convenience, new variables $M' = M/g\mu_B$ and $\Delta' = \Delta/(g\mu_B)^2\lambda$ are introduced, and the equation for the magnetization is written in the form

$$M' = \frac{\left(e^x - e^{-x}\right)}{\left(e^{x\Delta'/M'} + 1 + e^x + e^{-x}\right)}. \tag{7.5}$$

By solving this equation for various values of Δ', it was shown that for large Δ' the magnetic-order state is impossible, since the exchange interaction does not suffice to overlap the splitting due to the crystal field. For small values of Δ', the solutions for M' are analogous to those of the ordinary case, when the dependence of the magnetization of T and H is determined by the Brillouin function (Fig. 20) and the character of the variation of M' with T corresponds to a second-order phase transition. First-order phase transitions are possible only for definite values of Δ' lying in the interval $0.3662 < \Delta' < 0.5$. In this case the dependence of M' on x has the form shown in Fig. 21, from which it is seen that only in the region of high temperatures $T > T_C$ (curve 3) is there one solution for M', namely $M' = 0$. At low temperatures (curve 1) there are two solutions, and at values of T close to T_C (curve 2) there are three solutions for M'. The determination of the stable solutions was based on an analysis of the change of the thermodynamic Gibbs potential G as a function of the magnetization and the temperature:

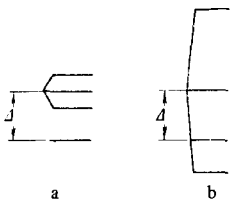

FIG. 19. Diagram of energy levels. a) Singlet-triplet splitting Δ is smaller than the splitting of the triplet due to the magnetic field; b) splitting of the triplet by the magnetic field is larger than the splitting Δ of the crystal lattice by the electric field.

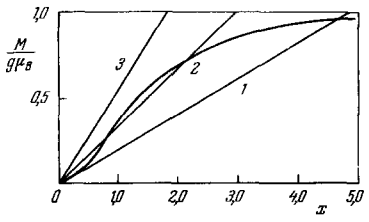

FIG. 20. Graphic solutions of Eq. (7.2) of Blum's theory [73] for the case when the magnetic transformation is a second-order phase transition.

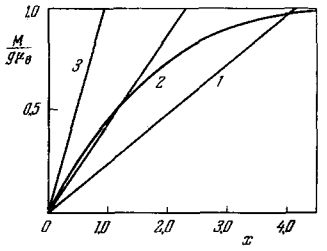

FIG. 21. Graphic solutions of Eq. (7.2) of Blum's theory [73] for the case $0.366 < \Delta' < 0.4$. The magnetic transformation is a first-order phase transition.

$$\frac{1}{\Delta}\{G(M',\ \tau)-G(0,\ \tau)\} = -\tau \ln\left[\frac{1+e^{-1/\tau}(1+e^{M'/\tau\Delta'}+e^{-M'/\tau\Delta'})}{1+3e^{-1/\tau}}\right]+\frac{1}{2\Delta'}M'^2. \quad (7.6)$$

Here $\tau = kT/\Delta$. Figure 22 shows the plots of the thermodynamic potential against the magnetization, determined from this formula, for various temperatures. In the region $T > T_c$ (curve for $\tau = 0.790$) there is a single extremum for the states with $M' = 0$; this corresponds to the curve 3 of Fig. 21. At low temperatures, as seen from the curve for $\tau = 0.770$ on Fig. 22, the stable state is the one with the finite value of M'. At temperatures close to the magnetic transformation point ($\tau = 0.780$ and $\tau = 0.786$) the plots of $1/\Delta\{G(M',\ \tau) - G(0,\ \tau)\}$ against M' have two minima and one maximum, corresponding to the intersection points of the straight line 2 in Fig. 21. If both minima are at the same level for a certain temperature (the curve for $\tau = 0.786$), then a first-order phase transition takes place, for in this case the magnetization drops suddenly from the finite value M' to zero.

The foregoing considerations were used by Blum as a basis for explaining the nature of the magnetic transformation in UO_2. Neutron-diffraction investigations[83] have shown that the character of the temperature dependence of the magnetization UO_2 in the region of the Neel point ($T_N = 30.8°$ K) corresponds to a first-order phase transition. The absence of volume changes of the crystal lattice during the transition, has led Blum to the assumption that the transformation in UO_2 is due to a change of the spin system only, and calls for a special analysis. In spite of the fact that Blum's calculations give a qualitative correspondence between the theory and experiment, recently doubts were advanced concerning the possible interpretation of the magnetic transition in UO_2 on the basis of the foregoing model representations. This is connected with the fact that recently published results[84] of dilatometric measurements (Fig. 23) and measurements of other properties of UO_2 (Fig. 24) indicate quite distinctly that the volume of the crystal lattice changes during the transformation, and the elastic constants decrease abruptly. These data indicate that it is necessary to review the mechanism of the magnetic phase transition in UO_2; this again raises the question of the exchange-striction nature of the magnetic transformation. For a final solution of this question further experimental investigations are needed, primarily measurement of the effect of the shift of the Neel temperature of UO_2 when the pressure is varied.

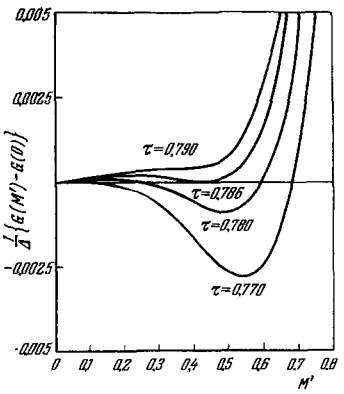

FIG. 22. Dependence of the free energy on the magnetization in accordance with Blum's calculation [73]. First-order phase transition for $\tau = 0.786$.

It must be noted that the antiferromagnetic transformation in Eu is also a first-order phase transition[85]. If account is taken of the fact that the picture of the splitting of the initially degenerate levels in Eu into "nonmagnetic" and "magnetic" sublevels is the same as in UO_2, and the magnitude of the dT_N/dP effect is small[86], then it would be of interest to verify the possibility of explaining this transition on the basis of the foregoing model.

8) Criterion of Ferromagnetism in Accordance with the Band Model, and Magnetic First-order Phase Transitions

Theoretical investigations of magnetic phenomena[87-89], based on the assumption of collectivization of "magnetic" 3d- and "valence" 4s- and 4p-electrons and their consideration as a single system of an electron gas have led to the creation of the band theory of magnetism. According to this theory, the occurrence of ferromagnetic order of the spin magnetic moments is possible only at definite relations between the kinetic and exchange energies; it is necessary here that the level density at the Fermi surface $\nu(\epsilon)$, and also the exchange energy, be sufficiently large. A calculation by Stoner[89] for the "normal" band, i.e., when the change of the density of states with energy has a parabolic form $\nu(\epsilon) \sim \sqrt{\epsilon}$, had shown that the ferromagnetism criterion for this case is $\alpha > \alpha_S$, where α is the constant of the Weiss molecular field and α_S is a constant characterizing the exchange interaction in the absence of a mole-

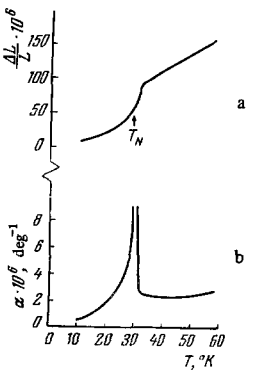

FIG. 23. Temperature dependences of $\Delta L/L$ and of the coefficient of thermal expansion of UO_2.

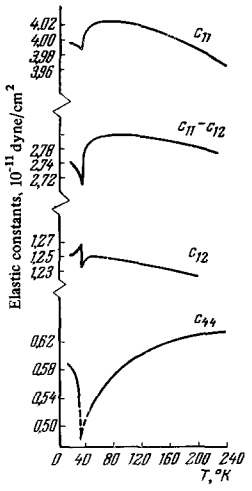

FIG. 24. Temperature dependence of the elastic constants of UO_2 in the region of the antiferromagnetic transformation.

cular field, and equal to the reciprocal of the paramagnetic susceptibility of the electron gas at 0°K ($\alpha_S^{-1} = \chi_0(0)$). Attempts were made subsequently to determine the conditions for the occurrence of ferromagnetism in a system of collectivized electrons with arbitrary dispersion law, i.e., for an arbitrary band, when the $\nu(\epsilon)$ dependence can have an arbitrarily complicated form. In an extensive investigation, Shimizu has shown[90,91] that the ferromagnetism criterion in the band model depends on the general topology of the density of states, the position of the Fermi level, and the magnitude of the molecular-field coefficient. It was established there that in a number of cases, when the Fermi level lies near the minimum of the density of state curve, the transition from the ferromagnetic into the paramagnetic state can be a first-order phase transitions.

In Shimizu's cited papers[90,91], he investigated the dependence of the kinetic and exchange energies on the spontaneous magnetization of the system of electrons. Figure 25 shows the change of the density of states as a function of the energy at 0°K. Here ζ_0 is the Fermi level for the paramagnetic state and $\nu_1(\epsilon)$ and $\nu_2(\epsilon)$ are the density of states for $\epsilon > \zeta_0$ and $\epsilon < \zeta_0$, respectively. The number of singly-occupied levels $n(\zeta)$, both above and below the Fermi level, is

$$n_1(\zeta_1) = \int_{\zeta_0}^{\zeta_1} \nu_1(\varepsilon)\, d\varepsilon, \quad n_2(\zeta_2) = \int_{\zeta_2}^{\zeta_0} \nu_2(\varepsilon)\, d\varepsilon. \tag{8.1}$$

Depending on the form of the $\nu(\epsilon)$ curve, the values of $n_1(\zeta_1)$ and $n_2(\zeta_2)$ differ. When spontaneous magnetization M occurs, some of the electrons occupying states below ζ_0 go over into states above ζ_0, and then

$$n_1(\zeta_1) = n_2(\zeta_2) = n_1 \tag{8.2}$$

$$M = 2\mu_B n. \tag{8.3}$$

When ferromagnetic order sets in, a change takes place in the kinetic energy E_k and in the exchange energy E_{ex}; the total change of the electron energy is then

$$E = E_k + E_{ex} = \int_{\zeta_0}^{\zeta_1} \varepsilon\nu_1(\varepsilon)\, d\varepsilon - \int_{\zeta_2}^{\zeta_0} \varepsilon\nu_2(\varepsilon)\, d\varepsilon + E_{ex}. \tag{8.4}$$

The equilibrium value of the energy is determined by minimizing E with respect to the magnetization:

$$\frac{\partial E}{\partial M} = \frac{\zeta_1 - \zeta_2}{2\mu_B} + \frac{\partial E_{ex}}{\partial M} = 0, \tag{8.5}$$

$$\frac{\partial^2 E}{\partial M^2} = \frac{\nu_1(\zeta_1)^{-1} + \nu_2(\zeta_2)^{-1}}{4\mu^2} + \frac{\partial^2 E_{ex}}{\partial M^2} > 0. \tag{8.6}$$

Following the Weiss hypothesis, it can be assumed that the dependence of the exchange energy on M is given by

$$E_{ex} = -\frac{1}{2}\alpha M^2; \tag{8.7}$$

and then

$$\frac{\partial E}{\partial M} = -\alpha M \quad \text{and} \quad \frac{\partial^2 E}{\partial M^2} = -\alpha;$$

taking (8.4) into account, we can conclude that E = 0 when M = 0. Inasmuch as the total energy should be negative following ferromagnetic ordering, it is necessary to determine the condition when E < 0 for M ≠ 0. To analyze the relations between E, E_k, E_{ex}, α, and M leading to a stable ferro- or paramagnetic state, Shimizu used a graphic method. Solving (8.4) by integrating by parts:

$$E = (\zeta_1 - \zeta_2)\, n - \int_{\zeta_0}^{\zeta_1} n_1(\varepsilon)\, d\varepsilon - \int_{\zeta_2}^{\zeta_0} n_2(\varepsilon)\, d\varepsilon + E_{ex}, \tag{8.8}$$

and plotting n against $\Delta\zeta$ to correspond to the investigated density of states curve, he determined the change of the total energy, and also of the individual contributions E_k and E_{ex}, as functions of the magnetization of the system. Figure 26 shows the change of n (number of singly occupied levels) for various values of the widths of the energy band near the Fermi level; it is seen from this figure that for the case when n = n′ and $\Delta\zeta = \zeta_1 - \zeta_2$, the area $OG_3G_2F_2n'O$, between the curve and the ordinate axis is equal to the change of the kinetic energy determined by the sum of the first three terms of (8.8). Taking into account (8.3), (8.5), and the functional dependence of the exchange energy on the magnetization (8.7), we can determine the relation between $\Delta\zeta = \partial E_{ex}(n)/\partial n$ and n (the straight lines OF_1, OF_2, OF_3, OF_4, and OF_5 on Fig. 26), and also the absolute value of the exchange energy E_{ex}, which equals the area between the indicated straight lines and the ordinate axes. For the case $\Delta\zeta = \zeta_1 - \zeta_2$, this is the area $OF_3n'O$. If the change of the kinetic energy is smaller than the contribution due to the exchange energy E_{ex} (the area $OG_3F_1F_2F_3n'O$ is smaller than the area $OF_3n'O$), then the total energy is negative and the system is in the ferromagnetic state. If the change of E_k is exactly equal to the change of E_{ex}, then the indicated two areas are equal and the state of the system can be characterized as critical. For the paramagnetic state, the total energy should be positive, and consequently E_k must be larger than E_{ex}. The dependence of E on M for all the cases indicated above is shown in Fig. 27. An analysis of the change of the coeffi-

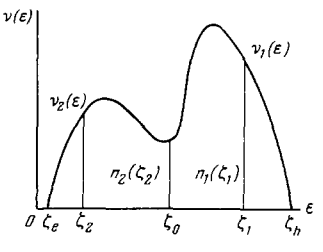

FIG. 25. Plot of the density of states vs. the energy.

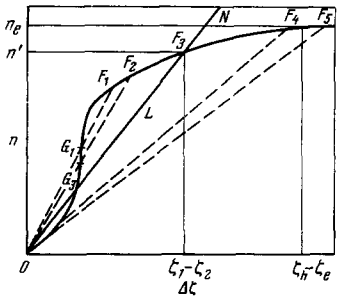

FIG. 26. Graphic solution of Eq. (8.8) in accordance with the Shimizu theory [91].

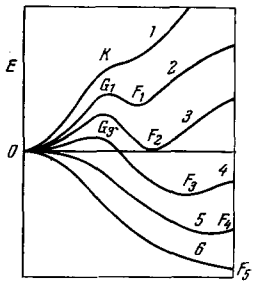

FIG. 27. Dependence of the energy on the magnetization M. Curves 1 and 2 – paramagnetic state, 5 and 6 – ferromagnetic state with the usual second-order phase transitions at the Curie point, 3 – critical state. 4 – the transition from the ferromagnetic into the paramagnetic state is a first-order magnetic phase transition.

cients of the molecular field α has shown that Stoner's ferromagnetism criterion $\alpha > \alpha_s$ is satisfied here, too (curves 5 and 6 of Fig. 27). There may be cases, however, (curve 4 of Fig. 27), when the ferromagnetic state is possible even when $\alpha < \alpha_s$, and the ferromagnetism criterion is $\alpha_c < \alpha < \alpha_s$, while that for paramagnetism is $\alpha < \alpha_c$ (α_c is the coefficient of the molecular field for the critical case).

It is seen from Fig. 27 that the dependences of E on M corresponding to the ferromagnetic state may differ in character (curve 4, on the one hand, and curves 5 and 6, on the other). This is of great significance, since it evidences that the character of the magnetic phase transitions is different for these cases. It can be assumed that the magnetic transformation is a first-order phase transition when E(M) is determined by curve 4 (Fig. 27), and an ordinary second-order phase transition of the Curie point type in the case of curves 5 and 6. The conditions for the occurrence of first-order magnetic phase transitions within the framework of the model of collectivized electrons are discussed in detail in[91]. It is noted there that for a band with an arbitrary dispersion law there can be realized conditions (depending on the position of the Fermi level) in which the ferromagnetic state has two temperature boundaries, i.e., the system is paramagnetic at high and low temperatures, and ferromagnetism arises in some intermediate temperature interval. It is important here that both the occurrence and the vanishing of the ferromagnetism, which occur on the boundaries of this temperature interval, are first-order phase transitions. A possible example of such transitions are the magnetic transformations in Mn_3Ge_2, observed by Fakidov, Grazhdankina, and Novogrudskiĭ[92] and investigated in[93-95]. A general qualitative verification of the theory was made by Shimizu by analyzing the experimental data obtained for MnAs. The experimentally observed strong decrease of the temperature of the magnetic transformation of MnAs with increasing pressure is explained on the basis of the foregoing model in the following manner. With increasing pressure, the degree of overlap of the wave functions of the "magnetic" electrons increases, and the curve of the dependence of the state density on the energy becomes less steep. This effect leads to an increase of the kinetic energy of the electrons, and by the same token weakens the ferromagnetism criterion. In this connection, the decrease of the temperature of the magnetic transition with increasing pressure can occur also in the case when the exchange energy and the coefficient of the molecular field do not change with increasing pressure.

Systems in which magnetic first-order phase transitions are observed are listed in Table III.

5. CONCLUSION

On the basis of the foregoing review we can conclude that the occurrence of magnetic first-order phase transitions is possible in a great variety of magnetic sys-

Table III. Substances in which magnetic first-order phase transitions were observed

Substance	Crystal structure	Magnetic transition	Temperature of magnetic transition, °K	Literature
MnAs	Hexagonal (type NiAs) orthorhombic 313-400°K	F → P	313 400	98, 99, 16, 17, 19, 20, 21, 26, 15, 96
$KMnF_3$	Monoclinic	AF → P	88.3	100, 101
Cr_3As_2	Tetragonal	F → P	213	102
$TiCl_3$	Rhombohedral	AF → P	210	103
$MnBr_2$	Hexagonal layered	AF → P	2.16	104, 105
NiO	$T < T_N$, Rhombohedral	AF → P	647	106, 107
	$T > T_N$, Cubic		523	
MnO	$T < T_N$, Rhombohedral	AF → P	122	106
	$T > T_N$, Cubic		115.9	
UO_2	Cubic f. c.	AF → P	30.8	83, 84
Eu	Cubic, b. c.	AF → P	90	85, 86
Cr	»	AF → P	311.5	77
$Mn_{2-x}Cr_xSb$ $(0,025 < x < 0,20)$	Tetragonal	AF → F	$T_s(x) = 200-350$	43, 41, 42, 40, 50, 52, 46, 51
$Mn_{2-x}Cr_xSb$	»	AF → H	$T_s(x) = 4.2-150$	46, 45, 42
$(0,025 < x < 0,035)$	»	H → F	$T_s(x) = 50-150$	44
Mn_3Ge_2		AF → F F → P	148 283	92, 93, 94, 63, 95
MnP	Rhombohedral	AF → F	50	108
FeRh	Cubic (type CsCl)	AF → F	350	53-55, 57, 58, 56, 59, 61, 62, 63, 64, 65, 66
Mn_3GaC	Cubic (perovskite type)	AF → F	150	67, 68, 69
α-Fe_2O_3	Rhombohedral	AF → F	250	97, 109
$CrS_{1.17}$	Hexagonal (type NiAs)	AF → F	158	110, 111, 63, 112, 113
$MnSn_2$	Tetragonal	AF → F	73	114
$Mn_{0.9}Li_{0.1}Se$	Cubic (NaCl type)	AF → F	71	115, 116

Table III (Cont'd.)

Substance	Crystal structure	Magnetic Transition	Temperature of magnetic transition, °K	Literature
Dy	Hexagonal	F → H	85	(see review on rare-earth ferro- and anti-ferromagnets [79,119])
Mn_3Pt	»	AF → AF	383	119
V_2O_3	»	AF → P	161	120, 121
Ti_2O_3	»	AF → P	473	122
NiS	»	AF → P	263	124

In the case when two transition temperatures are given, one of them (upper) corresponds to magnetic measurements and the other (lower) is established with the aid of thermal measurements.

Symbols: F – ferromagnetism or ferrimagnetism, AF – antiferromagnetism, P – paramagnetism, H – helical magnetic structure, WF – weak ferromagnetism of the Dzyaloshinskii-Morin type.

tems, and that the physical causes of this phenomenon are different. Most frequently magnetic first-order transitions are observed in substances in which effects of the shift of the magnetic-transformation temperature with increasing pressure are sufficiently large. In this connection, principal attention was paid in this review to the exchange-striction mechanism of magnetic transformations, which is based on the assumption that the exchange interaction depends strongly on the interatomic distances. This mechanism was used in the theory of Bean and Rodbell, and also in Kittel's theory for a quantitative treatment of magnetic transformations of two different classes: order-disorder type, connected with the destruction of the spin ordering, and order-order type, due to inversion of the exchange interaction. The agreement between the experimental results and the main conclusions of the indicated theories indicate that this mechanism is realized in a large number of magnetic systems that differ from one another in their crystal and magnetic structures, in the character of the exchange interactions, etc. Experimental investigations of the elastic properties and effects of the shift of the magnetic-transition temperature with increasing pressure are of principal significance for a verification of the initial premises of the considered theories. Besides neutron-diffraction investigations, great importance attaches also to measurements of the magnetic properties in strong magnetic fields, particularly for order-order transitions. These investigations yield important information concerning the magnitudes of the internal effective fields due to the magnetic and exchange interactions. A study of the character of the forces causing the magnetic ordering helps explain the causes of the change of this order, and determine the true nature of the magnetic transformation.

Magnetic transition models[70-78,90,91] not connected with the exchange-striction mechanism are of undoubted interest, and in many cases the factors considered in these models apparently exert a definite influence on the character of the magnetic transformations. Thus, for example, the experimentally established influence of the magnetic crystallographic anisotropy on the magnetic-transition in temperature MnAs[96] and in $Mn_{2-x}Cr_xSb$ alloys[44] serve to a certain degree as a proof of the validity of the ideas of Yosida and Miwa[70]. Since at present we have far from complete data on the structure of the electronic energy spectrum of transition metals and their alloys or compounds, it is impossible to draw any concrete conclusions concerning the influence of this factor on the character of the magnetic transformations. However the theories of Dzyaloshinskiĭ[71], Shimizu[90,91], and Blum[73] are sufficiently convincing examples demonstrating the great importance of the topology of the Fermi surface, of the density of states, and of the splitting of the energy levels in the crystalline magnetic fields to the magnetic transitions. In this connection, it can be assumed that in substances with a small volume dependence of the exchange integrals, the magnetic transitions are determined to a considerable degree by the indicated characteristics. Thus, the essential condition for further development of our concepts concerning the nature of magnetic transformations is comprehensive and purposeful research on the physical properties of various systems with spin ordering.

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