Itinerant metamagnetism

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The experimental and theoretical publications on itinerant metamagnetism—the jump-like transition, induced by a magnetic field, of a paramagnetic system of itinerant electrons into a magnetically ordered state—are reviewed. The conditions necessary for the appearance of the metamagnetic transition are formulated on the basis of Stoner's model, and a theory of itinerant metamagnetism for weak itinerant magnets is presented. The effect of fluctuations of the spin density on the properties of an itinerant metamagnet is examined. The results of experimental studies of itinerant metamagnetism, induced by both external and internal effective magnetic fields, in a system of electrons of a number of intermetallides are presented. The systems $Co(Se_{1-x}S_x)_2$, $Y(Co_{1-x}Al_x)_2$, and $Lu(Co_{1-x}Al_x)_2$, the compounds RCO_2 [1], $ThCo_5$, $CeCo_5$, and others are studied. Some other phenomena associated, like itinerant metamagnetism, with the sharp energy dependence of the density of states near the Fermi level are discussed.

CONTENTS

1. INTRODUCTION

Two opposite theoretical approaches are currently employed to describe the properties of magnets. One approach, first proposed by Heisenberg,[1] starts from the fact that the carriers of the magnetic moment (magnetic electrons) are localized and their energy spectrum is described by Boltzmann statistics. In the other model (called Stoner's model after the author who studied it most systematically)[2] it is assumed that the magnetic electrons are collectivized and obey Fermi-Dirac statistics. The use of one or the other model to describe the properties of a specific magnet depends on the energy structure of the magnet. If the width of the energy levels in the crystal is much smaller than the energy splitting between them, then Heisenberg's model of localized moments "operates"; if, however, the splitting between the electronic levels in the crystal is comparable to the width of these levels, then the magnetic properties are described by the itinerant model.

Although the itinerant model of magnetism was formulated at almost the same time as the model of localized magnetic moments, the magnetic properties of magnets were for a long time interpreted almost exclusively on the basis of Heisenberg's model. This happened because Stoner's model in its initial form was proposed for the simplest approximation, in which the magnetic electrons in the crystal were regarded as almost free, while collective excitations were ignored. This, of course, is completely unrealistic for most magnets.[1)]

In the last 10 to 15 years the situation changed radically. The band structure of many d metals and alloys has been determined by different methods, and their magnetic properties have been calculated in the collectivized-electron model taking into account the real band structure and spin-wave excitations. Significant progress has been achieved with the development of methods for calculating effects owing to fluctuations of the spin density (Fermi-liquid theory,[3] the functional-integral method,[4] etc.) in itinerant magnets.

All this led to the fact that the itinerant model is at the present time the generally accepted model of d magnets and is widely employed to describe the magnetic properties of d metals, alloys, and intermetallides.

One of the important features of the collectivized-electron model, properly perceived only recently, is the fact that the properties of an itinerant magnet depend very strongly on the structural characteristics of the d band. For example,

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in the simplest mean-field approximation (i.e., even neglecting spin-fluctuation effects) it is possible, by choosing the appropriate energy dependence of the density of d states, to describe the Curie-Weiss behavior of the paramagnetic susceptibility and to obtain Curie parameters of some d metals and alloys that are close to the experimental values[5] (these facts could not be explained on the basis of the simplest Stoner model). Unusual phenomena, such as the existence of itinerant ferromagnetism at temperatures between two paramagnetic phases (thermally induced ferromagnetism), can also be explained qualitatively in an analogous approximation.[6]

A specific manifestation of the itinerant nature of magnetism, first theoretically studied by Wohlfarth and Rhodes,[7] it the metamagnetism of collectivized electrons (itinerant magnetism of paramagnets). Wohlfarth and Rhodes showed[7] that is is possible to have a situation in which the magnetic system of itinerant electrons in a magnetic field (external or effective) transfers in a jump-like fashion into the ferromagnetic state.[2)] The theoretical ideas regarding itinerant metamagnetism later became significantly more profound and, most importantly, this phenomenon was discovered experimentally.

In this review we attempted to organize the published theoretical and experimental information on itinerant metamagnetism. We felt that this would be very useful, since itinerant metamagnetism is interesting not only in itself, but, in addition, by studying this phenomenon it is possible to understand more deeply some aspects of the itinerant theory of metamagnetism and open up the possibilities incorporated in this theory for describing different unusual effects observed in experiments.

The review is organized as follows. First, the basic assumptions of the theory of itinerant magnetism are formulated on the basis of Stoner's approximation. Then the conditions under which itinerant metamagnetism is possible in this model are examined qualitatively. The quantitative relations for the conditions for the appearance of and characteristics of an itinerant metamagnet are presented for the case of a weak itinerant magnet. The role of spin-fluctuation effects is briefly discussed. Then the data on itinerant metamagnetism in electronic paramagnets are presented systematically and the characteristics of the magnetic behavior of magnetically ordered materials, where the d subsystem exhibits metamagnetic properties, are discussed. The results of a numerical calculation of this phenomenon are presented for some intermetallides taking into account their specific band structure. Other effects whose nature is similar to that of itinerant metamagnetism are also examined.

2. STONER'S THEORY AND ITINERANT METAMAGNETISM (PHENOMENOLOGICAL DESCRIPTION)

2.1. Magnetism of collectivized electrons in Stoner's model

In the itinerant theory of magnetism a system of collectivized electrons is studied. Magnetization arises in this system because in a magnetic field the energy of electrons with spins oriented along the field (" + " spins) is less than the energy of electrons with spins oriented opposite to the field " − " spins), the subband of electrons with + and − spins is shifted downwards and upwards, respectively, on the energy scale, and some of the electrons from the " − " spin subband are transferred into the " + " spin subband.[2] Introducing the standard notation $N_\pm(\varepsilon)$, $n_\pm$, and $\zeta_\pm$ —the density of states at a given energy ε, the number of electrons, and the chemical potential in the subbands—the magnetization can be expressed as

$$M = \mu_B (n_+ - n_-), \tag{1}$$

$$n_\pm = \int_0^{\zeta_\pm} N_\pm(\varepsilon) f_\pm(\varepsilon)\, d\varepsilon, \tag{2}$$

where $f_\pm(\varepsilon)$ is the Fermi-Dirac distribution function in the " + " and " − " subbands.[8] The Pauli susceptibility of a noninteracting electron gas in the Stoner approximation equals[5,9]

$$\chi_p(T) = \chi_p(0)[1 - g_A T^2 + O(T^4)]; \tag{3}$$

here

$$\chi_p(0) = 2\mu_B^2 N(\varepsilon_F) \tag{4}$$

is the susceptibility at absolute zero. The temperature dependence of the susceptibility in the first approximation is quadratic and is determined by the coefficient g_A, given by

$$g_A = \frac{(k\pi)^2}{6}\left[\left(\frac{N'(\varepsilon_F)}{N(\varepsilon_F)}\right)^2 - \frac{N''(\varepsilon_F)}{N(\varepsilon_F)}\right]. \tag{5}$$

In the formulas (4) and (5) $N(\varepsilon_F)$, $N'(\varepsilon_F)$ are the density of states and its derivatives at the Fermi level ε_F.

If an exchange interaction exists between the electrons, then the susceptibility of the electron gas increases and the expression for the exchange-enchanced Pauli susceptibility has the form[9]

$$\chi(T) = \frac{\chi_p(T)}{1 - \lambda\chi_p(T)}, \tag{6}$$

where λ is the coefficient of the molecular field in the expression for the exchange energy

$$F_{exc}(M) = -\frac{1}{2}\lambda M^2. \tag{7}$$

Ferromagnetic ordering in the itinerant model will be thermodynamically stable, if on splitting of the subbands with " + " and " − " spins the magnetic part of the free energy consisting of the exchange energy $F_{ex}(M)$ and the additional kinetic energy $F_k(M)$ is nonpositive:

$$F(M) = F_k(M) + F_{exc}(M) \leqslant 0. \tag{8}$$

The equilibrium value of the magnetization M_s (spontaneous magnetization) and the condition for the ferromagnetic state to be stable (called the Stoner condition) are determined from (8) together with the equilibrium conditions $\partial F/\partial M = 0$, $\partial^2 F/\partial M^2 \geqslant 0$. For small energy splitting $\delta\varepsilon$ of the subbands in the exchange field, when it can be assumed that

$$F_c = \frac{1}{2}(n_+ - n_-)\,\delta\varepsilon,$$

$$N(\varepsilon_F)\,\delta\varepsilon = \frac{1}{2}(n_+ - n_-), \tag{9}$$

the condition for Stoner's itinerant ferromagnetism assumes the especially simple form

$$\lambda\chi_p(0) \geqslant 1. \tag{10}$$

This condition is sometimes written in terms of $N(\varepsilon_F)$ as

$$IN(\varepsilon_F) \geqslant 1 \tag{11}$$

($I = 2\mu_0^2\lambda$ is the exchange parameter).

We note that the relations presented, derived in the Stoner approximation, in many cases describe the experimental data for specific itinerant magnets quite well. Without making a detailed analysis of Stoner's model, we indicate only that a significantly better agreement between theory and experiment can be achieved by including in $F(M)$ the fluctuations of the spin density,[4,10] and keeping in mind the real structure of the energy band.[5,11] In particular, it is shown in Ref. 5 that the strong temperature dependence of the susceptibility in the itinerant model can be explained neglecting fluctuations (this question is most difficult for Stoner's "classical" theory) in magnets with a strong energy dependence of the density of states, having a singularity near the Fermi energy (for example, a singularity of the van Hove type: $\delta N'(\varepsilon_0) = N_2'(\varepsilon_0) - N_1'(\varepsilon_0)$, $|\varepsilon_0 - \varepsilon_F| \approx kT$). Moreover, the fluctuations themselves depend very strongly on the form of $N(\varepsilon)$, and they can apparently make a significant contribution on the magnetic properties in the same cases of sharp energy dependence $N(\varepsilon)$ for which a strong temperature dependence $\chi(T)$ arises.[10]

2.2. Possibility of ferromagnetism in an itinerant paramagnet in a magnetic field

The behavior of an itinerant paramagnet in a magnetic field depends on the form of the dependence $N(\varepsilon)$ near the Fermi level. It is possible to have a situation when an applied magnetic field increases the density of states at the Fermi level. If in such a paramagnetic system the Stoner condition[11] is close to being satisfied, then with a strong energy dependence $N(\varepsilon)$ the magnetic properties in the applied field can change significantly, right up to the appearance of magnetic ordering.

Figure 1 shows schematically sections of the curve $N(\varepsilon)$ near $\varepsilon = \varepsilon_F$ for some characterisic cases when $N(\varepsilon_F)$ decreases (case a) or increases (cases b–d) when the spin subbands are split in the field. As one can see from this figure, the condition

$$[N(\varepsilon_F) = N_+(\varepsilon_F) + N_-(\varepsilon_F)]_{H=0} < [N(\varepsilon_F) = N_+(\varepsilon_F) + N_-(\varepsilon_F)]_{H>0} \qquad (12)$$

holds, when the function $N(\varepsilon)$ can have a positive curvature near $\varepsilon = \varepsilon_F$, i.e., when $N''(\varepsilon_F) > 0$.

In a magnetic field, when the energy spin subbands are shifted relative to one another and the values of $N_+(\varepsilon)$ and $N_-(\varepsilon)$ are no longer equal for the same values of the energy, the Stoner condition in zero field (see the formula (11)) for the appearance of ferromagnetism must be replaced by the following relation (the "generalized" Stoner condition)[12]:

$$I\left(\frac{1}{N_+(\varepsilon_F)} + \frac{1}{N_-(\varepsilon_F)}\right)^{-1} \geqslant 1. \qquad (13)$$

It is obvious that for a paramagnetic system the relation (13) can hold in an external magnetic field only if the condition (12) holds.

2.3. Theory of itinerant metamagnetism

The theory of itinerant metamagnetism is simplest in the case when the resulting splitting of the subbands is much smaller than their width, i.e., in the case when Wohlfarth's approximation of weak itinerant magnetism is applicable.[13,14] Then the splitting of the subbands and therefore the magnetization are also small parameters, and expanding $F(M)$ in a series in powers of $F(M)$ in a series in powers of M we obtain for the magnetic part of the free energy

$$F(M) = \frac{(A-\lambda)}{2}M^2 + \frac{B}{4}M^4 + \frac{C}{6}M^6 - HM, \qquad (14)$$

where the expansion coefficients $A(T)$, $B(T)$, and $C(T)$ are determined by the properties of the curve of the density of states $N(\varepsilon)$ near the Fermi level and can be represented as series in even powers of the temperature:

$$A(T) = \chi_n^{-1}(T) = A(0)(1 + g_A T^2 + O(T^4))$$

(see formula (3)),

$$B(T) = B(0)(1 + g_B T^2 + O(T^4)),$$
$$C(T) = C(0)(1 + g_C T^2 + O(T^4)),$$

where

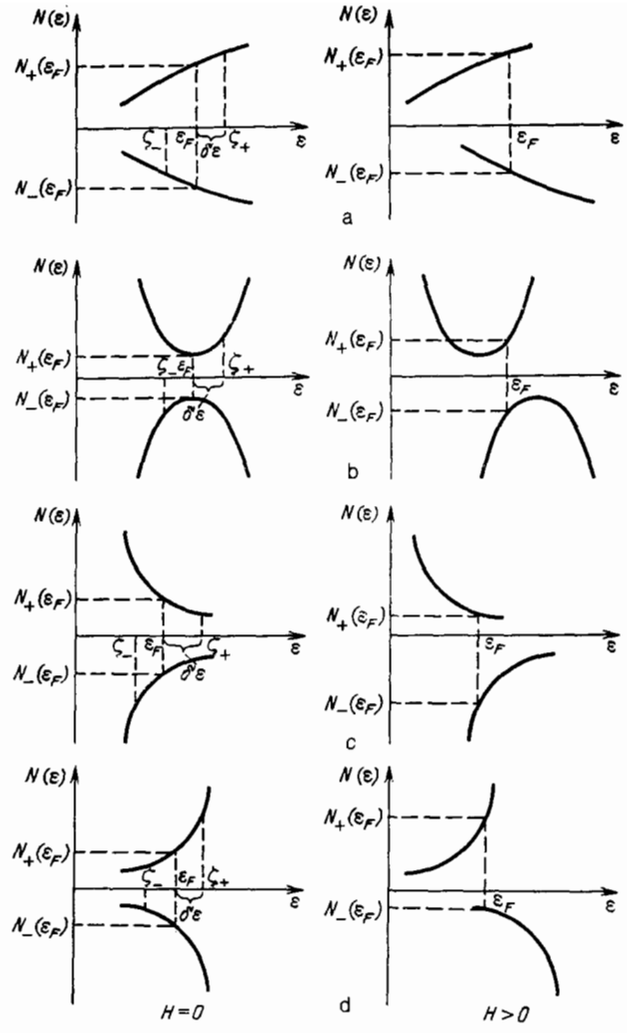

FIG. 1. Schematic diagrams of the dependence of the density of states on the energy $N(\varepsilon)$ near $\varepsilon = \varepsilon_F$ for cases of negative curvature of $N(\varepsilon)$ (a) and positive curvature of $N(\varepsilon)$ (b–d) for $H = 0$ (left) and $H > 0$ (right).

$$B(0)=\frac{1}{48\mu_B^4 N_F^3}\left[3\left(\frac{N_F'}{N_F}\right)^2-\frac{N_F''}{N_F}\right], \tag{15}$$

$$C(0)=\frac{1}{256\mu_B^6 N_F^5}\left[7\left(\frac{N_F'}{N_F}\right)^4-7\frac{N_F'^2N_F''}{N_F^3}+\frac{N_F'N_F'''}{N_F^2}+\frac{2}{3}\left(\frac{N_F''}{N_F}\right)^2-\frac{1}{15}\frac{N_F''''}{N_F}\right], \tag{16}$$

$$g_B=\frac{(k\pi)^2}{6\left[3(N_F'/N_F)^2-(N_F''/N_F)\right]}\left[15\left(\frac{N_F'}{N_F}\right)^4+25\frac{N_F'^2N_F''}{N_F^3}+4\left(\frac{N_F''}{N_F}\right)^2+7\frac{N_F'N_F'''}{N_F^2}-\frac{N_F''''}{N_F}\right]; \tag{17}$$

here the symbols N_F, N_F', N_F'', N_F''' and N_F'''' denote, for brevity, $N(\varepsilon_F)$ and its derivatives. The expression for q_C is very cumbersome, and we shall not write it out.

The Stoner condition for the appearance of weak itinerant ferromagnetism, derived from (14), has the form

$$A(0)-\lambda\leqslant 0. \tag{18}$$

The nature of the phase transition from the ferromagnetic into the paramagnetic state as the temperature is increased is determined by the sign of the coefficient $B(T_c)$ (T_c is the Curie temperature). If $B(T_c)>0$, the transition at T_c is a second-order phase transition and the Curie temperature is determined from the condition

$$A(T_c^{II})-\lambda=0. \tag{19}$$

If, however, $B(T_c)<0$, this transition becomes a first-order phase transition and T_c^I is given by the relation[12]

$$1=4(A(T_c^I)-\lambda)\left[1-\frac{4(A(T_c^I)-\lambda)C(T_c^I)}{B^2(T_c^I)}\right]. \tag{20}$$

In the case when $A(0)-\lambda>0$ the itinerant magnet will be a paramagnet at 0 K.

The dependence of the magnetization on the external field is found from the condition for the minimum of the free energy (14):

$$H=(A(T)-\lambda)M+B(T)M^3+C(T)M^5. \tag{21}$$

The character of this dependence for an itinerant paramagnet is determined by the signs of the coefficients $A(T)-\lambda$, $B(T)$, and $C(T)$ an the relations between their values. Let us see, for example, how the susceptibility of the paramagnet changes in a field. According to (21), it can be represented in the form[9]

$$\chi(T,H)\approx\chi(T,0)(1-B(T)\chi^3(T,0))H^2+\ldots), \tag{22}$$

where

$$\chi(T,0)=(A(T)-\lambda)^{-1} \tag{23}$$

is the exchange-enhanced susceptibility (see also (6)). One can see from here that together with the "trivial" case, when the susceptibility decreases as the field intensifies (this case is realized when $B(T)>0$), the susceptibility of the itinerant paramagnetic can increase as the field increases. For this the coefficient $B(T)$ must be negative. In the latter case, under some conditions, in an external field the paramagnet can transform into the ferromagnetic state. Analysis of the expression for the magnetization (21), performed in Ref. 14, shows that for $A(T)-\lambda>0$, $B(T)<0$, and $C(T)>0$ the magnetization curve is S shaped, i.e., a metamagnetic first-order transition occurs from the para- into the ferromagnetic state, if the following condition holds:

$$\frac{3}{16}<\frac{(A-\lambda)C}{B^2}<\frac{9}{20}. \tag{24}$$

Figure 2 shows the isotherms of the magnetization of an itinerant paramagnet for different cases, when the magnetization process is metamagnetic and when such a transition does not occur. Here the curve 1 corresponds to "normal" paramagnetic behavior of $M(H)$, which is realized with the energy dependence $N(\varepsilon)$ shown in Fig. 1a for the density of states at the Fermi level, decreasing as the field increases ($B(T)>0$). The linear dependence $M(H)$ (curve 2) is realized in the case when the change in $N(\varepsilon_F)$ in a magnetic field is not significant. Finally, the curves 3–5 illustrate different cases, when $B(T)<0$ and the density of states at the Fermi level increases as the magnetic field increases (they correspond to the dependences $N(\varepsilon)$ shown in Figs. 1b–d). For all these cases the susceptibility increases with the field, although the jump-like metamagnetic transition occurs only on the isotherm $M(H)$ shown by the curve 5 in Fig. 2. For such a paramagnet in an external field $H=H_c''$ the magnetization increases in a jump-like fashion, and the system transfers into the ferromagnetic state. The reverse transition occurs with hysteresis in the field $H_c'<H_c''$. The field H_c corresponds to the state when the free energies of the paramagnetic and ferromagnetic phases are equal to one another. This is the field of the phase transition, while the fields H_c' and H_c'' are the fields of lability of the paramagnetic and ferromagnetic phases, respectively. Curve 4 in Fig. 2 shows the limiting case $(A-\lambda)C/B^2=9/20$ (see formula (24)) of itinerant metamagnetism, when an inflection appears in the dependence $M(H)$. The other limit $(A-\lambda)C/B^2=3/16$ of the condition (4) corresponds to the case when the paramagnetic system transfers into the ferromagnetic state as the field increases, and when the external field exceeding H_c is removed, the system remains in the magnetically ordered state: $H_c'<0, H_c\geqslant 0$ (this case is not shown in Fig. 2).

The expressions for the critical fields H_c', H_c, and H_c'' and the corresponding values of the magnetization in the

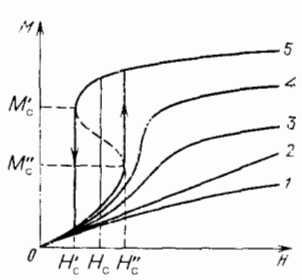

FIG. 2. Magnetization isotherms for an itinerant paramagnet ($A-\lambda>0$), described by Eq. (21).[9] 1($B>0$, $C>0$),2 ($B=0$, $C=0$)—no metamagnetic transition; 4 ($B<0$, $C>0$)—the critical case $(A-\lambda)C/B^2=9/20$; 5($B<0$, $C>0$)—metamagnetic behavior (the broken lines indicate the metastable states).

paramagnetic and ferromagnetic states, expressed in terms of $A-\lambda$, B, and C are given in Ref. 14:

$$M_c'^2 = -\frac{3B}{10C}\left\{1-\left[1-\frac{20}{9}\frac{(A-\lambda)C}{B^2}\right]^{1/2}\right\} \approx \frac{A-\lambda}{3B}, \tag{25}$$

$$M_c''^2 = -\frac{3B}{10C}\left\{1+\left[1-\frac{20}{9}\frac{(A-\lambda)C}{B^2}\right]^{1/2}\right\}, \tag{26}$$

$$H_c' = \frac{2}{5}\left[2(A-\lambda)+BM_c'^2\right]M_c' \approx \frac{2}{3\sqrt{3}}\left[\frac{(A-\lambda)^3}{|B|}\right]^{1/2}, \tag{27}$$

$$H_c'' = \frac{2}{5}\left[2(A-\lambda)+BM_c''^2\right]M_c'', \tag{28}$$

$$H_c \approx \left[\frac{7}{15}(A-\lambda)+\frac{3}{20}BM_c'^2\right]M_c' \approx \frac{5}{12\sqrt{3}}\left[\frac{(A-\lambda)^3}{|B|}\right]^{1/2}. \tag{29}$$

The formula presented are quite complicated, and it is difficult to analyze them completely. We point out only that (29) implies that the critical field of the transition into the metamagnetic state decreases as the paramagnetic susceptibility and the curvature of $N(\varepsilon)$ at the Fermi level increase.

It should be noted that in the model under study the first-order magnetic transitions induced by an applied field can also arise when the starting state is magnetically ordered $A(0)-\lambda<0$. These are transitions in a field from a weakly magnetic into a strongly magnetic state. As shown in Ref. 14 to describe such a transition the term $(D(T)/8)M^8$ must be included in the expansion of the free enegy (14). Then, if $B>0$, $C<0$, and $D>0$, for a definite ratio of the magnitudes of these coefficients this transition will be a first-order phase transition. The behavior of the magnetization of such a weakly ferromagnetic system in zero field is shown schematically in Fig. 3.

We note that the expansion (14) for the free energy of a weak itinerant magnet, from which, in particular, follows the phenomenon of itinerant metamagnetism, is analogous to the expansion of the free energy of a ferromagnet near the Curie temperature in Landau's theory of phase transitions, which describes both the magnetism of collectivized electrons and the magnetism of systems with localized moments. For this reason, if above the Curie temperature, when according to Landau's theory $A-\lambda>0$, because of the characteristics of the exchange interaction in a magnet with localized moments $B<0$, then in some range of temperature when the conditions (24) hold the transition in a field from the paramagnetic into the ferromagnetic state will be a first-order phase transition, i.e., phenomena analogous to itinerant metamagnetism are also possible in systems with localized moments.

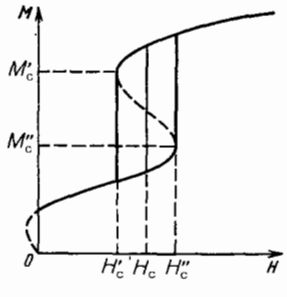

FIG. 3. Schematic dependence of the magnetization on the applied field for a weakly ferromagnetic system, undergoing a metamagnetic transition into the strongly ferromagnetic state in an external magnetic field.[9]

We call attention to the fact that ferromagnetism in a system of collectivized electrons is a threshold phenomenon: ferromagnetic ordering in such a system will occur only if the exchange interaction is strong enough for Stoner's condition to hold. This distinguishes qualitatively an itinerant magnet from a magnet with localized moments: according to Heisenberg's model ferromagnetism arises in a system of localized electrons even with a very weak exchange interaction (T_c in this model is proportional to the exchange parameter). For this reason, unlike itinerant magnets, a metamagnetic transition in a field from the paramagnetic into the ferromagnetic state almost always can occur only above 0 K.[3)]

2.4. Taking fluctuations into account

In the foregoing model we ignored the effect of fluctuations of the spin density on the properties of an itinerant paramagnet. It is well known, however, that in many cases spin-fluctuation mechanisms play a very large role, especially for systems with a strong energy dependence of the density of states $N(\varepsilon)$ near the Fermi energy.[10]

Different methods have now been developed for taking into account spin-fluctuation corrections for describing the magnetic properties of itinerant magnets,[4,9,16–19] but this falls outside the scope of this review. We shall examine the phenomenological approach, which enables understanding, at least qualitatively, the influence of spin fluctuations on the properties of an itinerant metamagnet.

When spin-fluctuation effects are ignored the magnetization can no longer be regarded as uniform over the volume and time-independent, and instead of the free energy (14) of an itinerant magnet the free energy density per unit volume $F(\mathbf{r})$ must be studied. Then the free energy of the magnet equals[9]

$$\mathcal{F} = \frac{1}{V}\int d^3\mathbf{r}F(\mathbf{r}) = \frac{1}{V}\int d^3\mathbf{r}\left[\frac{1}{2}(A(T)-\lambda)M^2(\mathbf{r}) + \frac{1}{4}B(T)M^4(\mathbf{r}) + \frac{1}{6}C(T)M^6(\mathbf{r}) + \ldots + \frac{1}{2}K|\nabla\mathbf{M}(\mathbf{r})|^2 + \ldots\right]; \tag{30}$$

here $\mathbf{M}(\mathbf{r}) = \mathbf{M}_0 + \delta\mathbf{M}(\mathbf{r})$, where $\mathbf{M}_0$ is the volume-averaged magnetization and $\delta\mathbf{M}(\mathbf{R})$ is the fluctuation of the spin density. The gradient term, describing the rate of change of the orientation of $\mathbf{M}(\mathbf{r})$ in space, causes the free energy to depend on the frequency of the fluctuations $\nu = 2\pi/q$ ($\mathbf{q}$ is the wave vector).

For relatively weak long-wavelength fluctuations (30) can be rewritten in the form[10]

$$\mathcal{F} \approx \frac{1}{V}\int d^3\mathbf{r}\left[\frac{A-\lambda}{2}M_0^2 + \frac{B}{4}M_0^4 + \ldots + \frac{A-\lambda}{2}(\delta\mathbf{M})^2 + \frac{B}{4}(\delta\mathbf{M})^4 + \frac{5}{6}BM_0^2(\delta\mathbf{M})^2 + \ldots + \frac{K}{2}(\nabla\delta\mathbf{M})^2\right]. \tag{31}$$

Introducing the statistical average $\xi^2_{i,q} = \langle \delta M_{i,q} \delta M_{i,-q} \rangle$ ($\delta M_{i,q}$ is the Fourier transform of $\delta \mathbf{M}_i$ ($i = x,y,z$), which is a function of the temperature, instead of the volume-average of $(\delta \mathbf{M})^2$ in (31) we obtain a new source for temperature and field dependences of the magnetization and susceptibility.

The equation of state of such a system is obtained by minimizing (31), and has the form of an expansion analogous to the one presented above for an itinerant magnet neglecting fluctuations (see formula (14))[9]:

$$H_i = (\tilde{A} - \lambda) M_i + \tilde{B} M_i^3 + \tilde{C} M_i^5, \qquad (32)$$

i.e., in this approximation the spin-fluctuation correction reduces to renormalization of the expansion coefficients in the equation of state (14):

$$\tilde{A} = A + \frac{5}{3}\left(B\xi^2 + \frac{7}{3} C\xi^4 + \ldots\right),$$
$$\tilde{B} = B + \frac{14}{3}\left(C\xi^2 + \frac{9}{2} D\xi^4 + \ldots\right),$$
$$\tilde{C} = C + 9(D\xi^2 + \ldots); \qquad (33)$$

here $\xi^2 = \sum_{i,q} \xi^2_{i,q}$ is the mean-square fluctuation of the magnetization, equal to[9]

$$\xi^2 = \frac{3}{2} \pi^{-2} k T q_m K^{-1} \{1 - q_m^{-1} (K\tilde{\chi})^{-1/2} \operatorname{th} [q_m (K\tilde{\chi})^{1/2}]\}, \qquad (34)$$

where q_m is the limiting wave vector, while $\tilde{\chi}(T) = (\tilde{A} - \lambda)^{-1}$ is the paramagnetic susceptibility taking into account fluctuations:

$$\tilde{\chi}(T) \approx \frac{\chi_p(T)}{1 - \lambda \chi_p(T)} \left(1 - \frac{1}{1 - \lambda \chi_p(T)} \frac{5}{3} B\xi^2\right). \qquad (35)$$

The foregoing theory shows that in an itinerant paramagnet the effect of fluctuations of the spin density becomes significant at high temperatures. However, in almost ferromagnetic systems, where the exchange enhancement coefficient $\lambda \chi_p(0)$ is close to unity fluctuations can play a large role in the formation of the magnetic properties also at comparatively low temperatures. This is true for itinerant metamagnets, which in most cases are almost ferromagnetic systems. Since in an itinerant metamagnet $B < 0$, the spin-fluctuation renormalization of the coefficients in the expansion of the free energy (14) increases the susceptibility and, therefore, decreases the critical field of the metamagnetic transition. In addition, fluctuation corrections can cause the criterion for itinerant metamagnetism to be satisfied above 0 K in systems where it does not hold at absolute zero.

3. METAMAGNETISM OF PARAMAGNETS IN AN EXTERNAL MAGNETIC FIELD: EXPERIMENTAL DATA AND BAND CALCULATIONS

3.1. Characteristic features of the paramagnetic behavior of itinerant metamagnets

Already in their earliest work[7] Wohlfarth and Rhodes formulated the conditions that enable prediction of metamagnetism of itinerant paramagnets from measurements in comparatively weak fields. These conditions essentially rest on the result of the theory of weak itinerant magnetism given above in Sec. 2, according to which in an itinerant metamagnet the coefficient B in the expansion of the free energy (14) is negative. As already pointed out, this condition implies that the susceptibility of an itinerant metamagnet in the paramagnetic state increases as the field increases (see the formula (22)). In addition, comparison of the formulas (3), (5), and (16) shows that if $B < 0$, the starting susceptibility should increase as the temperature increases from 0 K (and at higher temperatures passes through a maximum).

Starting precisely from these simple considerations, metallic palladium[7,20,21] and the intermetallic compound $TiBe_2$,[20] were proposed in the earliest works as "candidates" for itinerant metamagnets; both criteria were observed experimentally in them: the susceptibility increases when the field increases as well as when the temperature decreases. Attempts to observe a metamagnetic transition in these materials, however, have not been successful.

In palladium this is attributable primarily to the fact that based on theoretical estimates the field of the metamagnetic transition (1100 kOe according to Ref. 20 and 3220 kOe according to Ref. 21) is much stronger than the fields in which the magnetic properties of this metal were studied (up to 325 kOe[22]), and is hardly achievable at the present time.

The situation in $TiBe_2$ is more complicated. Measurements of the magnetization[23,24] show that in this compound a transition into the ferromagnetic state occurs in fields up to 200 kOe, but not in a jump-like fashion, as should happen with a metamagnetic transition, but rather gradually (as shown in curve 3 of Fig. 2). It would be possible to explain this on the basis of the theory of itinerant metamagnetism by the fact that the condition $B < 0$ is necessary but not sufficient for a metamagnetic transition and the relations (24), restricting the region of existence of metamagnetism, do not hold in $TiBe_2$.[4)]

The more important point, however, is that because of the lack of neutron-diffraction data the ground state of $TiBe_2$ cannot be definitely regarded as paramagnetic. In Ref. 25 the metamagnetic properties of this compound were interpreted starting from the assumption that it is an antiferromagnet with a Néel point of 10 K. Calculations of the band structure of $TiBe_2$ also do not give unique results.[26–28] The possibility of itinerant metamagnetism in $TiBe_2$ therefore requires further study.

The concept of itinerant metamagnetism is more useful for the analysis of the properties of the compounds $CoBe_2$ and RCo_2 (R = Y, Lu).[12,29–31] We shall examine below the metamagnetic transitions observed experimentally in the pseudobinary systems $Co(Se_{1-x}S_x)_2$, $Y(Co_{1-x}Al_x)_2$ and $Lu(Co_{1-x}Al_x)_2$.

3.2. Itinerant metamagnetism in the system $Co(Se_{1-x}S_x)_2$

The metamagnetism of collectivized electrons was apparently first observed experimentally in the metallic system of cobalt diselenide-dichalcogenide with a structure of the pyrite type: $Co(Se_{1-x}S_x)_2$.[32] In this system CoS_2 is a ferromagnet with a Curie temperature of 124 K and a saturation moment of $0.84\mu_B$ per cobalt atom.[33] When selenium is substituted for sulfur the phase transition into the ferromagnetic state becomes a first-order transition, and the transition temperature drops sharply to 0 K at $x = 0.85$ (Fig. 4). $CoSe_2$ does not exhibit spontaneous magnetization, its susceptibility passes through a maximum at approximately 40 K, and in the early papers this compound was regarded as an antiferromagnet.[34,35] For this reason, when the metamagnetic transition in mixed compounds $Co(Se_{1-x}S_x)_2$ was first observed in 1970[32] this transition was interpreted on the ba-

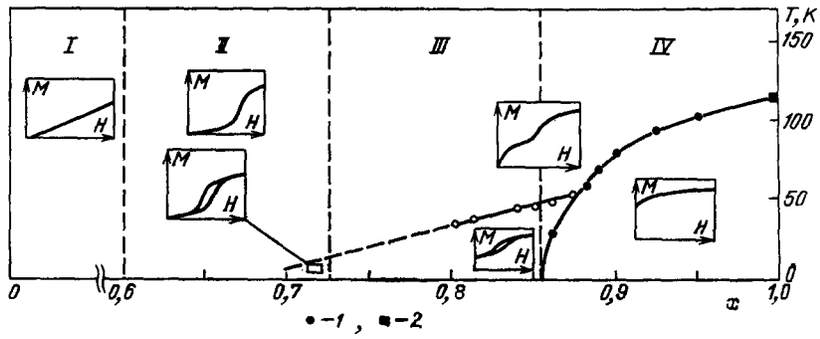

FIG. 4. The magnetic phase (x,T) diagram of the system $Co(Se_{1-x}S_x)_2$ based on the data of Refs. 38 and 42. I) Paramagnetic phase, II) paramagnetic phase with itinerant metamagnetism in an external field, III) weakly ferromagnetic phase, IV) strongly ferromagnetic phase. The dark symbols indicate the Curie temperatures (first-order transition (1) and second-order transition (2)), the light-colored circles indicate the temperature at which the form of the metamagnetic transition into the weakly ferromagnetic phase changes.

sis of the model of localized magnetic moments as a transition from the antiferromagnetic into the ferromagnetic state. In 1976, however, it was established by means of neutron-diffraction and NMR studies that both pure $CoSe_2$ and the selenium-rich mixed compounds are paramagnetic,[36] and it became obvious that a metamagnetic transition from the paramagnetic into the ferromagnetic state occurs in the mixed compositions $Co(Se_{1-x}S_x)_2$. The stimulated detailed theoretical and experimental studies of the compounds $Co(Se_{1-x}S_x)_2$.[37–44]

Figure 5 shows curves of the magnetization of the system $Co(Se_{1-x}S_x)_2$ ($x \geqslant 0.7$) at 4.2 K in fields up to 500 kOe. One can see that in an external magnetic field the paramagnetic compounds transform in a jump-like fashion into a magnetically ordered state. The field of this transition increases and the magnitude of the jump in the magnetization decreases as the selenium content increases, and the extrapolation performed in Ref. 42 showed that only compositions with $x \geqslant 0.6$ are metamagnetic, while composition with a higher selenium content are paramagnetic (see Fig. 5).

More careful studies[38,39] showed that the metamagnetic region of concentration contains compositions ($0.725 < x < 0.86$) in which metamagnetism is manifested against a small spontaneous background magnetization (inset in Fig. 6), i.e., ferromagnetism does not vanish abruptly at $x = 0.85$, rather there is a "tail" of spontaneous magnetization in the region of metamagnetism (see Fig. 6). The nature of this very weak magnetization is currently not fully understood. We feel that the conclusions drawn in Ref. 39, based on the results of neutron-diffraction and NMR studies, that this magnetization is associated with the magnetic inhomogeneity of the samples owing to the statistical effects of the local environment are very convincing. This is also indicated by the very high (of the order of 100 K) temperature of magnetic ordering of this weakly ferromagnetic phase and the very smeared character of the ferromagnetic ordering, which prevents a more accurate determination of the Curie temperature. The complete phase diagram of the system $Co(Se_{1-x}S_x)_2$ is shown in Fig. 4.

The itinerant model gives a convincing explanation of metamagnetism in the system $Co(Se_{1-x}S_x)_2$.[30,31,42] According to Asano's calculations of the band structure,[41,45] the Fermi level of CoS_2 lies near the peak in the density of states in the region where the curvature of $N(\varepsilon)$ is positive (see inset in Fig. 7). It is conjectured that the evolution of the magnetic properties in the system $Co(Se_{1-x}S_x)_2$ is determined by broadening of the 3d band as one transfers from CoS_2 to $CoSe_2$ (approximately by 30%) owing to the increase in the crystal lattice parameter (this broadening of the 3d band was recently observed experimentally by measurements of the optical reflection spectra of mixed compounds of this system[44]). As a result of this the value of $N(\varepsilon_F)$ decreases and there arises a situation in which itinerant magnetism is possible. To simplify the calculations performed in the Hartree-Fock approximation, it was assumed in Ref. 41 that the width of the 3d band is independent of the composition, and the effective Coulomb interaction integral

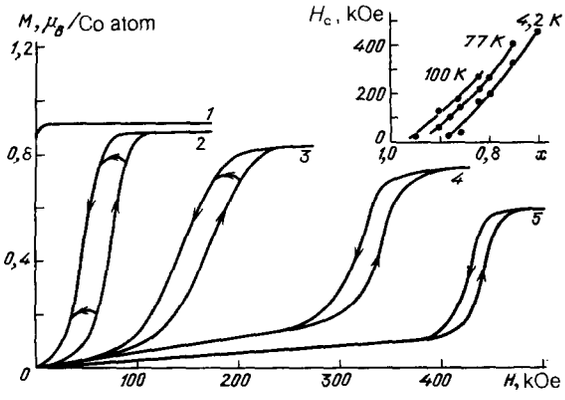

FIG. 5. Magnetization curves for $Co(Se_{1-x}S_x)_2$ at 4.2 K.[40] $x = 1.0(1)$, 0.86(2), 0.82(3), 0.75(4), and 0.70(5). The dependence $H_c(x)$ for different temperatures is shown in the inset.

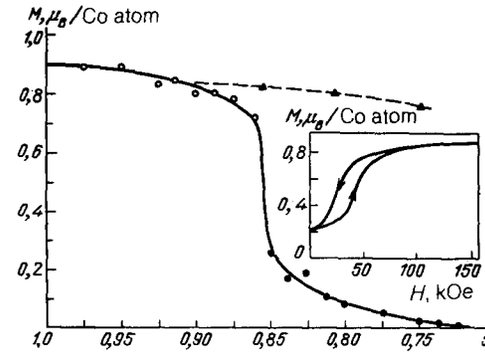

FIG. 6. Dependence of the spontaneous magnetization M_S (solid line) and the magnetization M_0 after the metamagnetic transition (broken curve) in the system $Co(Se_{1-x}S_x)_2$ on the sulfur content x at 4.2 K.[38,40] The magnetization curve for the compound $Co(Se_{0.163}S_{0.837})_2$ is shown in the inset.[38]

U was chosen as a parameter. Figure 7 shows the computed isotherms of the magnetization of the compounds $Co(Se_{1-x}S_x)_2$, whence one can see that in some interval of values of U/U_c (U_c is the critical value at which ferromagnetism appears) itinerant metamagnetism arises in them. The best agreement with experiment is obtained if it is assumed that for compositions with $x = 0.85$, 0.79, and 0.74 U/U_c equals 0.94, 0.92, and 0.91, respectively, while for U/U_c less than 0.9 metamagnetism vanishes.

Another important result obtained in Ref. 41 is that as the temperature increases spin fluctuation effects become significant. They cause the critical fields of the metamagnetic transition, observed in the system $Co(Se_{1-x}S_x)_2$, to be strongly temperature dependent, and they also enable explanation of the Curie-Weiss law for the paramagnetic susceptibility, observed in these compounds at high temperatures.

In spite of the convincing explanation of metamagnetism in the system $Co(Se_{1-x}S_x)_2$ in the itinerant model, it should be noted that quite successful attempts have been made to describe this phenomenon based on the model of localized moments, under the assumption that cobalt in paramagnetic compositions is in the nonmagnetic singlet ground state, while the first excited (triplet) state is magnetic and split from it by a narrow energy gap.[39] Although this model, in the opinion of Panissod *et al.*,[39] is not well founded and is hardly applicable to metallic systems, which $Co(Se,S)_2$ is, a more detailed analysis of this question is desirable.

In conclusion we point out that metamagnetic transitions, similar to those observed in the system $Co(Se_{1-x}S_x)_2$, have been observed in another mixed system with the structure of pyrite $Co_{1-x}Ni_xS_2$.[46] The situation here differs from the one described above, however, since both extreme compositions in this system are magnetically ordered (NiS_2 is an antiferromagnet), and the model of exchange-compensated paramagnetism of localized magnetic moments successfully describes the paramagnetism of mixed compositions and metamagnetic transitions in them.[34]

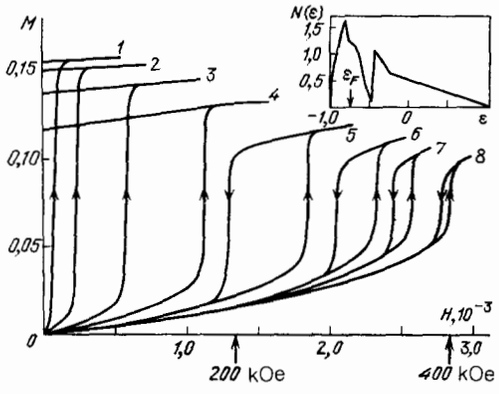

FIG. 7. Computed magnetization curves for the system $Co(Se_{1-x}S_x)_2$ (in relative units).[41] For different values of $U/U_c = 0.99(1)$, 0.98(2), 0.96(3), 0.94(4), 0.92(5), 0.91(6), 0.905(7), and 0.90(8). The schematic dependence $N(\varepsilon)$ for CoS_2 is shown in the inset.[45]

3.3. Itinerant metamagnetism in Laves phases $R(Co_{1-x}Al_x)_2$ (R=Y,Lu)

The next and, apparently, the last group of paramagnetic compounds in which metamagnetism of collectivized electrons has been observed in an applied magnetic field, are the compounds $R(Co,Al)_2$ (R = Y,Lu) with a cubic structure of the type observed in the Laves phase $MgCu_2$. Unlike the system $Co(Se_{1-x}S_x)_2$ described above, in which metamagnetism was first observed experimentally, and then later explained theoretically in the band model, the situation with the compounds $Y(Co,Al)_2$ and $Lu(Co,Al)_2$ was different: itinerant metamagnetism was predicted in them theoretically first, after which it was found experimentally.

The hypothesis that a transition in the field of exchange-enhanced itinerant paramagnets YCo_2 and $LuCo_2$ in a jump-like fashion into the ferromagnetic state is possible was first stated in Ref. 29, where it was established that these compounds exhibit the characteristic indications of itinerant metamagnets, pointed out by Wohlfarth and Rhodes[7]: their susceptibility increases as the temperature increases from absolute zero, and passes through a maximum at higher temperature (Fig. 8).[5)] The susceptibility also increases as the applied magnetic field is intensified.[51] Although the metamagnetic transition could not be observed experimentally in the fields studied (up to 380 kOe), the hypothesis that such a transition occurs in stronger fields turned out to be very fruitful in explaining the properties of magnetically ordered compounds RCo_2 with the magnetic rare earths[12,29] (we shall describe these studies below in Sec. 4).

The possibility of itinerant metamagnetism follows from the roughest qualitative analysis of the band structure of YCo_2 and $LuCo_2$.[12,52] The d band of these compounds is formed as a result of hybridization of the comparatively narrow (the width equals approximately 4 eV) low-energy 3d band of cobalt with a high density of states $N_{3d}(\varepsilon)$ near ε_F and the wider (the width equals approximately 7 eV) high-energy 5d (4d) band of Lu(Y) with a comparatively low density of states $N_{5d}(\varepsilon)$ ($N_{4d}(\varepsilon)$) near ε_F (Fig. 9a). The difference in the electronegativities of the elements formed (i.e., their Fermi levels) causes 5d(4d) electrons to be transferred into the unfilled 3d band. The total $n(\varepsilon)$ curve obtained contains a region with positive curvature $N''(\varepsilon) > 0$ (distinguished in Fig. 9a by the broken circle), and if the Fermi level lies in this region, then the case that we studied

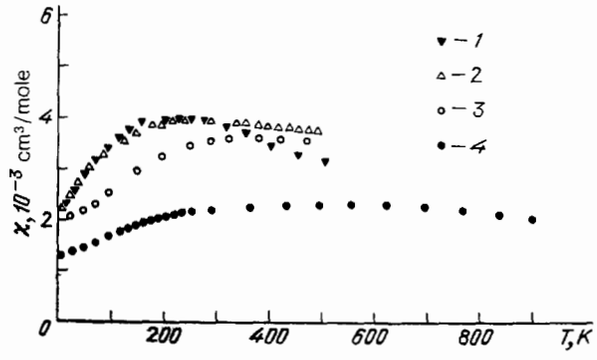

FIG. 8. The susceptibility of YCo_2(1)[47] and (2)[48], $LuCo_2$(3)[49] and $ScCo_2$(4)[50] as a function of the temperature.

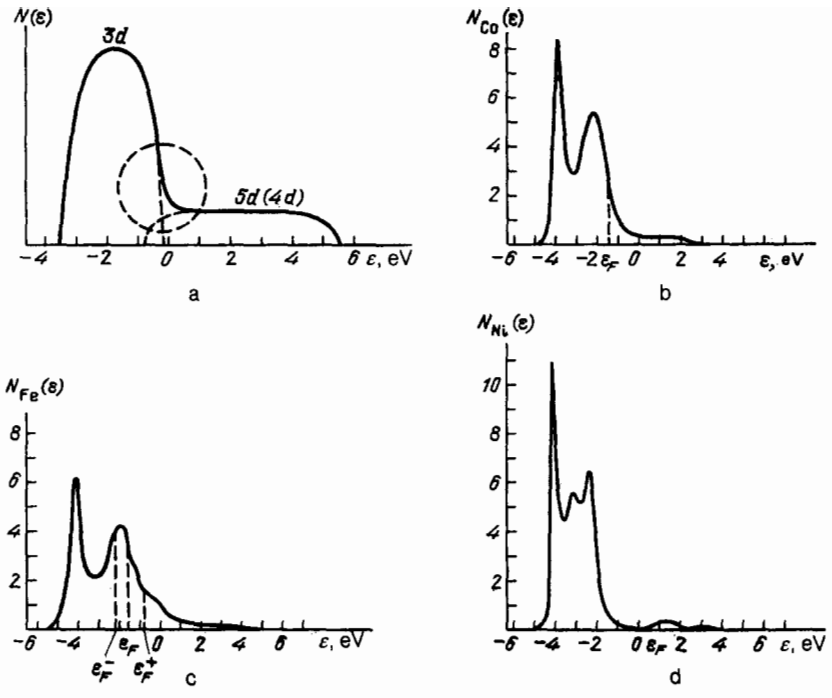

FIG. 9. (a) Hybridization of bands of the transition and rare-earth metals (R) in the RCo_2 compounds (the broken curve shows the region containing ε_F, satisfying the conditions of itinerant metamagnetism). b–d) Local density of states of d electrons of the YCo_2, YFe_2 and YNi_2 compounds, respectively.[12]

previously in Sec. 2 and shown in Fig. 1c is realized: in the applied magnetic field $N_-(\varepsilon_F)$ grows more strongly than $N_+(\varepsilon_F)$ decreases; the total density of states at the Fermi level $N(\varepsilon_F) = N_+(\varepsilon_F) + N_-(\varepsilon_F)$ increases and a transition into the ferromagnetic state is possible.

The density of states of the compound YCo_2 as well as the isostructural compounds YFe_2 and YNi_2 was first calculated by numerical methods in the tight-binding approximation in Ref. 12. To simplify the calculation Cyrot and Lavagna employed the same exchange parameter (4 eV) for all compounds. The number of d electrons contributed by cobalt, iron, and nickel atoms was assumed to be the same as in pure metals (8.3, 7, and 9.4 electrons per atom, respectively), while the number of d electrons per yttrium atom was assumed to equal 1.7. The dependences $N(\varepsilon)$ and positions of the Fermi level obtained for the three compounds studied are presented in Fig. 9b–d.

As one can see from Fig. 9b the Fermi level in YCo_2 lies on the decreasing section with positive curvature. The calculations show that the Stoner condition does not hold in YCo_2 ($IN(\varepsilon_F) = 0.85$), and this compound is an exchange-enhanced itinerant paramagnet. According to the calculations performed in Ref. 12, in YCo_2 the metamagnetic transition into the ferromagnetic state occurs in a field of 1000 kOe.

In YFe_2 the Fermi level lies near the peak of the density of states (Fig. 9c), Stoner's condition holds (the exchange-enhancement parameter $IN(\varepsilon_F) = 1.4$), and this compound, according to the calculations, is a ferromagnet with a moment of $1.48\mu_B$ per iron atom.

As one can see from Fig. 9d, the density of states at the Fermi level in YNi_2 is low (the exchange-enhancement parameter equals 0.033), and this compound is paramagnetic in the ground state.

The computed magnetic characteristics of YFe_2 and YNi_2 agree well with the experimental data; this confirms the conclusion, drawn in Ref. 29, that YCo_2 is an itinerant metamagnet.

We also call attention to the fact that the dependences $N(\varepsilon)$ of all three compounds are qualitatively analogous and the changes in the magnetic properties are determined primarily by the change in the degree of filling of the d band. This situation, as shown in Refs. 53 and 54, also occurs in intermetallides yttrium-3d-transition metal with a different stoichiometry. One can conclude from here that the rigid-band approximation is fully applicable for qualitative analysis of the magnetic properties of these compounds.

After Ref. 12 the calculations of the band structure of the compound YCo_2 were repeated many times by other authors using different, more accurate methods (taking into account the local density of states of 4d electrons of yttrium, the orbital contribution to the magnetic moment, etc.).[55–57] The energy dependences of the density of states, obtained in different calculations, agree qualitatively with the data of Ref. 12, presented in Fig. 9b, and they differ from one another only in details. It is important that all articles predict for YCo_2 a metamagnetic transition in a field from the paramagnetic into the ferromagnetic state, though the parameters of this transition obtained by the different authors differ very strongly (Table I).

The calculations of the band structure of exchange-enhanced paramagnets $LuCo_2$ and $ScCo_2$[58] indicate that their magnetic properties are similar to those of YCo_2, and they also predict a metamagnetic transition in strong magnetic fields (see Table I).

As follows from Table I, the theoretically expected fields of the metamagnetic transition from the paramagnetic into the ferromagnetic state in YCo_2, $LuCo_2$ and $ScCo_2$ in most estimates exceed 1000 kOe, and are obviously currently not achievable experimentally. According to the model of itinerant metamagnetism, presented above in Sec. 2, the critical field of the transition H_c can be lowered by increasing the density of states at the Fermi level (see formula (29)), and in so doing the paramagnetic susceptibility χ also increases. Since the Fermi level in YCo_2, $LuCo_2$,and $ScCo_2$

TABLE I. Computed values of the field of the metamagnetic transition H_c and the magnetization M_{Co} of the ferromagnetic state after the transition in the compounds RCo_2 (R = Y, Lu, Se).

Compound	H_c, kOe	M_{Co}, μ_B per Co atom
YCo_2	1000 [12]	1,0
	800 [52]	1.0
	3500 [55]	0.88
	1500 *) [58]	0.4
	900 [57]	0.38
$LuCo_2$	2000 *) [58]	0.4
$ScCo_2$	3000 [58]	Not evaluated

*)The metamagnetic transition into the ferromagnetic state is smooth and occurs without hysteresis.

lies on the descending section of the curve $N(\varepsilon)$, the density of states at the Fermi level can be increased by emptying the d band (if, in so doing, the rigid-band approximation holds).

The foregoing considerations motivated Aleksandryan *et al.*[59] to study the magnetic properties of the mixed intermetallides $Y(Co_{1-x}Al_x)_2$. It was conjectured that partial substitution of aluminum, with an unfilled 3d band (the electronic configuration is $3d^0$), for cobalt will decrease the density of d electrons and shift the Fermi level toward low energies with a high density of states. A superficially paradoxical phenomenon was thus expected: introduction of "nonmagnetic" aluminum into YCo_2 instead of the "magnetic" cobalt should intensify the magnetism.

Figure 10 shows the curves of the magnetization of compounds in the system $Y(Co_{1-x}Al_x)_2$ as a function of the field at 4.2 K in fields up to 450 kOe. One can see from the figure that in the fields studied YCo_2 and the composition with a low aluminum content $Y(Co_{0.95}Al_{0.05})_2$ remain in the paramagnetic state—their magnetization varies almost linearly with the field. The magnetization of compositions with a high aluminum content ($x \geqslant 0.075$) behaves differently: it increases sharply in some interval of fields—this indicates that a metamagnetic transition into the ferromagnetic state occurs in the field. As one can see from the inset in Fig. 10, as the temperature increases the region of the transition becomes smeared over a larger interval of fields with virtually no displacement.

In agreement with the foregoing considerations, as the aluminum content increases the susceptibility in the paramagnetic state increases, the metamagnetic transition shifts toward weak fields, and the region of the transition becomes wider. In the concentration interval $0.075 \leqslant x \leqslant 0.15$ the parameters of the metamagnetic transition (the fields at the start and end of the transition, the magnetization at the start and end of the transition, etc.) depend linearly on the aluminum concentration. This enabled Aleksandryan *et al.*[59] to "reconstruct" the magnetization curve for YCo_2 (shown by the broken curve in Fig. 10) by linear extrapolation. According to this extrapolation the metamagnetic transition in YCo_2 occurs in a jump-like fashion in a field of 660 kOe, and its moment in the ferromagnetic state equals $0.7\mu_B$ per cobalt atom. These parameters qualitatively agree with the results of band calculations (see Table I). Incidentally, the linear extrapolation is not theoretically well founded and other methods for extrapolating the experimental data can be employed. Thus in Ref. 60 the critical fields of $Y(Co_{1-x}Al_x)_2$ were extrapolated according to a power law and for YCo_2 the critical field $H_c = 1000$ kOe was obtained.

As we have already indicated, the paramagnetic susceptibility of $Y(Co_{1-x}Al_x)_2$ increases when aluminum is substituted for cobalt. It turned out that the inverse susceptibility at 4.2 K depends linearly on the concentration x and vanishes at $x = 0.13$; therefore compositions with $x \geqslant 0.13$ should be ferromagnetic. Indeed, as one can see from Fig. 10, the spontaneous magnetization of compounds with a high content of aluminum is of the order of 0.1–$0.3\mu_B$ per formula unit. We note that metamagnetic transitions are also observed in ferromagnetic compounds (see Fig. 10).

The ferromagnetic state in the system $Y(Co,Al)_2$ was studied in greater detail in Ref. 61. It was established that the Curie temperature and the spontaneous magnetization depend nonmonotonically on the aluminum concentration and pass through a maximum at $x = 0.15$. The properties of these compounds are described very well by Wohlfarth's model of weak itinerant ferromagnetism[13] (the dependence of the magnetization on the field in the entire region of existence of the ferromagnetic state obeys the Belov-Arrot relation $H/M = A + BM^2$, the ratio of the effective moment in

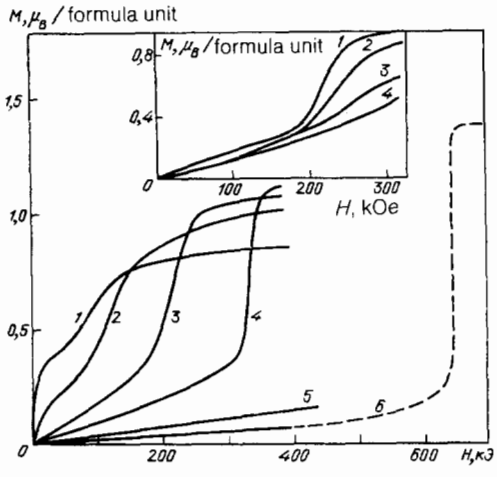

FIG. 10. Magnetization curves for the system $Y(Co_{1-x}Al_x)_2$ at 4.2 K.[59] $x = 0.15(1), 0.125(2), 0.10(3), 0.075(4), 0.05(5)$, and 0(6) (the broken curve represents an extrapolation). $M(H)$ for the compound with $x = 0.1$ at the temperatures (K) 4.2(1), 40(2), 60(3), and 80(4) is shown in the inset.

the paramagnetic state to the saturation moment in the ferromagnetic state is much greater than unity, etc.). Some features of the behavior of the ferromagnetic compounds of the system $Y(Co,Al)_2$ at high temperatures were explained on the basis of Moriya's theory of spin fluctuations.[62,63]

Figure 11 shows the magnetic phase diagram of the system $Y(Co,Al)_2$ in the entire region of existence of the cubic crystalline phase of $MgCo_2$ (the limiting concentration $x_{lim} = 0.2$), constructed from the data in Refs. 59 and 61.

The appearance of itinerant metamagnetism in the system $Lu(Co,Al)_2$[64] is in many ways reminiscent of the features observed in the system $Y(Co,Al)_2$. One can see from Fig. 12, which shows the magnetization curves for the compounds $Lu(Co,Al)_2$ at 4.2 K, that increasing the aluminum content leads to the appearance of ferromagnetic ordering; in addition, in some compounds metamagnetic transitions, smeared over a wide range of fields and occurring with hysteresis, are observed. Unlike the system with yttrium, in the lutecium system with a high aluminum content ($x \geqslant 0.1$) the magnetically ordered state becomes strongly magnetic: the magnetic moment reaches $0.55\mu_B$ per cobalt atom.

Figure 13 shows the magnetic phase diagram of the system $Lu(Co_{1-x}Al_x)_2$ (in the region of cubic compositions up to $x_{lim} = 0.2$). Compositions with $x \leqslant 0.07$ are paramagnetic; weak ferromagnetism with a metamagnetic transition in a field into the state of strong ferromagnetism is observed in compositions with $0.075 \leqslant x \leqslant 0.095$. We note that in the strongly magnetic state there is a region of concentrations ($0.1 \leqslant x \leqslant 0.12$) where the transition at the Curie point is a first-order phase transition, and in some temperature interval the paramagnetic and ferromagnetic phases coexist.

The foregoing discussion shows that itinerant metamagnetism in $Co(Se_{1-x}S_x)_2$, $Y(Co_{1-x}Al_x)_2$, and $Lu(Co_{1-x}Al_x)_2$ has many common features, which can be explained in the itinerant model. As x increases the exhange-enhancement factor increases, i.e., we approach the situation when Stoner's condition for itinerant ferromagnetism holds. At the same time the critical field of the metamagnetic transition shifts into the region of weaker, experimentally accessible, fields. In all systems the transition from paramagnetism to weak ferromagnetism is observed on substitution, and in mixed compounds based on $CoSe_2$ and $LuCo_2$ with a further change in the concentration x a strongly ferromagnetic state with a magnetic moment of 0.9 and $0.55\mu_B$ per cobalt atom, respectively, arises (in compounds based on YCo_2 the strongly ferromagnetic phase did not arise, probably because of the fact that the critical concentration at which it appears exceeds the limiting value $x_{lim} = 0.2$ for the existence of the critical cubic phase of $MgCu_2$ in $Y(Co_{1-x}Al_x)_2$).

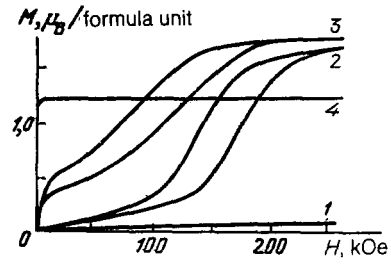

FIG. 12. Magnetization curves for the system $Lu(Co_{1-x}Al_x)_2$ at 4.2 K.[64] $x = 0(1), 0.05(2), 0.09(3)$, and $0.12(4)$.

The origin of first-order phase transitions at the Curie point, which are observed in compounds with large substitutions of the systems $Co(Se_{1-x}S_x)_2$ and $Lu(Co_{1-x}Al_x)_2$ (see Fig. 4 and 13), can be understood based on the theory of itinerant metamagnetism. Like in the case of metamagnetic compositions, the coefficient $B(T)$ in the expansion of the free energy (14) is negative in them.

The nature of the weakly ferromagnetic phase in the systems $Co(Se,S:)_2$ and $Lu(Co,Al)_2$ is apparently the same: it appears to be the "tail" of the strongly ferromagnetic phase, owing to effects of the local enivornment, leading to magnetic heterogeneity at low temperatures. This is indicated by the characteristics of the properties of this phase in both systems, such as the strong smearing of the ferromagnetic transformation, the high Curie temperature (of the order of the Curie temperature of the strongly ferromagnetic phase), etc.

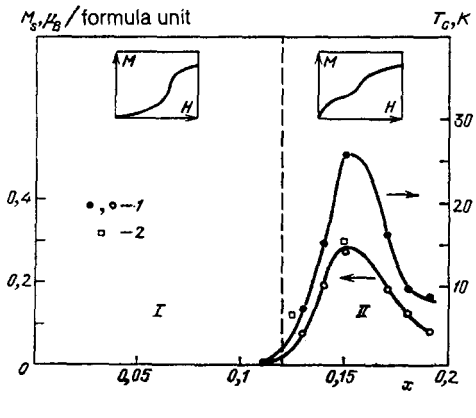

FIG. 11. Magnetic phase (x,T) diagram of the system $Y(Co_{1-x}Al_x)_2$ at 4.2 K based on the data of Ref. 61(1) and Ref. 59(2). The insets show the schematic form of the curves $M(H)$ in the paramagnetic phase with itinerant metamagnetism (I) and in a weakly ferromagnetic (II) phase.

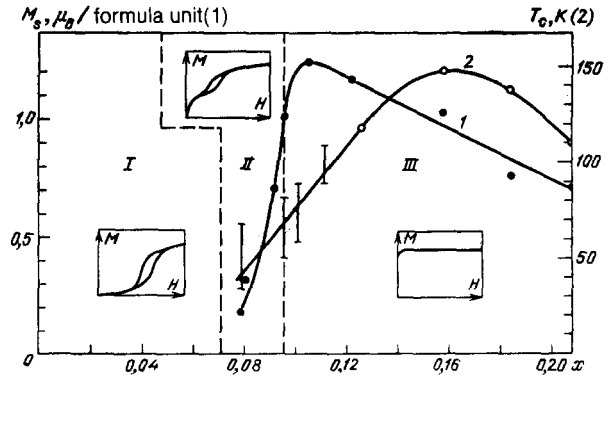

FIG. 13. Magnetic phase (x,T) diagram of the system $Lu(Co_{1-x}Al_x)_2$ at 4.2 K.[64] The insets show the schematic form of $M(H)$ in the paramagnetic phase with itinerant metamagnetism (I), weakly ferromagnetic (II) and strongly ferromagnetic (III) phases. The vertical solid and broken segments show the regions of coexistence of the magnetic and nonmagnetic phases near the temperature of magnetic ordering.

Conversely, according to Ref. 61, the weakly ferromagnetic state in the system $Y(Co,Al)_2$ can be described very well on the basis of the model of weak itinerant ferromagnetism, and the effects of magnetic heterogeneity are insignificant here. An analogous contribution could also possibly exist in the systems $Co(Se,S)_2$ and $Lu(Co,Al)_2$ in the region of the weakly ferromagnetic state, but it is masked by the contribution owing to the magnetic heterogeneity. In this connection, it would be very interesting to follow the change in the parameters of the weakly ferromagnetic phase of the systems studied as the conditions of synthesis and homogenizing annealing change.

We note that the nature of the appearance of itinerant metamagnetism in the systems studied is different. In the system $Co(Se,S)_2$ the number of d electrons remains constant. For this reason, the assumption that itinerant metamagnetism in $CoSe_2$ arises as the sulfur content increases owing to the narrowing of the 3d band (as a result of the increase in the cobalt-cobalt distances accompanying the substitution) and the resulting increase in the density of states at the Fermi level appears to be very well founded. The same mechanism is the chief mechanism for the decrease in the field of the metamagnetic transition. In the systems $Y(Co,Al)_2$ and $Lu(Co,Al)_2$ as the amount of the aluminum is increased the number of d electrons decreases, and this, as conjectured, increases the density of states at the Fermi level. In these systems, however, substitution with aluminum leads, in addition, to an increase in the volume of the unit cell (i.e., an increase in the cobalt-cobalt distance). For this reason, the mechanism of narrowing of the d band accompanying substitution could also increase $N(\varepsilon_F)$. It would be very interesting to separate the contributions of these mechanisms both experimentally, by studying the effect of other substitutions on the properties of YCo_2 and $LuCo_2$, and theoretically by calculating the band structure of the mixed compounds.

3.4. Thermally induced ferromagnetism in itinerant systems with a paramagnetic ground state

The phenomenon of thermally induced ferromagnetism in electronic systems that are paramagnetic at 0 K is closely related to the phenomenon of itinerant metamagnetism examined above.

The phenomenon of thermally induced ferromagnetism (first studied theoretically in Ref. 6 and then from a somewhat different point of view in Ref. 65) can be qualitatively understood based on the simplest considerations. In a system with a paramagnetic ground state the Stoner condition for itinerant ferromagnetism does not hold: $I(\varepsilon_F) < 1$. If the susceptibility increases as the temperature increases, then the system approaches one in which the Stoner condition does hold and at a temperature T_S, when $IN(\varepsilon_F) = 1$, the paramagnet transforms into the ferromagnetic state. Thus, in this state, ferromagnetism exists in a bounded temperature range from T_S up to the Curie point T_c.

Up to now thermally induced ferromagnetism has been observed experimentally in only one compound—the intermetallide Y_2Ni_7 (rhombohedral structure of the type Gd_2Co_7).[66,67] Figure 14 shows the temperature dependences of the spontaneous magnetization and the paramagnetic susceptibility of this compound. One can see that below the Curie temperature $T_c = 58$ K the magnetization increases,

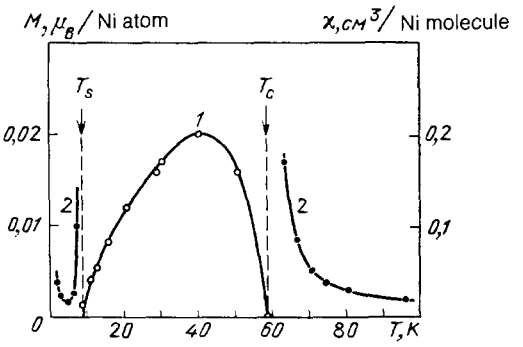

FIG. 14. Temperature behavior of the susceptibility (dark circles) and spontaneous magnetization (open circles) of Y_2Ni_7.[66]

passes through a maximum at 40 K and vanishes at $T_S = 7$ K. The absence of ferromagnetic ordering at lower temperatures as confirmed in Ref. 66 by means of experiments on depolarization of a neutron beam passing through the Y_2Ni_7 sample.

The possibility of thermally induced ferromagnetism in Y_2Ni_7 is confirmed by calculations of the band structure.[53] The Fermi level of the d band of this compound lies on the section where $N(\varepsilon_F)$ has a sharp, positive curvature. The thermal smearing of the Fermi surface increases the density of states at the Fermi level and, under certain conditions, causes Stoner's condition to hold.[53]

It should be noted, however, that Stoner's approximation, employed in the articles enumerated above in the discussion of thermally induced ferromagnetism, is rough, since at finite temperatures the role of spin fluctuations becomes important. Moriya[68] recently examined this phenomenon taking into account the long-wavelength spin fluctuations. He showed that such fluctuations impose much more stringent restrictions on the condition for the appearance of thermally induced ferromagnetism. Moriya also found, by comparing the experimental data with the theoretical relations, that in this model thermally induced ferromagnetism in Y_2Ni_7 can arise only if the curvature of $N(\varepsilon)$ at the Fermi levels is very strong and, apparently, unrealistic ($N'(\varepsilon_F)/N(\varepsilon_F) \approx N''(\varepsilon_F)/N(\varepsilon_F) \approx 4000$ eV^{-2}). It is possible that with the appearance of thermally induced ferromagnetism in this compound shorter wavelength antiferromagnetic modes of spin fluctuations play a significant role.[68]

The question of thermally induced ferromagnetism of itinerant systems requires further theoretical and experimental study.

4. METAMAGNETISM IN MULTISUBLATTICE MAGNETS

4.1. Itinerant metamagnetism in an effective field

We examined above the metamagnetic transitions in itinerant paramagnets. It follows from the results presented that in most cases in pure compounds the critical fields of these transitions are very high and itinerant metamagnetism can be observed only in a narrow interval of concentration in mixed compounds, by selecting their components so as to lower the transition field into an accessible range of magnetic fields.

Together with the most obvious, but, unfortunately, not easily accessible method, enabling expanding the range of materials in which itinerant magnetism can be studied—in-

creasing the intensity of the applied magnetic field, there also exists another, more effective, though not so obvious method—studying magnetically ordered multisublattice materials, one of whose subsystems exhibits the properties of an itinerant metamagnet.

Indeed, in multisublattice magnetically ordered magnets the itinerant subsystem is subjected to, in addition to the external field **H**, the internal molecular field $\mathbf{H}_M$, owing to the interaction with other magnetic subsystem, and the total effective field equals

$$\mathbf{H}_{eff} = \mathbf{H}_m + \mathbf{H}. \quad (36)$$

By varying (changing the composition or temperature) the value of H_M so that $H_M \approx h_c$ a metamagnetic transition can in principle be induced with a comparatively weak, experimentally achievable, external field. In addition, even if such a transition cannot be observed in an external magnetic field, the metamagnetic character of the itinerant subsystem strongly affects the magnetic properties of the multisublattice magnet, leading to a number of unusual phenomena.

Itinerant metamagnetism in an effective field has now been studied in great detail (possibly in even greater detail than metamagnetism of itinerant paramagnets) both theoretically and experimentally. We shall describe below the most salient manifestations of this phenomenon.

4.2. Laves phases of RCo_2 (R—a magnetic rare earth)

In these intermetallides, which are isostructural to the compounds YCo_2 and $LuCo_2$ described above, the itinerant d subsystem, formed by the 3d electrons of cobalt and the 5d electrons of the rare earth (in what follows, for brevity, we shall refer to it as the cobalt subsystem), is located in an internal field generated by the magnetic subsystem formed by the localized 4f electrons of the rare earth. If the d subsystem of the compounds RCo_2 (just like in YCo_2 and $LuCo_2$) is metamagnetic (this is apparently the case, at least for compounds with heavy rare earths[12]), then here the effects of itinerant metamagnetism in an internal effective field should be observed.

The magnetic properties of the compounds RCo_2 have been well studied by different methods.[69] At low temperatures, in these intermetallides both magnetic subsystems are ordered (with light rare earths the magnetic moments of the rare earth and cobalt are parallel, while with heavy rare earths they are antiparallel to one another). The main magnetic characteristics of these intermetallides are given in Table II.

The unusual experimental magnetic behavior of the compounds RCo_2 with heavy rare earths, which cannot be explained on the basis of the model of localized moments (the Bean-Rodbell model of strain-dependent exchange interaction,[81] theory of epamagnetism[82] etc.) and adequately described on the basis of the model of itinerant metamagnetism in an internal field, consists of the following. In $GdCo_2$ and $TbCo_2$, which have high Curie points, the transition into the magnetically ordered state is a second-order phase transition, as in the case of the usual ferro- and ferrimagnets—the magnetization varies smoothly in the course of the transition; however, in other compounds with heavy rare earths ($DyCo_2$, $HoCo_2$, $ErCo_2$, $TmCo_2$), whose Curie temperatures are lower, the magnetization at the point of magnetic ordering arises in a jump-like fashion—a first-order phase transition occurs (see the review in Ref. 69 and Table II). The magnetization curves of the compounds of the second group above the temperature of magnetic ordering have a metamagnetic character.[47,83] As an example, Fig. 15 shows the magnetization isotherms and the temperature dependence of the spontaneous magnetization of an $ErCo_2$ single crystal.[84]

We shall describe the characteristic features of the behavior of RCo_2 on the basis of the simplest theory, proposed in Ref. 29, where the possibility of a metamagnetic transition in the itinerant subsystem of a many sublattice magnet in an effective field was apparently first demonstrated.

We shall assume that the structure of the d band is the same in all RCo_2 and that among the exchange interactions

TABLE II. The basic magnetic characteristics of the compounds RCo_2.

R	M_s, μ_B per formula unit	M_{Co}, per Co atom	M_R, μ_B per R atom	T_c, K	Type of magnetic transition
Pr	3,0 [70] 3,5 [71]	0,3 [71]	2,9 [71]	46 [70] 34 [72]	Second-order
Nd	3,4 [70]			98 [72] 116 [73]	»
	3,1 [71]	0,2 [71]	2,7 [71]	115 [74] 211 [70]	»
Sm	1,5 [70]	0,5 [70]	0,5 [70]	204 [72] 395 [70]	
Gd	4,96 [70]	—1,02 [70]	7,0 [70]	405 [47] 398 [72] 237 [73]	»
Tb	6,25 [75] 6,65 [76]	—1,34 [73]	8,93 [76]	240 [75] 230 [74]	»
Dy	6,8 [70]	—1,0 [70]	8,8 [70]	135 [70] 140 [70]	First-order
Ho	7,5 [73]			74 [70]	»
	7,7 [78]	—1,0 [73]	9,5 [73]	87 [73] 78 [77]	
Er	6,9 [73]	—1,0 [73]	8,9 [73]	33 [70] 30 [72]	»
Tm	3,8 [80]	—0,8 [80]	5,4 [80]	4—7 [79] 4 [72]	»

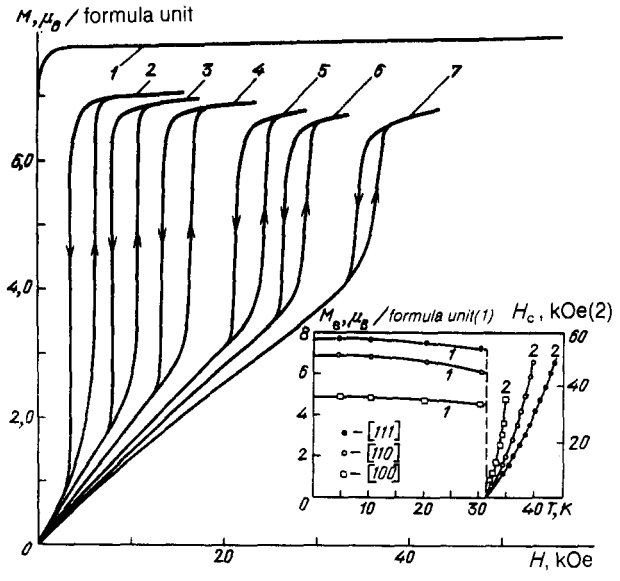

FIG. 15. Magnetization curves for an $ErCo_2$ single crystal along the [111] axis at different temperatures.[84] $T(K) = 4.2(1)$, 36.2(2), 34.1(3), 35.9(4), 38.0(5), 38.9(6) and 41.0(7). The inset shows the temperature dependence of the spontaneous magnetization M_S (1) and of the critical field of the metamagnetic transition H_c (2) along the [111], [110], and [100] axes. The vertical broken line shows the Curie temperature T_c.

only the interaction of the rare earth and cobalt is important, and we shall neglect the crystal field. Then the equation of state for the itinerant cobalt subsystem assumes a form analogous to that in Ref. 21:

$$(A-\lambda)M_d + BM_d^3 + CM_d^5 = H_{eff}, \qquad (37)$$

where M_d is the magnetization of the cobalt subsystem. The effective field H_{eff} is described by the formula (36), while the molecular field acting on the cobalt subsystem from the side of the rare earth is proportional to the magnetization of the rare-earth subsystem:

$$H_M = \lambda_{R\text{-}Co} M_R;$$

here the molecular-field coefficient $\lambda_{R\text{-}Co}$ can be expressed in terms of the exchange spin-spin interaction parameter $I_{R\text{-}Co}$, which is the same for the entire series of rare earths:

$$\lambda_{R\text{-}Co} = \frac{g_R - 1}{g_R} I_{R\text{-}Co}.$$

The magnetization of the rare-earth subsystem equals

$$M_R = g_R J_R \mu_B B_J\left[\frac{g_R J_R \mu_B}{kT}(\lambda_{R\text{-}Co} M_d + H)\right], \qquad (38)$$

where g_R is the g factor, and J_R is the total quantum number of the rare earth.

Expanding the right side of (37) in a series we find (with $H = 0$)

$$(A'-\lambda)M_d + B'M_d^3 + C'M_d^5 = 0, \qquad (39)$$

where

$$A' = A - (g_R\mu_B\lambda_{R\text{-}Co})^2 (kT)^{-1} J_R (J_R+1)\cdot\frac{1}{3},$$

$$B' = B + (g_R\mu_B\lambda_{R\text{-}Co})^4 (kT)^{-3}[(2J_R+1)^4 - 1]\cdot\frac{1}{720},$$

$$C' = C + (g_R\mu_B\lambda_{R\text{-}Co})^6 (kT)^{-5}[(2J_R+1)^6 - 1]\cdot\frac{1}{30240}. \qquad (40)$$

Thus the role of the rare-earth subsystem in this model reduces to the fact that it modifies the parameters of the expansion of the free energy A, B, C, describing the magnetism of the cobalt subsystem of the itinerant metamagnets YCo_2 and $LuCo_2$. At low temperatures the cobalt subsystem in RCo_2 with magnetic rare earths is magnetically ordered, and therefore $A' - \lambda < 0$ (we recall that $A - \lambda > 0$, since YCo_2 and $LuCo_2$ are paramagnets). The character of the transition into the magnetically ordered state, as already pointed out (see Sec. 2.3), depends on the sign of B'. If $B'(T_c) > 0$, then this transition is a second-order phase transition and the Curie temperature is determined from the formula (19). Taking into account (40), it can be represented in the form

$$T_c = \frac{I_{R\text{-}Co}^2}{\mu_B^2}\chi(T_c)(g_R - 1)^2 J_R, \qquad (41)$$

where χ is the exchange-enhanced susceptibility of the cobalt subsystem. If $B'(T_c) < 0$, then the transition into the magnetically ordered state becomes a first-order phase transition and the Curie temperature is determined from the formula (20). It can be expressed approximately in terms of the parameters of the metamagnetic transition of the cobalt subsystem H_c and M_c in the form[12]

$$T_c \approx \frac{I_{R\text{-}Co}^2 (g_R-1)^2 J_R (J_R+1) M_K(T_c)}{6k\mu_B^2 H_K(T_c)} \times\left[1 - \frac{3\mu_B^2 H_K(T_c)[(2J_R+1)^4 - 1]}{20 I_{R\text{-}Co}^2 (g_R-1)^2 J_R^3 (J_R+1)^3}\right]. \qquad (42)$$

The different character of the magnetic transformation in the compounds RCo_2 (a second-order transition in $GdCo_2$ and $TbCo_2$ and a first-order transition in $DyCo_2$, $HoCo_2$, $ErCo_2$, $TmCo_2$ is caused by the fact that the sign of B' is a function of the temperature. This behavior is fully understandable physically: as the temperature is increased, thermal effects, leading to "smearing" of the Fermi level, increase (in other words, states above the Fermi level are populated), and the metamagnetic character of the magnetization of the cobalt subsystem vanishes. This interpretation is confirmed by the experimental data for YCo_2 and $LuCo_2$: a change in the sign of the coefficient B as a result of thermal effects leads to a decrease in the susceptibility of these compounds at high temperatures (see Fig. 8).

The theory developed explains in a natural manner the experimentally observed metamagnetism of RCo_2 above the temperature of the first-order phase transition into the magnetically ordered state, whose nature is the same as in itinerant paramagnets. In this case, however, the cobalt subsystem is subjected to, in addition to the external field, the internal field owing to the magnetized rare-earth subsystem.

In addition to calculations, the metamagnetism of the cobalt subsystem in RCo_2 is confirmed by neutron-diffraction studies of the magnetic moment of cobalt in $TmCo_2$ and $HoCo_2$ at different temperatures[80] (Fig. 16a). One can see from the figure than increasing the internal field of the rare-earth subsystem acting on the cobalt subsystem (in these experiments the change in the internal field is determined by the temperature dependence of the magnetization of the rare-earth subsystem (see Ref. 36)), causes the magnetic moment of this subsystem to grow in a nonlinear fashion.

The metamagnetic character of the magnetization of the cobalt subsystem is also indicated by the dependence of

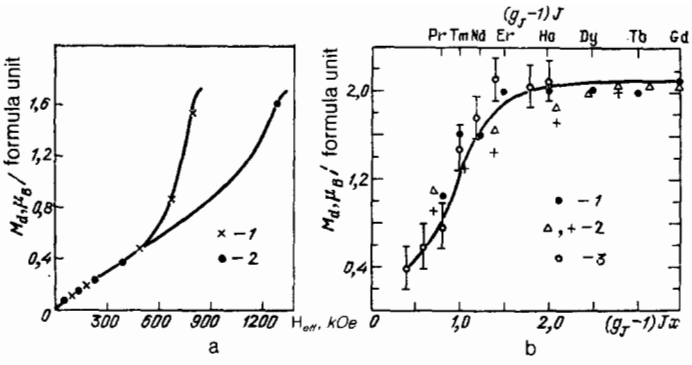

FIG. 16. The magnetization of the cobalt subsystem in RCo_2 as a function of the effective field. a) neutron diffraction data for $TmCo_2(1)$ and $HoCo_2(2)$.[80] b) magnetic data for $RCo_2(1)$, and the systems $Gd_{1-x}Y_xCo_2(2)$ and $Ho_{1-x}Y_xCo_2(3)$.[85]

its magnetic moment in different RCo_2 on the parameter $(g_R - 1)J_R$, characterizing, according to (37), the internal field acting on this subsystem (Fig. 16b). We call attention to the fact that the magnetic moment of ferromagnetic cobalt in RCo_2 equals $\sim 1\mu_B$ per atom and is approximately twice the moment of cobalt in the ferromagnetic state in YCo_2 and $LuCo_2$, as found experimentally (see Fig. 10 and 12) and computed theoretically (see Table I), though the parameters of the paramagnetic d band in both groups of compounds are identical.[56] This difference is caused by the roughness of the model employed, in which it was assumed that the exchange field in RCo_2 affects the band structure just like the external field: it shifts the subbands with + and − spins relative to one another as a whole. The fact that the exchange interaction modifies the atomic potential of cobalt must also be taken into account. This leads to the fact that when the subbands are shifted in the exchange field they are deformed, which increases the magnetic moment of the cobalt subsystem.

The nonlinear dependence of the magnetization of the itinerant subsystem in the exchange field generated by the rare-earth moments has also been observed in the system $(Gd_{1-x}Y_x)Co_3$.[86] According to the latest studies the compound Y_4Co_3 (because of the existence of a narrow region of homogeneity its formula is sometimes written in the form Y_9Co_7) is an itinerant paramagnet.[87] When gadolinium is substituted for yttrium in the system $(Gd_{1-x}Y_x)Co_3$ ferrimagnetic ordering arises (the moments of the gadolinium and cobalt subsystems are antiparallel), and in addition the magnetic moment of cobalt increases sharply from $0.1\mu_B$ to $0.6\mu_B$ for gadolinium concentrations ranging from 70 to 100 at. %. Thus the dependence of the magnetic moment of cobalt on the gadolinium concentration and therefore also on the internal field acting on the cobalt subsystem is nonlinear and qualitatively analogous to the dependence $M_d(H)$ for RCo_2, shown in Fig. 16b. It is possible that the cobalt subsystem in the system $(Gd_{1-x}Y_x)_4Co_3$ is also metamagnetic.

Important experimental data, confirming the model of itinerant metamagnetism of d electrons in RCo_2, were obtained for mixed compounds $Tb_{1-x}Y_xCo_2$ and $Er_{1-x}Y_xCo_2$.[89-91]

Studies of the first system $Tb_{1-x}Y_xCo_2$ enable checking the theoretical idea that the change in the nature of the transition into the magnetically ordered state is associated with the influence of thermal effects on the parameters of the d band. If this is true, then, reducing the terbium content in the mixed compounds, thereby shifting the point of the magnetic transition to lower temperatures, would change the transition from a second-order transition, as in $TbCo_2$, to a first-order transition. Indeed, the results of Refs. 89 and 91 confirm this: changing the composition from $x = 0.5$ to $x = 0.6$ changes the character of the magnetovolume anomaly as well as the character of the temperature behavior of the starting susceptibility near T_c (Fig. 17). The magnetovolume anomaly of the first composition ($x = 0.5$), as in other terbium-rich compounds, increases smoothly as the temperature is lowered, as should happen with a second-order phase transition. In the composition with $x = 0.6$ the magnetovolume anomaly changes more sharply in a small temperature interval, which is characteristic for "smeared" first-order phase transitions. This smearing is caused by the statistical distribution of ytterbium and terbium atoms in mixed compounds, as a result of which magnetic heterogeneity arises[89] (an analogous mechanism was discussed above when we studied the characteristics of the magnetic properties of mixed systems $Co(Se,S)_2$ and $Lu(Co,Al)_2$).

Studies of the system $Er_{1-x}Y_xCo_2$[91] pursued an analogous goal: to show that the first-order phase transition in RCo_2 compounds is determined by the state of the cobalt subsystem. According to ideas about itinerant metamagnetism the change in the type of transition from first- to second-order in compositions of the system $Er_{1-x}Y_xCo_2$ will occur owing to the substitution-induced reduction of the molecular field, when the condition $H_M < H_c$ holds (i.e., at 0 K the cobalt subsystem is in the paramagnetic state). The

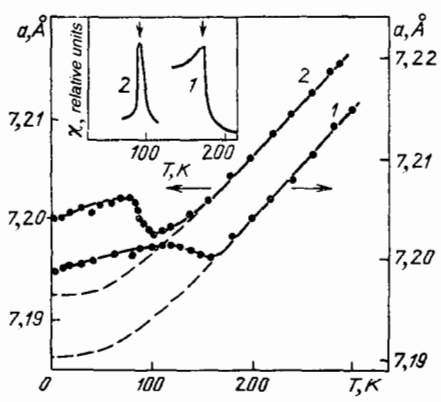

FIG. 17. Temperature dependence of the lattice parameter of the compounds $Tb_{0.5}Y_{0.5}C_{02}$ (1) and $Tb_{0.4}Y_{0.6}Co_2(2)$.[89] The inset shows $\chi(T)$ for the same compounds.

change in the type of transition should lead to anomalies in the concentration dependences of different magnetic parameters. In Fig. 18 the experimental changes in T_c, the magnetovolume anomaly, and the anisotropic-magnetostriction constants as a function of the yttrium content in the system $Er_{1-x}Y_xCo_2$ at 5.5 K are compared with the changes computed theoretically on the basis of a somewhat improved theory[91] (exchange within the rare-earth subsystem was taken into account together with the rare-earth–cobalt exchange). One can see that indeed as the erbium content is reduced to $x = 0.3$ the transition into the ferromagnetic state becomes a second-order phase transition, and at this concentration anomalies appear in the dependences of different magnetic characteristics on x. The theoretical dependences describe these anomalies at least qualitatively.

Thus far we have discussed the manifestations of the metamagnetism of the cobalt subsystem in RCo_2 in the internal field acting on this subsystem from the side of the rare-earth subsystem. Meanwhile it is possible, in principle, to transfer the cobalt subsystem in these compounds from the ferromagnetic into the paramagnetic state by means of an external field (we recall that in RCo_2 with heavy rare earths of the magnetic moment of the cobalt subsystem is antiparallel to the moment of the rare-earth subsystem, and therefore, to the field also). Until recently such phenomena were not observed. This is largely attributable to the experimental difficulty of performing measurements in strong magnetic fields, of weak magnetizations, owing to the change in the magnetic moment of the cobalt subsystem, against the background of the high magnetization of RCo_2. In addition, in polycrystalline samples of the compounds RCo_2 with anisotropic rare earths the transition of the cobalt subsystem into the unmagnetized state should be "smeared" over some interval of fields, owing to the anisotropy of H_c along different crystallographic directions (such an anisotropy is indicated by the experimental data on the metamagnetic transitions above T_c in $ErCo_2$[84]). In spite of these difficulties, it was possible to observe the growth of magnetostriction of a textured sample of $Er_{0.7}Y_{0.3}Co_2$ in strong magnetic fields,[91] which is interpreted as being caused by the metamagnetic transition of the cobalt subsystem from the ferro- into the paramagnetic state.

4.3. Systems based on $ThCo_5$ and $CeCo_5$

Another group of compounds in which the metamagnetism of itinerant d subsystem can be observed because of the action of the internal molecular field are the intermetallides based on $ThCo_5$ and $CeCo_5$, in which the 6d and 5d bands of the quadrivalent thorium and cerium, respectively, are hybridized with the 3d band of cobalt.[92]

In RCo_2 the localized moments of the rare-earth subsystem act on the itinerant metamagnetic subsystem, whereas in the intermetallic compounds $ThCo_5$ and $CeCo_5$ both the metamagnetic and the magnetizing magnetic subsystems, consisting of cobalt atoms occupying two nonequivalent 3g and 2c positions of the hexagonal crystalline structure of the $CaCu_5$ type, are itinerant. The magnetic moments M_{3g} and M_{2c} of these subsystems are parallel to one another.[93]

An important point for us is the existence of a significant region of homogeneity in $ThCo_5$: some of the thorium atoms can be replaced by "dumbbells" consisting of two cobalt atoms and, correspondingly, the general formula for $ThCo_5$ can be represented in the form $Th_{1-\delta}Co_{5+2\delta}$, where $0 \leqslant \delta \leqslant 0.09$.[94] Thus by varying the cobalt concentration in the region of homogeneity it is possible to change the magnitude of the molecular field acting on the 3g and 2c cobalt subsystems (and, in part, on the parameters of the d bands).

As experiments show,[92,93] in the entire region of homogeneity of $Th_{1-\delta}Co_{5+2\delta}$ for the cobalt 2c subsystem in the intrinsic internal field the Stoner condition holds—this subsystem is ferromagnetic. For the 3g metamagnetic cobalt subsystem Stoner's condition in the intrinsic field does not hold, and the state of the subsystem depends on the magnitude of the exchange interaction between the 2c and 3g subsystems, and changes as the stoichiometry changes. For this reason, the magnetic behavior of the compounds $Th_{1-\delta}Co_{5+2\delta}$ depends strongly on x.

Figure 19 shows the magnetization isotherms of the three typical compositions of the system $Th_{1-\delta}Co_{5+2\delta}$,

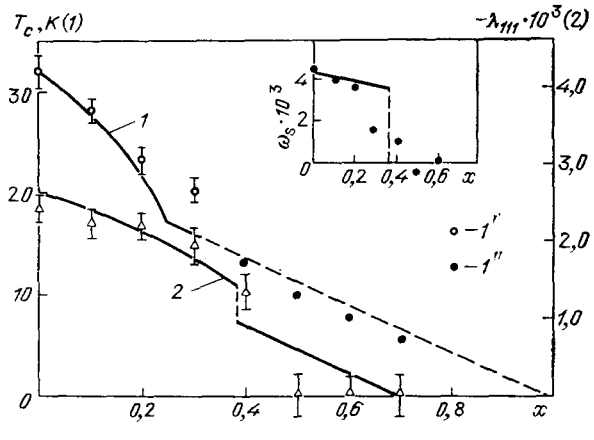

FIG. 18. Concentration dependences of some magnetic characteristics of the system $Er_{1-x}Y_xCo_2$.[91] 1) T_c (1' is a first-order phase transition, 1" is a second-order phase transition), 2) anisotropic magnetostriction constant λ_{111}. The inset shows the magnetovolume anomaly $\omega_S = \Delta V/V$. The solid and broken lines show the theoretical calculations.

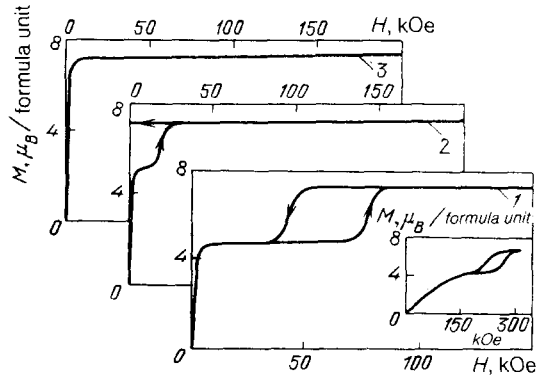

FIG. 19. Magnetization curves for the compounds $Th_{1-\delta}Co_{5+2\delta}$ at 4.2 K.[92] $\delta = 0.035(1)$, 0.04(2), and 0.05(3). The inset shows $M(H)$ for the compound with $\delta = 0.035$ along the difficult magnetization axis.[95]

measured at 4.2 K on single crystals along the direction of easy magnetization (the hexagonal axis of the crystal).[92] One can see that the spontaneous magnetization of the compound with a large excess of cobalt ($\delta = 0.05$) is significantly higher than in the two other compounds: the molecular field H_M, acting on the 3g subsystem of this compound, is stronger than the critical metamagnetic-transition field H_c, and the 3g subsystem is ferromagnetic. For compounds with $\delta = 0.04$ and $\delta = 0.35$ $H_M < H_c$ and the 3g subsystem is paramagnetic. This interpretation is confirmed by the evolution of the magnetization of compounds with $\delta = 0.035$ and 0.04 in a field: as the field increases their magnetization increases in a jump-like fashion; this is attributable to the transition of the 3g subsystem in a field from the paramagnetic into the ferromagnetic state. The transition occurs with hysteresis, and in the compound with $\delta = 0.04$ the 3g subsystem remains in the ferromagnetic state when the field is removed. This picture has been directly confirmed experimentally in experiments on the study of the magnetic structure of the compound $\delta = 0.035$ by the neutron-diffraction method in an external magnetic field.[96] It was shown that the magnetic moment of the 3g subsystem primarily increases in a field.

We call attention to the fact that in the $ThCo_5$ compounds there is a large anisotropy of the field of the metamagnetic transition along different directions (see inset in Fig. 19, where the magnetization curve for the compound with $\delta = 0.035$ in the direction of difficult magnetization in the basal plane of the crystal is shown).[95] The strong increase of the critical field of the metamagnetic transition in the direction of difficult magnetization is linked, as shown in Ref. 95, with the significant magnetic anisotropy in the cobalt 3g subsystem.

Since the magnetic moments of the 2c and 3g subsystems in $ThCo_5$ are parallel, an external field always increases the effective field acting on the metamagnetic 3g subsystem. Effects determined by the decrease in the internal field can be observed on the temperature dependences of the spontaneous magnetization of the $Th_{1-\delta}Co_{5+2\delta}$ compounds.[92] Since the magnetization of the 2c subsystem increases as the temperature increases, at some temperature in the compound with $\delta = 0.05$ H_M, acting on the 3g subsystem, becomes less than H_c. This leads to a transition of the 3g subsystem into the paramagnetic state and a jump-like decrease in the magnetization of the compound with $\delta = 0.05$ to a magnitude close to the magnetization of the other two compounds.

In the system $Ce_{1-\delta}Co_{5+2\delta}$ it was expected that the composition dependence of the magnetic properties would, in principle, be analogous to that studied above in $Th_{1-x}Co_{5+2\delta}$ (quadrivalent cerium, like quadrivalent thorium, is nonmagnetic). It turned out, however, that in $CeCo_5$ both magnetic subsystems are in the ferromagnetic state in the entire region of existence of a crystalline structure of the $CaCu_5$ type (the difference between the two systems is attributable to the fact that the 5d electrons of cerium are more localized than the 6d electrons of thorium, so that the density of states near ε_F is higher in $CeCo_5$). Nevertheless the characteristics of the d band in $ThCo_5$ are preserved in $CeCo_5$. This follows from studies of the mixed compounds $Ce(Co_{1-x}Ni_x)_5$.[92]: increasing the nickel content sharply reduces the magnetization, and in addition in the compound with $x = 0.075$ a metamagnetic transition, qualitatively analogous to the transition observed in the system $Th_{1-\delta}Co_{5+2\delta}$, is observed. The evolution of the properties of $Ce(Co_{1-x}Ni_x)_5$ can be understood by assuming that, as the content of nickel (which is nonmagnetic in 1:5 compounds[97]) increases, the 3g cobalt subsystem transforms from the ferromagnetic into the paramagnetic state, while in the compound with $x = 0.075$ the opposite transition occurs in an external magnetic field.

The result presented demonstrate the metamagnetic character of the magnetization of the d-band subsystem in $ThCo_5$ and $CeCo_5$. The structure of this band in $ThCo_5$ and $CeCo_5$ as well as in the isostructural rare-earth compounds RCo_5 is described by the qualitative scheme shown in Fig. 9a.[92] Within the framework of the rigid band the difference in the magnetic properties of compounds from these two groups ($ThCo_5$ and $CeCo_5$, on the one hand, and RCo_5 on the other) is caused by the fact that in RCo_5 with trivalent rare earths the Fermi level of the d band lies in the region of the maximum of the density of states, so that the d subsystem in these compounds is ferromagnetic. In $ThCo_5$ and $CeCo_5$ with quadrivalent thorium and cerium, respectively, the presence of one additional 6d (5d) electron shifts the Fermi level of the d band into the region of higher energies with low density of states and with a high positive curvature of $N(\varepsilon)$ (the broken circle in Fig. 9a), which encourages the appearance of itinerant metamagnetism.[12,92]

Unfortunately, at the present time this qualitative picture has not been confirmed by quantitative calculations of the band structure of $ThCo_5$ and $CeCo_5$. For this reason, the roles of different mechanisms in the formation of the magnetic properties of these compounds have not been completely determined.

4.4. Some other cases of itinerant metamagnetism in an effective field

As one can see from the foregoing discussion, itinerant metamagnetism is most conveniently studied in cobalt compounds, although this phenomenon can also be observed in compounds of other 3d transition metals. In this section we shall examine some other systems, where metamagnetism is linked not only with cobalt, but also with nickel or iron.

4.4.1. The intermetallides Y_2Ni_{17}

These compounds have much in common with the system $ThCo_5$ described above. In the hexagonal crystalline structure of Y_2Ni_{17} (of the Th_2Ni_{17} type) pairs of nickel atoms in one of four nonequivalent sites (4f) can be replaced by yttrium atoms, and this gives rise to a region of homogeneity (the general formula is $Y_{2+x}Ni_{17-2x}$).

The compounds $Y_{2+x}Ni_{17-2x}$ are ferromagnetic at low temperatures, and their magnetic properties depend strongly on the amount of excess yttrium.[98] Thus as x increases from 0 to 0.36 the spontaneous magnetization decreases from 0.25 to 0.15 μ_B per nickel atom, and the Curie temperature drops from 150 to 120 K.

In a compound with an intermediate yttrium concentration ($x = 0.16$) at low temperatures the magnetization is observed to increase in strong fields, which is reminiscent of the analogous phenomenon in $ThCo_5$ and, especially, in $Ce(Co,Ni)_5$ at a metamagnetic transition (Fig. 20).

A significant confirmation of the proposition of Ref. 98 that Y_2Ni_{17} is an itinerant metamagnet are the results of

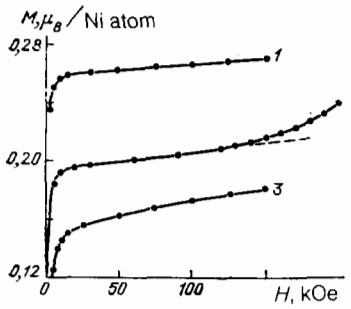

FIG. 20. Magnetization curves for the compounds Y_2Ni_{17}(1), $Y_{2.17}Ni_{16.66}$ (2) and $Y_{2.36}Ni_{16.28}$ (3) at 4.2 K.

calculations of the band structure of the intermetallides Y_2Ni_{17}.[53] According to these calculations the Fermi level of the d band of compounds of the type Y_2Ni_{17} lies near the peak in the density of states as a function of energy. This peak is determined, primarily, by the local density of states of nickel in the 4f positions, and therefore the substitution of yttrium for nickel in these positions, which decreases the local density of states and therefore the density of states at the Fermi level, strongly affects the magnetic properties. It follows from Ref. 53 that in the stoichiometric compound Y_2Ni_{17} one stable ferromagnetic state with a moment 0.29 μ_B per nickel atom is possible. In $Y_{2.17}Ni_{16.33}$ together with the weakly ferromagnetic ground state (with a moment of 0.18 μ_B per nickel atom) there is one other state, corresponding to minimum energy, with a large magnetic moment (0.26μ_B per nickel atom), separated from the ground state by a low energy barrier.

The imposition of an external magnetic field transfers the system from a weakly magnetic into a strongly magnetic state.

4.4.2. The system $Sc_{1-x}Ti_xFe_2$

In compounds of this system, in a narrow region of homogeneity near $x = 0.65$ below the Curie point (360 K), as the temperature is lowered to 70 K a transition arises from the weakly ferromagnetic into the strongly ferromagnetic state (the iron moment increases in a jump-like fashion from 0.9 to 1.3μ_B), while somewhat above the transition temperature the strongly ferromagnetic state can be induced by an external field,[9] i.e., the behavior of $Sc_{1-x}Ti_xFe_2$ is qualitatively analogous to that of $Th_{1-\delta}Co_{5+2\delta}$.

The results obtained were analyzed in Ref. 100 on the basis of the spin-fluctuation theory, and it was shown that the transition into the strongly magnetic state is accompanied by an increase in the degree of localization of the d electrons, though the nature of the magnetic phase transition was not established in this work. Based on the most qualitative considerations the structure of the d band of $Sc_{1-x}Ti_xFe_2$, formed by the 3d electrons of iron and titanium, as well as the 4d electrons of scandium, should have the form shown in Fig. 9a. Taking into account the fact that in the crystalline structure of $Sc_{1-x}Ti_xFe_2$ (hexagonal of the $MgZn_2$ type) there are two types of nonequivalent sites for iron atoms (6h and 2a), it is very likely that one of the magnetic subsystems manifests itinerant metamagnetism in an effective field. However the question of itinerant metamagnetism in (Sc, Ti)Fe_2 must be regarded as open until calculations of the band structure of these compounds are performed and the manner in which the magnetic moments of both subsystems change with a transition into the strongly ferromagnetic state is established experimentally (for example, by means of neutron diffraction).

4.4.3. The hydrides YCo_3H_x and $Y_2Co_7H_x$

A sharp change in the parameters of the d band of transition metal compounds can be achieved by hydrating them. First of all, hydration narrows the d band and increases $N(\varepsilon_F)$ owing to an increase in the interatomic distances. In addition, the 1s electron of hydrogen can appear as a donor or acceptor for the d band and shift ε_F along the curve $N(\varepsilon)$. In materials in which the energy dependence $N(\varepsilon)$ is sharp this leads to a significant change in the density of states at the Fermi level and, under certain conditions, can give rise to the appearance of metamagnetic properties.

Unfortunately, thus far no systematic theoretical and experimental studies of the effect of hydration on the band structure of intermetallides of d metals have been performed, while observations of metamagnetism in the hydrides of intermetallic compounds are very sporadic and admit other interpretations. We note only the two systems $Y_2Co_7H_x$ ($0 \leqslant x \leqslant 6.6$) and YCo_3H_x ($0 \leqslant x \leqslant 3.8$).[101] In the first system, depending on the hydrogen content, both the transitions paramagnetism–weak ferromagnetism and weak-strong ferromagnetism were observed in a field, while in YCo_3H_x only transitions of the second type were observed.[102,103]

5. CONCLUSIONS

The phenomenon of metamagnetism of collectivized electrons, which is the subject of this review, is one of the consequences of the sharp energy dependence of the density of states, when the curvature of $N(\varepsilon)$ is positive near the Fermi energy. The use of a simple qualitative model for interpreting the experimental data makes it possible to establish the general properties of itinerant metamagnets, belonging to different classes of compounds, and to point out the indicators according to which the phenomenon of itinerant metamagnetism can be predicted from measurements in comparatively weak fields. In spite of the fact that in its pure form (as a transition of a paramagnet into the ferromagnetic state in an external magnetic field) itinerant metamagnetism is a quite exotic phenomenon, the characteristic indicators formulated in this review make it possible to perform a more directed search for such magnets. In particular, an undoubtedly important factor, giving rise to the appearance of the positive curvature of $N(\varepsilon)$, is the hybridization of the d bands of components with different electronegativity.

The phenomenon of itinerant metamagnetism is attracting increasingly persistent attention because of the successful calculations of the band structure of different materials. Such calculations are continuously being refined and depended, and a number of new studies,[104–107] devoted to both the theoretical and experimental study of itinerant metamagnetism, have already been published after this review was prepared. The existence of theoretical prerequisites greatly simplifies the search for metamagnetic transitions in a system of itinerant electrons. In particular, the recent discovery of anomalous metamagnetic magnetization curves in the systems $Y_{1-x}La_xCo_2$,[106] $Sc(Co_{1-x}Al_x)_2$,[107] as well as

$Y(Co_{1-x}Fe_x)_2$[106] was made possible largely by the theoretical explanation of the structure and properties of the d band in the YCo_2 and $ScCo_2$ compounds.

The current situation indicates that the jump-like change in the ground magnetic state of a system of itinerant electrons in an external field, a particular case of which is itinerant metamagnetism, may turn out to be a widespread effect, and the small number of experimental facts confirming this phenomenon is primarily attributable to the inadequacy of the existing information on the band structure of the d electrons in different compounds.

It should be noted that itinerant metamagnetism does not exhaust all qualitative mechanisms which are determined by the structural characteristics of the d band near the Fermi level (even without knowing its analytical form). We have already mentioned in this review of the phenomenon of thermally induced magnetism. The recently discovered gigantic increase in the Curie temperature in the mixed compounds $R(Co,Al)_2$, also due to the sharp energy dependence of the density of states at the Fermi level,[108] etc., is closely related to the phenomenon of metamagnetism of collectivized electrons.

The general laws, following from the structure of the d band, can obviously also be formulated for itinerant systems in which a transition from the antiferromagnetic into the ferromagnetic state occurs in an external field (such systems were recently discovered in $La(Fe,Al)_{13}$, $(Y,Th)Fe_3$, $FePt_3$ and other materials.[109-111]

We would like to emphasize that in order to make well-founded assertions about the true nature of the magnetic phase transitions observed it is necessary to have information about the nature of the magnetic state, since these transitions can be explained not only in the itinerant model, but also in the model of localized moments. It is undoubtedly very important to confirm the itinerant character of the transition by quantitative calculations of the band structure.

[1)]It is interesting to note that Stoner himself clearly understood the approximate nature of this approach. In his fundamental work[2] he wrote: "Owing to the peculiarities in the forms of the electronic energy bands of particular metals, it cannot be claimed that the results will necessarily be strictly applicable to any actual ferromagnetic. . . . It is difficult to say how much the results obtained in this approximation [free electron approximation] can be generalized . . . . In any case, every metal must have its own specific form of the band."

[2)]We call attention to the qualitative difference between the concept of itinerant metamagnetism and the concept of metamagnetism in the model of localized moments, where the metamagnetic transition is a transition in a field from the antiferromagnetic into the ferromagnetic state.

[3)]Systems with a singlet ground state, which can be paramagnetic at 0 K are an exception (see Ref. 15 for a more detailed discussion).

[4)]In addition, in real samples extraneous phenomena (local nonuniformities, features of nucleation, etc.) can lead to "smearing" of the transition over a finite interval of fields. In what follows, in describing the experimental data we shall examine also such transitions from the paramagnetic into the ferromagnetic state, calling them, for brevity, metamagnetic.

[5)]Figure 8 also shows the dependence $\chi(T)$ for $ScCo_2$, which, as follows from theoretical calculations (see below), can be an itinerant metamagnet.

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