Spin-flop transitions in itinerant metamagnets

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A study is made of phase transitions induced by a magnetic field in itinerant ferrimagnets of f–d compounds in which the d sublattice is unstable, i.e., undergoes a metamagnetic phase transition. In particular, a first-order phase transition of a new type is predicted. It is a transition from a weak ferrimagnetic state directly into an angular structure, without the stage of a collinear ferrimagnetic structure.

1. Magnetic-field-induced phase transitions from a collinear ferrimagnetic phase to an angular phase (spin-flop transitions in ferrimagnets) have been studied in detail both theoretically and experimentally.[1-3] The most common materials, which have been the setting for most of the research on these phase transitions so far, are compounds of rare-earth elements and transition metals of the iron group: the iron garnets $R_3Fe_5O_{12}$ and the intermetallic compounds R_nT_m, where R is a rare-earth element, and T a transition metal.[3] Such systems are generally described in the approximation of a "rigid" d-sublattice, in which the magnetization of the d-sublattice is assumed to be independent of the external magnetic field and of the exchange field exerted on it by the rare-earth sublattice. Much interest has recently been attracted to itinerant f–d metamagnets, which in a sense are the opposite of the materials mentioned above.[4] In them, the d-subsystem is a weak itinerant ferromagnet and can undergo a metamagnetic phase transition with a substantial jump in magnetization. Some typical members of this family are YCo_2, $LuCo_2$, and RCo_2, which exhibit metamagnetic transitions in the electronic d-subsystem from a paramagnetic state to a ferromagnetic state under the influence of a magnetic field. Magnetic-field-induced transitions of this sort were predicted by Wohlfarth and Rhodes.[5] According to the theory of Refs. 6–8, such a transition is possible in YCo_2; it was indeed observed[9,10] comparatively recently, in fields on the order of 100 T. The critical field decreases in the compounds $R_xY_{1-x}FeO_3$, since the metamagnetic transition arises in an effective field which is the sum of the external field and the molecular field exerted on the d-ions by the rare-earth ions.[5,7,11-14] Another possibility for a decrease in the critical field of a metamagnetic transition is realized in compounds of the type[14] $(RY)Co_{2-x}Al_x$.

Our purpose in the present study was to learn about magnetic-field-induced phase transitions and the phase diagrams in itinerant metamagnets with an unstable d-sublattice. This problem is important to the magnetism of f–d intermetallic compounds in general, since according to the present understanding of itinerant ferromagnetism the d-subsystem in such compounds is frequently an unsaturated (weak) ferromagnet with all the characteristic features of this situation.

2. We first consider the ground state of an f–d ferrimagnet at $T=0$. The thermodynamic potential of the d-subsystem of a weak itinerant ferrimagnet is cus-

tomarily written as an expansion in powers of the magnetization:[4,5]

$$F=\frac{1}{2}am^2+\frac{1}{4}bm^4+\frac{1}{6}cm^6, \tag{1}$$

where a, b, and c are coefficients whose temperature dependence is determined by the particular band structure and/or by spin fluctuations. Let assume, as is customarily done in the theory of itinerant metamagnetism, that the following relations hold: $a>0$, $b<0$, $c>0$. We consider the case in which the d-subsystem is itself paramagnetic down to $T=0$. It would seem at first glance that in this case the f–d system as a whole should also be paramagnetic, since the molecular field created by the d-subsystem at the f ions must be zero. However, we will show that this is not the case. Actually, the paramagnetic state (i.e., a state with a zero spontaneous magnetization) of such a subsystem is unstable in the presence of an f ion with a degenerate ground state, and a spontaneous magnetization arises in the f–d system. The onset of a spontaneous magnetization below the threshold, i.e., formally, in the paramagnetic phase, can be seen directly on the magnetization curves reported in Ref. 13. The physical meaning of this phenomenon can be explained as follows. We consider a spin fluctuation in a system of d ions surrounding an f ion of interest. We assume that this fluctuation causes a splitting of the ground state of the f ion. The meaning here is that this f ion becomes magnetized, and it in turn causes a further magnetization of the surrounding ions by virtue of the f–d interaction. A spontaneous magnetization thus arises in the d–f system. In other words, the symmetry under time reversal is spontaneously broken. (In the case of an isolated ion, of course, quantum fluctuations should lead to a restoration of the symmetry under time reversal, but for the case of the cooperative instability discussed below this symmetry breaking has a completely real meaning.)

This conclusion can be thought of as a consequence of a more general position—as a manifestation of a crossover instability in magnetically ordered systems.[15,16] The lowering of the energy due to the splitting of the ground state of the f ion is equal to $-\lambda m M_f$, where M is the magnetic moment of the f ion, m is the amplitude of the magnetization of the cloud of magnetized ions around the f ion, and λ is the f–d exchange constant. When the paramagnetic d -subsystem becomes magnetized, its energy increases by an amount $\frac{1}{2}Vm^2/2\chi_d$, where $\chi_d=a^{-1}$ is the magnetic susceptibility of the d-subsystem, and V is the volume of the magnetized region around the f ion. The instability of the uniform state ($m=0$) is obvious even for an arbitrarily weak interaction, since the improvement in terms of energy is linear in m, while the degradation is quadratic. If the concentration of m ions is high enough, i.e., if the magnetization clouds around the f ions overlap (more on this below), there will be a cooperative spontaneous magnetization of the f- and d-subsystems in the system. In this case the total energy per molecule is

$$E=\tfrac{1}{2}m^2/\chi_d-t\lambda mM, \tag{2}$$

where t is the relative concentration of f ions. Minimizing (2), we find

$$m=\chi_d t\lambda mM. \tag{3}$$

This discussion can easily be generalized to nonzero temperatures H_{eff}. The thermodynamic potential Φ of this system is

$$\Phi = 1/2am^2 + 1/4bm^4 + 1/6cm^6 - t\int_0^{H_{\text{eff}}} M(h)dh, \tag{4}$$

where $M(h)$ is the magnetization of the f-sublattice expressed as a function of the effective field $H_{\text{eff}} = \mathbf{H} - \lambda\mathbf{m}$ (in this case, the external field $\mathbf{H}$ is assumed to be zero), of the temperature T, and of the magnetic moment μ of the f ion. In particular, for the Gd^{+3} ion we have $M(h) = \mu B_{7/2}(\mu h/T)$, where $B(x)$ is the Brillouin function, and $\mu = 7\mu_B$. Minimizing (1), we find

$$am + bm^3 + cm^5 - t\lambda M(\lambda\mu m/T) = 0. \tag{5}$$

This equation determines two phase-transition points: the magnetic-ordering temperature T_c, which is determined by the condition $\chi_d\chi_f\lambda^2 t = 1$, and the (usually lower) temperature of the metamagnetic transition to a "strong ferrimagnetic" state, T_M.

3. The threshold concentration for the t^* transition to a cooperative behavior of the system can be estimated on the basis of the following qualitative considerations, which are based on arguments regarding the size of the magnetized cloud around the f ion. This size is determined by the correlation radius of the fluctuations in the d -subsystem. To find it we work from the Ginzburg–Landau energy

$$E = \int (A(\text{grad}m)^2 + m^2/2\chi_d)dV, \tag{6}$$

where A is the nonuniform-exchange constant (the exchange stiffness) of the d-subsystem, and the integration is over the entire volume except a small volume around the f ion with a diameter on the order of the interatomic distance. We assume $m(r) = m$ at the boundary of this small volume, and at infinity we naturally assume $m(r) \to 0$. Using these boundary conditions, we then find the following from the Euler–Lagrange equations for functional (6): using these boundary conditions, we then find

$$m(r) = (ma/4\pi r)\exp(-r/\rho), \tag{7}$$

where $\rho = (A\chi_d)^{1/2}$ is the correlation radius which we are seeking. Setting $A = 5\times10^{-9}$ esu/ion and $\chi_d \approx 2\times10^{-7}$ esu/ion,[13] we find $\rho = 3$ Å . This value is of course too small for the continuum approximation to be reliable, but it will do for a qualitative argument. The magnetization distribution described by (7) is obviously degenerate under the direction of the spins of the f ion and the d-subsystem (the matrix). The actual wave function of this composite formation is therefore a linear combination of all possible wave functions which are included in the degeneracy space, i.e., which are characterized by different spin orientations. A wave function of this sort describes a localized spin-wave mode which includes a joint motion of f and d spins. A detailed description of this mode goes beyond the scope of the present letter, but we would like to point out that this picture of an isolated f ion in a d-matrix may be observed at low concentrations of f ions, at which local spin modes do not overlap. A mode overlap determines an interaction of centers, and if the concentration of centers is sufficiently

high, it will lead to cooperative effects. The threshold concentration t^* can be estimated with the help of the percolation model. If the distance between two nearest f ions is smaller then ρ, then these ions perturb each other substantially. As a result, a correlation arises in the directions of spins. The percolation threshold can then be found approximately from $N^*\rho^3=q$, where q is a numerical factor on the order of one; for our purposes we can set it equal to one. The threshold critical concentration is thus $t^*\approx(a/\rho)^3\approx 0.1$, where a is the average interatomic distance in the compound.

4. We turn now to phase transitions induced by a magnetic field and to phase diagrams at $T=0$, assuming that the concentration of f ions is large enough that the behavior of the system can be assumed to be cooperative. In other words, we assume $t>t^*$. In this case we can ignore the nonuniform-exchange energy, and we can write the thermodynamic potential in the form

$$\Phi=\Phi_d(m)-MH\cos\psi-m(H^2+\lambda^2M^2-2\lambda M\cos\psi)^{1/2}, \tag{8}$$

where Φ_d is the energy of the d-subsystem found from (1), and ψ is the angle between the magnetic field H and magnetization M of the f-sublattice. The last term in (8) is the energy of the interaction of d -subsystem with the effective field acting on it. Expression (8) is the thermodynamic potential minimized as a function of the angle between the magnetization of the d-sublattice and the effective field acting on it. The order parameter of this system is determined by the values of m and ψ. Minimizing (8) with respect to m and ψ, we find

$$h_d(m)=H_{\text{eff}}(M,\psi), \tag{9}$$

$$MH\sin\psi(1-\lambda m/H_{\text{eff}})=0, \tag{10}$$

$$m(h)=\begin{cases}\chi_d h, & h<H_p,\\ m_1, & h>H_p,\end{cases} \tag{11}$$

where H_p is the threshold field for the metamagnetic transition in the d-subsystem. From (11) we can directly determine the functional dependence $h(m)$. It is simple to verify by direct calculation that the values of the magnetization on the descending slope of the $m(h)$ curve [or of the $h(m)$ curve] determined by Eq. (1), i.e., the values corresponding to a negative differential susceptibility $\partial m/\partial h<0$, correspond to unstable states of the system. For this reason, the interval of magnetization values from $\chi_d H_p$ to m_1 is of no interest for our purposes, in our approximation of $m(h)$, i.e., (11). For simplicity we will also ignore the hysteresis on the $m(h)$ curve. We will come back to this question below. We should also mention that in a real metamagnet the magnetization of the d-subsystem is not a constant in the ferromagnetic phase, instead increasing slightly with increasing field. This point is simple to deal with mathematically, but taking it into account makes the analysis more complicated without leading to any qualitatively new facts. Since it tends to obscure the overall picture, we will ignore it.

Equations (9) and (10), along with the stability conditions ($\delta^2\Phi>0$), determine the following solutions (phases) and the regions in which they exist:

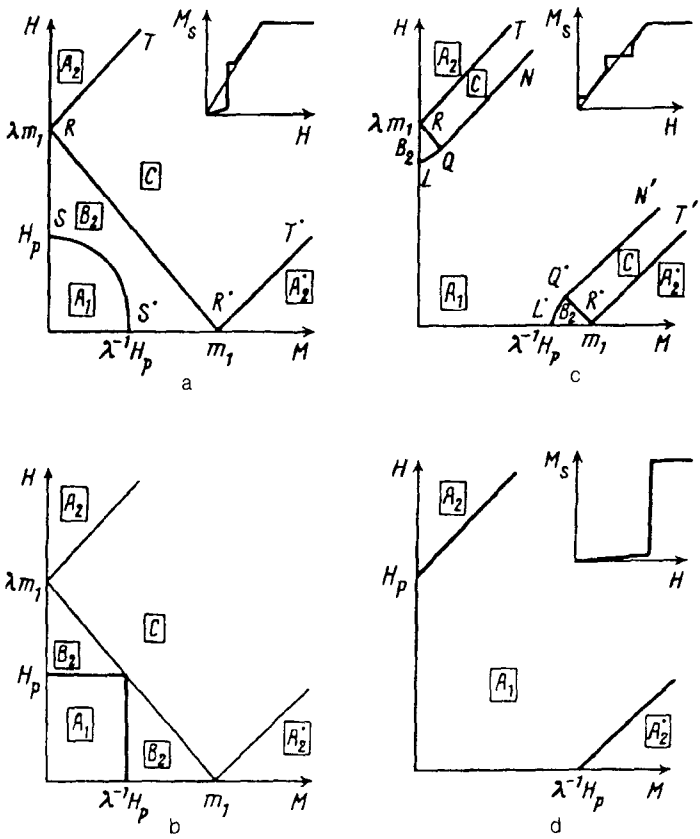

FIG. 1. Phase diagrams of an itinerant ferrimagnet with an unstable d subsystem. a—$H_p<\lambda m_1/2$; b—$H_p=\lambda m_1$; c— $H_p<\lambda m_1/2$; d—$H_p>\lambda m_1$. The insets are schematic diagrams of the corresponding magnetization curves.

$$
\begin{aligned}
&A_1\text{:} && \psi=0, && m=\chi_d(H-\lambda M), && H<H_p+\lambda M,\\
&A_2\text{:} && \psi=0, && m=m_1, && H>H_p+\lambda M,\\
&B_1\text{:} && \psi=\pi, && m=\chi_d(H+\lambda M), && H<H_p-\lambda M,\\
&B_2\text{:} && \psi=\pi, && m=m_1, && H>H_p-\lambda M,\\
&C\text{:} && 0<\psi<\pi, && m=m_1, && \lambda|m_1-M|<H<\lambda|\ m_1+M|\ .
\end{aligned}
$$

The phases $A_1(A_2)$ and $B_1(B_2)$ can be defined as weak (strong) ferrimagnetic collinear phases, while phase C is an angular phase. To plot $H-M$ phase diagrams, we need to equate the energies of the coexisting phases and find the lines of first-order phase phase transitions from these equations. As $\Phi_d(m)$ in our approximation we should use the quantity $\Phi_d=\int_0^m h_d(m)dm$.

The phase diagrams in Fig. 1 give a general picture of the magnetization curves

and critical fields of itinerant metamagnets. The nature of the H–M phase diagrams depends on the relation between H_p and λm_1. If $H_p < \lambda m_1$, the phase diagram will have, in addition to the "ordinary" lines of second-order phase transitions between collinear and angular phases (which are determined by the known expressions for the critical fields $H_{c1} = \lambda |m_1 - M|$ and $H_{c2} = \lambda |m_1 + M|$), lines of a first-order transition, which are determined by the equation (under the condition $\lambda \chi_a \ll 1$)

$$H_M = (H_p - \lambda M)/(1 - 2M/m). \tag{12}$$

At $H_p = \lambda m_1/2$, this line transforms into the boundary of a rectangle (Fig. 1b) bounding a region of absolute stability of the A_1 phase. In the interval $\lambda m_1 < H_p < \lambda m_1$ the phase diagram (Fig. 1c) has two interesting features. There can be not only $A_1 - B_2$ phase transitions here, which occur on lines LQ and $L'Q'$, but also first-order transitions from the weak ferrimagnetic phase A_1 to the angular phase C, which occur on lines QN and $Q'N'$. Transitions of this sort have not previously been seen in isotropic systems. This is a distinctive feature of itinerant ferrimagnets with an unstable d-subsystem. Lines QL and $Q'L'$are determined by Eq. (12), and lines QN and $Q'N'$by

$$H = \lambda |M + \epsilon m_1|, \quad H = \lambda |M - \epsilon m_1|, \tag{13}$$

where $\epsilon = ((2H_p/\lambda m_1) - 1)^{1/2}$. The points Q and Q' have the coordinates $M = \frac{1}{2} m_1(1 \pm \epsilon)$, $H = \frac{1}{2}\lambda m_1(1 \mp \epsilon)$.

The second unusual feature of this diagram is that there can be an "inverse transition" from the strong ferrimagnetic phase to the weak ferrimagnetic phase. This transition would occur as the magnetic field is increased.[17] The same feature is seen, even more clearly, at $H_p > \lambda m_1$ (Fig. 1d), where the inverse transition occurs abruptly, without an intermediate angular phase.

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