Itinerant electron metamagnetism

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Classification
Physics Abstracts
75.10L — 75.20E — 75.30C

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(*Reçu le 10 août 1981, accepté le 17 septembre 1981*)

Résumé. — Les conditions rigoureuses pour les transitions métamagnétiques entre l'état paramagnétique et l'état ferromagnétique ou entre l'état ferromagnétique faible et l'état ferromagnétique normal sont déduites. Les expressions de ces conditions et celles des champs critiques sont obtenues dans un modèle simple pour un système d'électrons itinérants, et également pour un système plus complexe de moments magnétiques locaux et d'électrons itinérants. Les résultats sont appliqués à $TiBe_2$, YCo_2, Pd, à certains composés entre les métaux de terres rares et de transition, à $Co(S, Se)_2$, etc. Ils permettent d'expliquer que $TiBe_2$ et, sans doute, YCo_2 et Pd ne présentent pas la transition métamagnétique, en accord avec les résultats expérimentaux.

Abstract. — Rigorous conditions for the metamagnetic transitions between the paramagnetic and ferromagnetic states and between the weak ferromagnetic and normal ferromagnetic states are derived. The expressions for the conditions and the critical field are derived in the simple model for an itinerant electron system and for a combined system of localized magnetic moments and itinerant electrons. The results are applied to $TiBe_2$, YCo_2, Pd, compounds of rare earth metals and transition metals, $Co(S, Se)_2$, etc. It is explained that $TiBe_2$ and perhaps YCo_2 and Pd will not show the metamagnetic transition in consistent with the experimental results.

1. **Introduction.** — The metamagnetic transition (MT) from the paramagnetic state to the ferromagnetic state by applying the magnetic field was first discussed by Wohlfarth and Rhodes [1] for the itinerant electron model. They showed that the paramagnetic metals or alloys will show MT, if there is a maximum in the temperature variation of the paramagnetic susceptibility as in Pd, or as a more strict condition, if the coefficient a_3 in the expansion of the magnetic energy E given by

$$E = \tfrac{1}{2} a_1' M^2 + \tfrac{1}{4} a_3 M^4 - MH,$$

where H is the applied magnetic field, as a power series of the magnetization M, is negative. They defined the critical field H_c for MT from the paramagnetic state to the ferromagnetic state by the inflection point in the plot of E against M as a function of H.

Recently, using the same definition of H_c as before, Wohlfarth [2] has predicted the value of H_c for Pd, YCo_2 and $TiBe_2$ as 1 100, 170 and 58 kOe, respectively. However, experimentally MT has so far never been observed for Pd up to 325 kOe [3], for YCo_2 up to 150 kOe [4] and 380 kOe [5] and for $TiBe_2$ up to 190 kOe [6] and 213 kOe [7]. In the cases of YCo_2 and $TiBe_2$ the highest fields used in experiment are much higher than the values predicted by Wohlfarth [2]. Cyrot and Lavagna [8] have also predicted MT for YCo_2 at about 1 000 kOe, using their calculated density of states. In our estimation from their calculated density of states, MT seems to be impossible in YCo_2. Recently, Jarlborg and Freeman [9] have also predicted MT in Pd at 3 220 kOe from the calculation of its electronic structure under the magnetic field.

In this paper it is shown that the condition for MT, $a_3 > 0$ is not complete and the previous estimations of H_c are not reliable. We should include the higher order terms at least up to the M^6 term in the expansion of the magnetic (free) energy E in order to discuss MT, as shown below. It is possible that even if $a_3 < 0$ the second minimum corresponding to the ferromagnetic state in addition to the first minimum corresponding to the induced paramagnetic state in the plot of E against M does not appear even at very high field when the contribution from the higher order terms to E is large. The condition for MT is more strict than $a_3 < 0$. It is well-known that in the case $a_3 < 0$ the paramagnetic susceptibility χ increases with increasing H. Therefore, the increase of χ with increasing H, as observed in Pd [3], YCo_2 [4, 5]

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and $TiBe_2$ [6, 7], does not necessarily mean the occurrence of MT, although it is one of the necessary conditions.

On the one hand, there are many intermetallic compounds of rare earth metals and transition metals, e.g. RCo_2 [10, 11], where R means the rare earth metals and is Dy, Ho or Er, (Ho, Y)Co_2 [12], etc., which show MT from the paramagnetic state to the ferromagnetic state and also many compounds, e.g. $ThCo_5$ [13], Y_2Ni_{16} [14], Co(S, Se)$_2$ [15, 16], (Co, Ni)S_2 [17], etc. show MT from the weak ferromagnetic state to the ferromagnetic state with a larger magnetization.

On the other hand, there are many alloys and rare earth compounds which also show MT from the antiferromagnetic state to the ferrimagnetic or ferromagnetic state or from the ferrimagnetic state to the ferromagnetic state and which show the dependence on H of M very similar to the one of MT that can be explained by the model of narrow domain wall [18]. In this paper we will discuss only the former case and will no discuss the latter case, There are review articles for the magnetic properties of intermetallic compounds of rare earth metals and transition metals [10, 19-21].

Especially, in some of RCo_2 compounds, $ErCo_2$, $HoCo_2$ and $DyCo_2$ the first-order transition was observed [10, 11, 22] and MT was observed only in a very narrow temperature range, 5 ~ 10 K [10, 11]. The first-order transition, which corresponds to the case $H_c = 0$ in MT, in these compounds was qualitatively explained by the combined model of the localized magnetic moment on R atoms and itinerant electrons on Co atoms or the so-called s-d model [4], where the expansion of free energy with respect to M only due to the itinerant electrons was taken into account. Recently, it has been pointed out that the expansion of the magnetic free energy with respect to the total magnetization given by the sum of the magnetization due to the localized moments and that due to the itinerant electrons is very important to discuss the first-order transition and to derive this transition temperature [23]. This expansion of the free energy with respect to the total magnetization is also very important to discuss MT in various kinds of rare earth compounds, as shown below.

In the case of Co(S, Se)$_2$ [15, 16] and (Co, Ni)S_2 [17], the simple Heisenberg model seems to be appropriate, because the magnetization changes very little at very high field or the high-field susceptibility is very small and the temperature variation of χ at high temperatures obeys the Curie-Weiss law. However, all the coefficients except the first coefficient of the M^2 term in the expansion of the free energy as a power series of M^2 in the molecular field approximation are always positive in the simple Heisenberg model, where the average of the magnetic interaction is proportional to M^2, so that we cannot expect MT and the first-order transition in this model. Therefore, in order to explain MT in the Heisenberg model we have to introduce some modifications of the model, e.g. the magnetic interaction with higher powers of M than M^2, the temperature dependence of the molecular field coefficient, the complicated magnetic structures, the distribution of the magnetic moments, etc. In the case of $Co(S_xSe_{1-x})_2$ compounds the distribution of cobalt atoms with and without magnetic moment has been ascertained in experiment [16] and MT has been discussed in terms of the distribution of the two kinds of Co atoms with and without magnetic moment [24, 25].

In section 2, general conditions for MT based on the thermodynamics are shown without regard to any specific model for MT. In section 3, MT between a simple paramagnetic state and a ferromagnetic state is discussed in the simplest model, that is, the least number of terms in the expansion of the free energy in a power series of M^2 and the analytical expressions of the conditions for MT and of the critical fields which show a hysteresis are obtained. In section 4, MT between a weak ferromagnetic and normal ferromagnetic states is discussed in terms of the least number of terms in the expansion of the free energy and the conditions for this kind of MT and the critical fields are obtained. In section 5, from the experimental results of the field dependence of M for $TiBe_2$, YCo_2 and Pd the values of the coefficients in the expansion of the free energy with respect to M are estimated and the conditions for MT are examined. It is concluded that $TiBe_2$ will not show MT and for Pd and YCo_2 it is very difficult to predict whether they show MT or not from our present knowledge for the dependence on H of M. Even if it exists it occurs at very high fields higher than 325 kOe for Pd and 380 kOe for YCo_2. In section 6, the reason for the occurrence of the variety of MT in various rare earth compounds and the character of MT are discussed and some conclusions are given.

2. **General conditions for the metamagnetic transition.** — The magnetic free energy f can be given as a function of the temperature T, the volume V, the concentration c, if necessary, and the magnetization M of a metal, alloy or compound. By the thermodynamic relations the magnetic field $H(M)$ is given as a function of T, V, c and M as

$$H(M) = \partial f/\partial M . \tag{1}$$

For the moment we consider the dependence only on M of f and $H(M)$. In the itinerant electron system $H(M)$ can be written as [26, 27] :

$$H(M) = \Delta\zeta/2\,\mu_B - \alpha M , \tag{2}$$

where $\Delta\zeta$ is the so-called exchange splitting, i.e. the difference between the chemical potentials of electrons with up (+) and down (−) spins when the magnetization M exists and α is the molecular field coefficient. We can obtain the dependence on M of $\Delta\zeta$ from the calculated density of states and actually $\Delta\zeta$

shows a very complicated dependence on M, as shown schematically before [28] and for $ZrZn_2$ recently [29]. $\Delta\zeta$ should be a monotonically increasing function of M, i.e. $\partial\,\Delta\zeta/\partial M \geqq 0$ and it can be expanded when M is small as

$$\Delta\zeta/2\,\mu_B = a_1\,M + a_3\,M^3 + a_5\,M^5 + a_7\,M^7 + \cdots, \tag{3}$$

where the coefficients a_1, a_3, a_5, a_7, etc. are in general functions of T, V and c and they can be expressed in terms of the electronic density of states and its derivatives [27]. All coefficients except a_1 are possible to become negative. However, we must remember that these coefficients at finite temperature are modified by the effect of spin fluctuations in the itinerant electron system as shown in [27, 30]. Then $H(M)$ is expanded as

$$H(M) = a_1'\,M + a_3\,M^3 + a_5\,M^5 + a_7\,M^7 + \cdots,$$

where $a_1' = a_1 - \alpha = 1/\chi_d$. (4)

On the other hand, for a Heisenberg system of N magnetic moments with spin S and Landé factor g, $H(M)$ can be written as

$$H(M) = (g\mu_B\,S\beta)^{-1}\,B_s^{-1}(M/Ng\mu_B\,S) - KM, \tag{5}$$

where $\beta = 1/k_B\,T$, B_s^{-1} is the inverse Brillouin function and K is the molecular field coefficient between the localized moments. The right-hand side of equation (5) can also be expanded as a power series of the magnetization M as [23]

$$H(M) = b_1'\,M + b_3\,M^3 + b_5\,M^5 + b_7\,M^7 + \cdots, \tag{6}$$

where

$$b_1' = b_1 - K = 1/\chi_i$$

and

$$\begin{aligned}
b_1 &= 3\,\beta^{-1}\,N^{-1}(g\mu_B)^{-2}\,S^{-1}(S+1)^{-1},\\
b_3 &= \frac{9}{20}\,\beta^{-1}\,N^{-3}(g\mu_B)^{-4}\,\{(2S+1)^2+1\}\,S^{-3}(S+1)^{-3},\\
b_5 &= \frac{27}{2\,800}\,\beta^{-1}\,N^{-5}(g\mu_B)^{-6}\,\{11(2S+1)^4+32(2S+1)^2+11\}\,S^{-5}(S+1)^{-5},\\
b_7 &= \frac{81}{56\,000}\,\beta^{-1}\,N^{-7}(g\mu_B)^{-8}\,\{19(2S+1)^6+107(2S+1)^4+107(2S+1)^2+19\}\,S^{-7}(S+1)^{-7}.
\end{aligned} \tag{7}$$

It is seen that all coefficients b_i are proportional to T and positive. In general, K may depend on T, V, c and M. In the case of the Heisenberg model all the coefficients b_i are of course modified by the effect of the spin fluctuations in the same way as in the itinerant electron system [27, 30].

For a combined system of the localized magnetic moments and itinerant electrons, such as Pd-Fe and Pd-Co alloys and compounds of rare earth metals and transition metals, $H(M)$ can be expanded as a power series of the total magnetization M as [23]

$$H(M) = c_1\,M + c_3\,M^3 + c_5\,M^5 + c_7\,M^7 + \cdots, \tag{8}$$

where M is the sum of the magnetization of the localized moments and that of the itinerant electrons and the coefficients c_1, c_3, c_5 and c_7 are given by

$$\begin{aligned}
c_1 &= Q_d\,Q_i\,Q^{-1} - J,\\
c_3 &= (a_3\,Q_i^4 + b_3\,Q_d^4)\,Q^{-4},\\
c_5 &= (a_5\,Q_i^6 + b_5\,Q_d^6)\,Q^{-6} - 3(a_3\,Q_i^3 - b_3\,Q_d^3)^2\,Q^{-7},\\
c_7 &= (a_7\,Q_i^8 + b_7\,Q_d^8)\,Q^{-8} - 8(a_5\,Q_i^5 + b_5\,Q_d^5)(a_3\,Q_i^3 - b_3\,Q_d^3)\,Q^{-9} +\\
&\quad + 8(a_3\,Q_i^2 + b_3\,Q_d^2)(a_3\,Q_i^3 - b_3\,Q_d^3)^2\,Q^{-10}
\end{aligned} \tag{9}$$

with

$$Q_d = \chi_d^{-1} + J, \quad Q_i = \chi_i^{-1} + J$$

and

$$Q = Q_d + Q_i,$$

where J is the molecular field coefficient between the localized moments and itinerant electrons.

Now, we discuss the possibility of MT between the paramagnetic and ferromagnetic states by assuming a proper dependence of $H(M)$ on M for several cases, (for example, $a_1' \geqq 0$, $a_3 < 0$ and $a_5 > 0$ in the itinerant electron model or $c_1 \geqq 0$, $c_3 < 0$ and $c_5 > 0$ in the combined model), as shown by schematic curves in figure 1, here and hereafter × shows an inflection point and a small vertical bar shows the position of a maximum or minimum. This figure gives

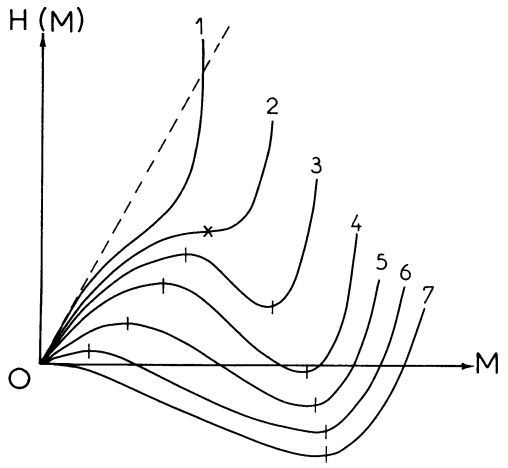

Fig. 1. — Schematic dependences on the magnetization of the magnetic field $H(M)$ for the cases of the metamagnetic transition between the paramagnetic and ferromagnetic states, e.g. for the cases, $a'_1 > 0$, $a_3 < 0$ and $a_5 > 0$ in the expansion of $H(M) = a'_1 M + a_3 M^3 + a_5 M^5$. Here and hereafter × shows an inflection point and small vertical bars show a maximum or minimum.

of course the variation of M with respect to the external field H as usually observed in experiment. Here and hereafter, we make use of only the expansion of $H(M)$ given by equations (4) for the itinerant electron system and the same discussion can be applied to the combined system of the localized moments and itinerant electrons by replacing equation (4) by equation (8). There is an inflection point at $M = M_0$ and $H = H_0$ in the curve 2, there are a maximum and a minimum in the curves 3, 4, 5 and 6 and there is only a minimum in the curve 7 (e.g. if $a'_1 = 0$ or < 0). It is easily seen from figure 1 that in the cases corresponding to the curves 3-6 MT occurs and there are hysteresis in the plot of M against H and in the case of the curve 1 MT does not occur.

The critical condition for the occurrence of MT corresponds to the curve 2 and it is given by the relation which satisfies two equations

$$\partial H(M)/\partial M = 0\,, \tag{10}$$

and

$$\partial^2 H(M)/\partial M^2 = 0\,. \tag{11}$$

And the critical value M_0 of M and the corresponding value H_0 of the magnetic field H are also obtained. Analytical expressions of this critical condition obtained from the expansion of $H(M)$ in equation (4) or (8) will be given in § 3.

For each case corresponding to each curve in figure 1 the effect of H is examined in the following way. The magnetic free energy f for any magnetic system under H can be written as

$$f = \int_0^M H(M)\,\mathrm{d}M - HM \tag{12}$$

besides a constant term. Then, we can get the dependence on M of f with H by integrating the curves in figure 1 with respect to M. The schematic dependences of f on M as a function of H and the schematic dependences of M on H are shown in figures 2*a*, *b*, *c*, *d*, *e* and 3*a*, *b*, *c*, *d*, *e*, which correspond to the curves 1 and 2 (case I), curve 3 (case II), curve 4 (case III), curve 5 (case IV) and curve 6 (case V) in figure 1, respectively.

In the case I (Figs. 2*a* and 3*a*) there is no minimum of f at finite value of M when $H = 0$. With increasing H the paramagnetic state at $M = 0$ when $H = 0$ simply shifts to a larger value of M, as there is only one solution $H(M) = H$ in this case. There is no MT and the dependence of M on H is simply given by curve 1 or 2 in figure 1 or 3*a*. This type of curve 1 in figure 3*a* has been found experimentally for $TiBe_2$ [6, 7]. In Pd [3] and YCo_2 [4, 5] the bend of the curve toward H axis has not yet been observed.

In the case II (Figs. 2*b* and 3*b*) f does not show any minimum at finite M when $H = 0$. The cross points between the curve and vertical straight lines $H =$ constant in figures 3 give the inflection point, maximum or minimum in the curve of f against M in figures 2. Therefore, in the case II, MT occurs and the hysteresis appears. The lower and higher critical fields and the critical field in the equilibrium, where the values of f at the induced paramagnetic and ferromagnetic states are equal, are denoted by H'_c and H''_c and H_c, respectively, in figures 2*b* and 3*b*. The largest value of M corresponding to H''_c in the induced paramagnetic state and the smallest value of M corresponding to H'_c in the ferromagnetic state are denoted by M''_c and M'_c, respectively, in figure 3*b*. Analytical expressions of H_c, H'_c, H''_f, M'_c and M''_c obtained in the simple model are given in § 3. The slope of the curve of M at $M = 0$ in figures 3, gives the paramagnetic susceptibility and that at high H gives the high-field susceptibility. The MT in the case II (Fig. 3*b*) was observed in experiment for many rare earth compounds, RCo_2 [10, 11], (Ho, Y)Co_2 [12], Co(S, Se)$_2$ [15] and (Co, Ni)S_2 [17]. In Co(S, Se)$_2$ the transition seems to be between the weak ferromagnetic and normal ferromagnetic states [16].

In the case III (Figs. 2*c* and 3*c*), there is a minimum of f at $M \neq 0$ even when $H = 0$ and the lower critical field H'_c does not exist. In the case IV (Figs. 2*d* and 3*d*), the minimum values of f at $M = 0$ and at $M \neq 0$ are equal to zero when $H = 0$ and we have $H_c = 0$. In the case V (Figs. 2*e* and 3*e*), the minimum value of f at $M \neq 0$ is already negative when $H = 0$ and we have only the critical field H''_c. The magnetization curves against H in the cases III, IV and V (Figs. 3*c*, *d*, *e*) were observed in experiment for RCo_2 [10, 11] and (Ho, Y)Co_2 [12].

Now, we discuss MT between the weak ferromagnetic state and the ferromagnetic state with a larger M. The relations between $H(M)$ and M for several cases, (for example, in the conditions that $a'_1 < 0$, $a_3 > 0$, $a_5 < 0$ and $a_7 > 0$ or $c_1 < 0$, $c_3 > 0$, $c_5 < 0$ and

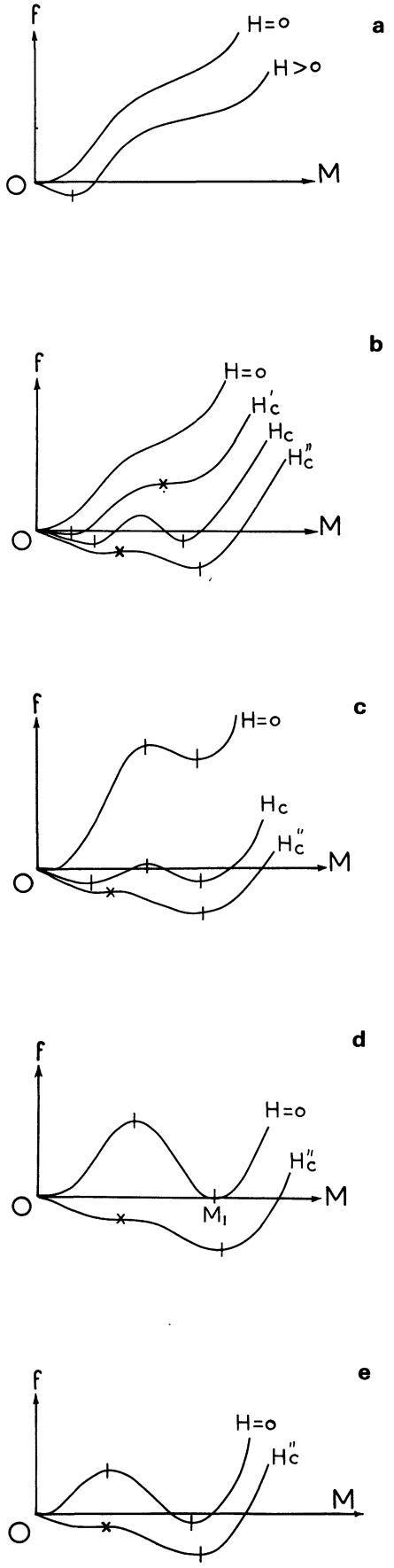

Fig. 2. — Schematic dependences on the magnetization M of the magnetic free energy f under the magnetic field H, where the figures *a*, *b*, *c*, *d* and *e* correspond to the curves 1 and 2, 3, 4, 5 and 6 in figure 1, respectively, H_c' and H_c'' are the lower and higher critical fields and H_c is the critical field in equilibrium.

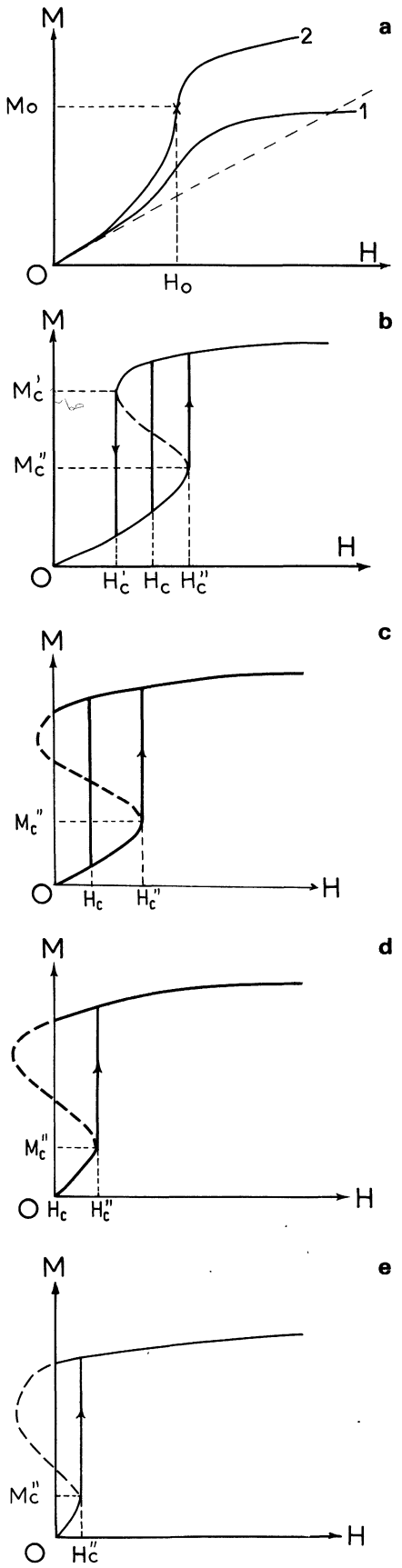

Fig. 3. — Schematic dependences on the external magnetic field H of the magnetization M, where the figures *a*, *b*, *c*, *d* and *e* correspond to the curves 1 and 2, 3, 4, 5 and 6 in figure 1, respectively, M_0 and H_0 are the magnetization and the magnetic field at the critical condition for the metamagnetic transition and M_c' and M_c'' are the magnetizations corresponding to the critical fields H_c' and H_c'', respectively.

$c_7 > 0$), are shown schematically in figure 4. In this case there is always a minimum of $H(M)$ at a low value of M. The corresponding dependences of M on H are shown in figure 5.

The curve 1 in figures 4 and 5 shows the relation between M and H at the critical condition where MT occurs or does not occur. In the cases of the curves 2, 3 and 4 in figures 4 and 5, MT occurs and the hysteresis appears. The critical condition for MT is similarly given as above by the relation which satisfies two equations (10) and (11) and the critical value M_0' of M and the corresponding critical value H_0' of H are also obtained. Analytical expressions for the critical condition and the critical fields H_0', H_c', H_c'' and H_c obtained in the simple model are shown in § 4. In the case of the curve 4 in figures 4 and 5 two minimum values of f are equal and we have $H_c = 0$. In the case of the curve 5 in figures 4 and 5, the ferromagnetic state with a large M is always stable. This type of MT was observed in $ThCo_5$ [13], Y_2Ni_{16} [14] and $Co(S, Se)_2$ [16].

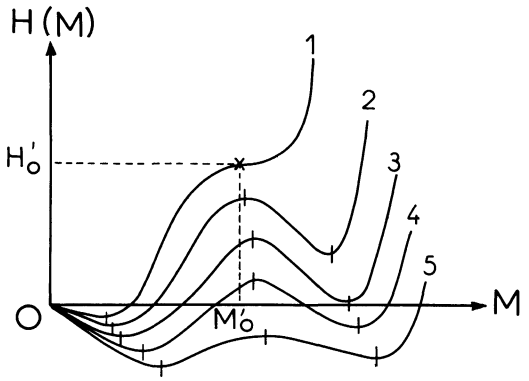

Fig. 4. — Schematic dependences on the magnetization M of the magnetic field $H(M)$ for the cases of the metamagnetic transition between the weak ferromagnetic and normal ferromagnetic states, e.g. for the cases $a_1' < 0, a_3 > 0, a_5 < 0$ and $a_7 > 0$ in the expansion of $H(M) = a_1' M + a_3 M^3 + a_5 M^5 + a_7 M^7$. The curve 1 shows the critical condition for the metamagnetic transition.

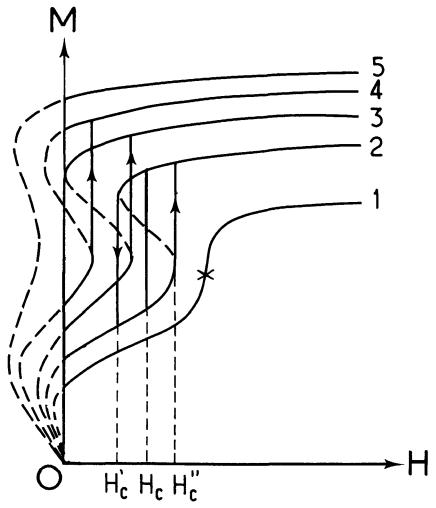

Fig. 5. — Schematic dependences on the external magnetic field H of the magnetization M, where the curves 1, 2, 3, 4 and 5 correspond to the curves 1, 2, 3, 4 and 5 in figure 4.

3. **Metamagnetic transition between the paramagnetic and ferromagnetic states.** — It is clear from the discussion given in § 2 that at least we should retain three terms in equation (4) or (8) as

$$H(M) = a_1' M + a_3 M^3 + a_5 M^5 , \qquad (13)$$

and we can expect the same dependences on M of $H(M)$ as those shown by the curves in figure 1, when $a_1' > 0$, $a_3 < 0$ and $a_5 > 0$. We discuss this case below.

The critical condition for MT in the case I (curve 2 in figure 1) is easily obtained from two equations (10) and (11) as

$$a_1' a_5/a_3^2 = 9/20 \qquad (14)$$

and M_0^2 and H_0^2 at the inflection point are given, respectively, by

$$M_0^2 = -\frac{3}{10} a_3/a_5 \qquad (15)$$

and

$$H_0^2 = -\frac{54}{3\,125} a_3^5/a_5^3 . \qquad (16)$$

The condition that the critical field H_c in equilibrium becomes zero in the case III (curve 5 in figure 1) in § 2 or the condition that the two minimum values of f at $M = 0$ and $M = M_1 \neq 0$ are equal was already obtained before [26] and it is written as

$$a_1' a_5/a_3^2 = 3/16 . \qquad (17)$$

The value of M_1 is given by

$$M_1^2 = -\frac{3}{4} a_3/a_5 . \qquad (18)$$

Therefore, the condition for MT to occur is given from equations (14) and (17) as

$$\frac{3}{16} < a_1' a_5/a_3^2 < \frac{9}{20} \qquad (19)$$

besides the conditions $a_1' = a_1 - \alpha = 1/\chi_d > 0$, $a_3 < 0$ and $a_5 > 0$. For the combined model of localized moment and itinerant electrons a_1', a_3 and a_5 in equation (19) are replaced by c_1, c_3 and c_5, respectively.

The critical fields H_c' and H_c'' and the corresponding critical values M_c' and M_c'' in figure 3*b* for the hysteresis of MT can be calculated from equation (10) and are given by, respectively,

$$H_c' = \frac{2}{5}(2 a_1' + a_3 M_c'^2) M_c' , \qquad (20)$$

$$H_c'' = \frac{2}{5}(2 a' + a_3 M_c''^2) M_c'' , \qquad (21)$$

$$M_c'^2 = \frac{1}{10}(-3 a_3 + \sqrt{9 a_3^2 - 20 a_1' a_5})/a_5 , \qquad (22)$$

$$M_c''^2 = \frac{1}{10}(-3a_3 - \sqrt{9a_3^2 - 20a_1' a_5})/a_5 . \quad (23)$$

The critical field H_c in equilibrium is calculated approximately from the condition

$$f(M_c') - H_c M_c' = 0$$

and is given by

$$H_c \simeq \left(\frac{7}{15}a_1' + \frac{3}{20}a_3 M_c'^2\right) M_c' . \quad (24)$$

The definition of the critical field by Wohlfarth [2] is similar to H_c'' in this paper, but the expansion of H_c'' in equation (21) for the case of small a_5 does not coincide with his result. The condition that H_c' becomes zero is obtained from equations (20) and (22) as

$$a_1' a_5/a_3^2 = \frac{1}{4}, \quad (25)$$

and the value of $M_c'^2$ and $M_c''^2$ are given, respectively, by

$$M_c'^2 = -\frac{1}{2}a_3/a_5 \quad (26)$$

and

$$M_c''^2 = -\frac{1}{10}a_3/a_5 . \quad (27)$$

The condition that H_c becomes zero is given approximately from equation (24) as

$$a_1' a_5/a_3^2 = \frac{135}{784}. \quad (28)$$

As long as a_1' is positive, H_c'' always exists. Therefore, if any ferromagnet shows the first-order transition at $H = 0$ in the case $a_1' > 0$ it should always show the hysteresis like that shown in figure 3*d*.

4. **Metamagnetic transition between the weak ferromagnetic and usual ferromagnetic states.** — From the discussion given in § 2, we should retain at least four terms in equation (4) or (8) as

$$H(M) = a_1' M + a_3 M^3 + a_5 M^5 + a_7 M^7 , \quad (29)$$

with

$$a_1' < 0 , \quad a_3 > 0 , \quad a_5 < 0 \quad \text{and} \quad a_7 > 0 ,$$

in order to describe the curves shown in figure 4.

Similarly as in § 3, the critical conditions for MT in the case shown by the curve 1 in figure 4 is obtained from equations (10) and (11) as

$$a_1' + \left(2a_3 + \frac{5}{3}a_5 M_0'^2\right) M_0'^2 = 0 , \quad (30)$$

where M_0' is the value of M at the inflection point and is given by

$$M_0'^2 = \frac{1}{21}(-5a_5 + \sqrt{25a_5^2 - 63a_3 a_7})/a_7 \quad (31)$$

and the corresponding value of H_0' at the inflection point is given by

$$H_0' = (a_1' + a_3 M_6'^2 + a_5 M_0'^4 + a_7 M_6'^6) M_0' . \quad (32)$$

The condition that the critical field H_c in equilibrium becomes zero in the case given by the curve 4 in figure 4 is obtained from the fact that two minimum values of f at M_1 and M_2 are equal, where M_1^2 and M_2^2 are given by the smallest and largest positive roots of the equation

$$H(M) = a_1' + a_3 M^2 + a_5 M^4 + a_7 M^6 = 0 ,$$

respectively, and it is given by

$$a_1' - \frac{1}{9}a_3 a_5/a_7 + \frac{1}{9}(3a_3 - a_5^2/a_7)(M_1^2 + M_2^2) = 0 . \quad (33)$$

Then the condition for MT between the weak ferromagnetic and normal ferromagnetic states can be written from equations (30) and (33) as

$$\frac{1}{9}a_3 a_5/a_7 - \frac{1}{9}(3a_3 - a_5^2/a_7)(M_1^2 + M_2^2) < a_1' < -\left(2a_3 + \frac{5}{3}a_5 M_0'^2\right) M_0'^2 . \quad (34)$$

This condition can be rewritten approximately as

$$-\frac{3}{8}\frac{a_3^2}{a_5} + \frac{17}{48}\frac{a_3 a_5}{a_7} + \frac{93}{288}\frac{a_5^3}{a_7^2} < a_1' < -\frac{3}{4}\frac{a_3^2}{a_5} + \frac{10}{7}\frac{a_3 a_5}{a_7} - \frac{500}{1\,323}\frac{a_5^3}{a_7^2} . \quad (35)$$

The critical fields H_c' and H_c'' are defined by $H_c' = H(M_3)$ and $H_c'' = H(M_1)$, respectively, where $H(M)$ is given by equation (29) and M_3 and M_1 are the largest and smallest positive roots of the equation $dH(M)/dM = 0$. The critical field H_c in equilibrium is given by the solution of equation

$$H_c = \left\{\frac{1}{2}a_1' + \frac{1}{4}a_3(M_1^2 + M_3^2) + \frac{1}{6}a_5(M_1^4 + M_1^2 M_3^2 + M_3^4) + \frac{1}{8}a_7(M_1^6 + M_1^4 M_3^2 + M_1^2 M_3^4 + M_3^6)\right\}(M_1 + M_3) ,$$

where M_1 and M_3 are the smallest and largest positive roots of the equation $H(M) = H$. The analytical expressions in this section are very complicated, because the analytical roots of the cubic equation have complicated expressions, but the numerical calculations of the critical conditions and the critical fields are very easy if the numerical values of all the coefficients a'_1, a_3, a_5 and a_7 are given.

5. **Comparison with the experimental results.** — From the experimental results obtained by Monod *et al.* [6] on the field dependence of M at 4.2 K up to 180 kOe for $TiBe_2$, which is similar to the curve 1 in figure 3*a*, the values of a'_1, a_3 and a_5 are estimated as

$$a'_1 = 1.18 \times 10^2 \text{ Oe (mole/emu)},$$

$$a_3 = -4.50 \times 10^{-5} \text{ Oe (mole/emu)}^3$$

and

$$a_5 = 6.58 \times 10^{-11} \text{ Oe (mole/emu)}^5,$$

where the unit of emu/mole for M is used, and we obtain the value of $a'_1 a_5/a_3^2 = 3.83$. From the experimental data obtained by Acker *et al.* [7] similar values of a'_1, a_3 and a_5 are obtained. Therefore, $TiBe_2$ does not satisfy the condition for MT given by equation (19). However, the recent data [31] shows that the relation between M and H cannot be described by a simple expansion like equation (13).

From the recent calculated results of the density of states for $TiBe_2$ the values of a_3 and a_5 at 0 K can be determined, but we obtain $a_3 > 0$ and $a_5 < 0$ from the calculated results by Jarborg and Freeman [32] and $a_3 \lesssim 0$ and $a_5 \gtrsim 0$ from the results by de Groot *et al.* [33].

For YCo_2 the values of a'_1 and a_3 are estimated as

$$a'_1 = 5.88 \times 10^2 \text{ Oe (mole/emu)}$$

and

$$a_3 = -1.53 \times 10^{-4} \text{ Oe (mole/emu)}^3,$$

respectively, from the data of Schinkel [5], but the value of a_5 cannot be determined, as the field is still not high enough to determine the value of a_5. Therefore, it is very difficult to say at present whether YCo_2 shows MT or not. If MT would occur in YCo_2, the critical field should be much higher than 380 kOe. Using the calculated density of states for YCo_2, Cyrot and Lavagna [8] predicted MT at 1 000 kOe, but from their calculated density of states a positive value of a_3 and a negative value of a_5 are estimated which are in contradiction with the conditions for MT and also with the experimental results of Schinkel [5], $a_3 < 0$.

For Pd the values of $a'_1 = 1.39 \times 10^3$ mole/emu [34] and $a_3 = -1.6 \times 10^{-4}$ Oe (mole/emu)^3 [3] are obtained experimentally, but the value of a_5 cannot be estimated as in YCO_2. Therefore, it is also very difficult to say at present whether Pd as well as YCo_2 shows MT or not. If MT would occur, the critical field should be much higher than 325 kOe. However, it seems that the calculated density of states for Pd [35] does not satisfy the condition $a_3 < 0$ and this fact is not favourable to MT in Pd.

6. **Discussion and conclusions.** — The MT has been found for many intermetallic compounds of the rare earth metals and transition metals, as shown in § 1. The MT is not necessarily sharp [10, 11] and the field dependence of M is very similar to that given by the curve 1 or 2 in figure 3*a*. However, as the first-order transition has been found in other properties of these compounds at $H = 0$ and therefore MT should occur. The broad transition may be attributed to the effect of defects, distribution of concentration, magnetostriction or any micro-structure in these compounds.

For the compounds of the heavy rare earth metals and transition metals the combined model of the localized moment on the rare earth atoms and itinerant electrons on transition metals will be appropriate and the expression of f in equations (8) and (9) is useful to discuss MT in these compounds. In order to satisfy the condition of MT given by equation (19), where a'_1, a_3 and a_5 should be replaced by c_1, c_3 and c_5, respectively, the value of c_3 or a_3 must be largely negative and the values of c_1 and c_5 must be small. It is easily seen from equation (9) these conditions can be much easily satisfied in the combined model than in the simple itinerant electron model, especially the values of c_1 and c_5 are reduced in this combined model. Sometimes c_5 may become negative at low temperature and in this case we have to take into account the higher order terms than $c_5 M^5$ in the expansion of f in equation (8), as the values of M are always limited.

In the combined model of the localized moments and itinerant electrons the coefficients given by equation (9) always change their sign at high temperature if they are negative at low temperatures. The temperatures where these coefficients change their sign depend on the values of g, S, N, K, J, α and the shape of the density of states for the itinerant electrons. These facts will be the main reasons for the appearance of the various kinds of MT in the rare earth compounds. In this paper we have discussed only a few simple cases and we can easily extend the present discussions to more complicated MT.

In heavy rare earth-cobalt compounds the value of c_1 becomes negative below the temperature T_c, where the paramagnetic susceptibility is expected to diverge and which should be just below the first-order transition temperature T'_c, where $H_c = 0$, and the value of c_3 when $a_3 < 0$ becomes positive above a certain temperature higher than T'_c, as seen from equation (9). Therefore, the range of temperature, where the conditions for MT, i.e. equation (19) for c_1, c_3 and c_5 with $c_1 > 0$, $c_3 < 0$ and $c_5 > 0$, in the combined model are satisfied, is rather narrow and this result is consistent with the experimental results for RCo_2 [10, 11]. The detailed comparison between the present theory

and the experimental results for MT in RCo_2 will be published elsewhere.

Moreover, it is seen from equation (9) that c_3 can change its sign from the negative value due to a_3 at low temperature to the positive values with increasing temperature, even if a_3 does not become positive at high temperature, although the change of the sign in a_3 was assumed before to explain the first-order transition in RCo_2 [4]. As the dependence on H of M in YCo_2 does not show any bend toward the H-axis at 300 K [4], the value of a_3 in YCo_2 and also for itinerant electrons in RCo_2 will be always negative at least below 300 K.

It is interesting to note that MT in $Co(S, Se)_2$ compounds is rather sharp [15, 16], though there is a random distribution of two kinds of cobalt atoms with and without local moment. This result will be explained in the following way. The effect of the magnetostriction in the magnetizing process or any micro-structure is averaged out by the random distribution of two kinds of cobalt atoms and MT becomes sharp.

It is seen from the discussions in the previous sections the condition $a_3 < 0$ in the simple itinerant electron system, i.e. the paramagnetic susceptibility χ increases with the increasing field, is not sufficient to show MT. When $a_3 < 0$ at low temperature, χ at low temperature always increases with increasing temperature and shows a maximum, but even if χ shows a maximum in its temperature variation a_3 is not necessarily negative. Therefore, the existence of a maximum of χ in its temperature variation is, of course, not a sufficient condition for MT. The range of the values of the coefficients a'_1, a_3 and a_5 which satisfy the condition for MT given by equation (19) with $a'_1 > 0$, $a_3 < 0$ and $a_5 > 0$ is rather narrow and this will be the reason why there exist no simple materials which show MT, such as the transition metals to which the simple itinerant electron model can be applied.

Although $TiBe_2$, YCo_2 and Pd show a maximum in the temperature variation of χ and χ increases with increasing H, $TiBe_2$ clearly does not satisfy the condition for MT given by equation (19), then it is concluded that $TiBe_2$ will not exhibit MT. For YCo_2 and Pd there are not enough data at present to judge whether they exhibit MT, but it seems that these substances are also unlikely to exhibit MT.

Acknowledgments. — I wish to acknowledge stimulating discussions with D. Bloch, G. Chouteau, D. Gignoux, D. Givord, C. Lacroix, R. Lemaire and J. Voiron. I am also grateful to the University of Grenoble and C.N.R.S. for the support of my working in Grenoble. I am also grateful to F. Acker for discussions and a report of work prior to publication.

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