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# Density of states and magnetic properties of the rare-earth compounds RFe<sub>2</sub>, RCo<sub>2</sub> and RNi<sub>2</sub>

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**Résumé.** — La densité d'états des composés d'yttrium  $YM_2$  (M = Fe, Co, Ni) est calculée dans l'approximation des liaisons fortes. L'utilisation du modèle de Stoner permet d'en déduire leurs propriétés électroniques et magnétiques. Dans  $YCo_2$ , nous montrons qu'il importe d'introduire les effets des paramagnons pour expliquer leurs propriétés électroniques. L'interaction supplémentaire d-f introduite par les atomes de terres rares (R) dans  $RM_2$  est traitée dans une approximation Hartree-Fock. On a peu de changement pour les composés de fer et de nickel. Au contraire, dans les composés  $RCo_2$ , le champ d'échange dû aux atomes de terres rares peut produire un métamagnétisme collectif comme celui décrit par Wohlfarth et Rhodes [1] et le cobalt peut devenir magnétique. Cet effet vient de la position du niveau de Fermi de ces composés dans une large décroissance de la densité d'états. La température de Curie, l'ordre de la transition, l'effet d'un champ magnétique externe sont étudiés de la même façon. D'autres conséquences sont tirées du modèle.

Abstract. — The density of states of yttrium compounds  $YM_2$  (M = Fe, Co, Ni) is calculated within a tightbinding scheme. Using the Stoner model, conclusions are drawn about their magnetic and electronic properties. In  $YCo_2$ , we show that one has to introduce paramagnon effects in order to explain the electronic properties. The additional d-f interaction introduced by rare-earth atoms (R) in  $RM_2$  is treated with a Hartree-Fock approximation. Little change is obtained in iron and nickel compounds. Conversely, in  $RCo_2$  compounds, the exchange field due to the rare-earth atoms can produce collective metamagnetism as described by Wohlfarth and Rhodes [1] and cobalt becomes magnetic. This effect stems from the position of the Fermi level of these compounds in a steep decrease of the density of states. Curie temperature, order of the transition and effect of an external magnetic field are studied following this method. Other consequences are drawn from the model.

1. Introduction. — The study of the magnetic properties of  $RM_2$  (R = rare-earth and M = transition metal) is a subject of great interest. Although all possess the same MgCu<sub>2</sub> cubic Laves phase structure with very similar lattice parameters, they exhibit a wide variety of magnetic behaviour. Iron is magnetic in the RFe<sub>2</sub> compounds and Curie temperatures are always high; the magnetic moment of iron is nearly constant in all these compounds : it is of the order of 1.45  $\mu_B$  in YFe<sub>2</sub> and LuFe<sub>2</sub>, and reaches 1.6  $\mu_B$  in GdFe<sub>2</sub> [2]. On the other hand, nickel is never magnetic in the RNi<sub>2</sub> compounds [3], [4], [5]. YNi<sub>2</sub> and LuNi<sub>2</sub> are Pauli paramagnets, and the Curie temperatures of the others are particularly small. Finally RCo<sub>2</sub> are intermediate compounds : cobalt atoms possess magnetic moments only if the alloyed rare-earth is magnetic. So, YCo<sub>2</sub> and LuCo<sub>2</sub> exhibit Pauli paramagnetism [6], [7] and the cobalt magnetization is about 1  $\mu_{\rm B}$  in the other compounds [8].

These properties make the  $RM_2$  compounds particularly interesting for the study of the appearance of 3d magnetism. Magnetic transitions are generally of second order, except for  $DyCo_2$  [9],  $HoCo_2$  [6], and  $ErCo_2$  [10] which exhibit first order transitions.

Up to now, only cobalt compounds have received much attention from a theoretical point of view. In order to explain their paramagnetic behaviour, Bloch and Lemaire [11] developed a theory based on a collective electrons model. The cobalt moment is not intrinsic but induced in the d band by the exchange field due to the rare-earth. Along the same line, Bloch *et al.* [12] have related the order of the transition in  $RCo_2$  (i.e. the sign of the Landau parameter *B*) to the behaviour of the susceptibility in high magnetic fields. They also suggested that the Fermi level in  $YCo_2$  lies in a minimum of the density of states and fitted various experimental results to derivatives of the density of states at the Fermi level. This theory based on expansion does not permit a precise treatment of the first order transitions.

The aim of this paper is to go beyond such a theory by making full calculations and to extend it to the understanding of Ni and Fe compounds. In the first part, we calculate the density of states of the Laves phases YM<sub>2</sub> within a tight-binding scheme. We find that simple application of the Stoner criterion can explain the magnetic properties of these compounds. We show in a second part that this model accounts for the electronic properties of YFe<sub>2</sub> and YNi<sub>2</sub> but one needs to introduce paramagnon effects in order to explain those of  $YCo_2$ . In a third part, we are interested in the rare-earth compounds where a rare-earth replaces yttrium. This substitution introduces an additional interaction between the spin of the rare-earth and the spin of the conduction electrons. Within the Hartree-Fock approximation, this interaction is equivalent to an exchange field acting on the d electrons. We show that for iron and nickel compounds, this induces little change in the magnetic properties of the transition metal. The calculated values of the magnetizations agree with the CPA calculations of Szpunar and Kozarzewski [13] in  $Gd_{1-x}Ni_x$ ,  $Gd_{1-x}Fe_x$ ,  $Gd_{1-x}Co_x$  and  $Y_{1-x}Co_x$ . However, for cobalt compounds, we find that the exchange field can produce itinerant metamagnetism as described by Wohlfarth and Rhodes [1]. For large enough exchange field, cobalt becomes magnetic. This stems from the particular position of the Fermi level in these compounds which lies in a steep decrease of the density of states. In the last section, the order of the magnetic transitions is discussed. We find that the magnetic transition is second order except for the cobalt compounds with low Curie temperatures (DyCo<sub>2</sub>, HoCo<sub>2</sub>, ErCo<sub>2</sub>) where the shape of the density of states at the Fermi level induces a first order transition. This metamagnetism can also explain the magnetization curves above the Curie temperatures for these three compounds. In every case, Curie temperatures are calculated and agree with experimental results. We finally give experimental evidences for the particular position of the Fermi level in cobalt compounds.

2. Density of states of yttrium compounds. — The band structure of transition metals and alloys (or rare-earth) are well described in a Mott-Slater model [14] : a wide s band mixed with a narrower d band in which the Fermi level is located. Generally, one can neglect the s-d hybridization and the problem is reduced to the study of the single d band which can be described in a tight-binding approximation [15]. The density of states can then be computed from its moments [16], [17]. This is the case of intermetallic compounds between yttrium and 3d transition metals. The problem is treated here in two steps : first, the calculation of the paramagnetic density of states is carried out self-consistently on the atomic levels within a Hartree-Fock approximation in order to take account of the charge transfer [18]. Then, the magnetism of the compound is accounted for by splitting the up and down spin bands in a Stoner model : Stoner criterion can be used and the splitting value is

$$(Um + 2 \mu_{\rm B} B_{\rm a})$$

where :

U is the average Coulomb integral,

*m* is the average magnetization per atom and per orbital in  $\mu_{\rm B}$  and,

 $B_{\rm a}$  is the applied field.

2.1 DETERMINATION OF THE TIGHT-BINDING PARA-METERS. — Since yttrium is similar to rare-earths, we discuss at the same time the choice of the parameters for yttrium and rare-earth compounds. All of them crystallize in the MgCu<sub>2</sub> cubic Laves phase structure. There is equivalence between all the crystallographic sites of the transition metals and of the rare-earths. We have therefore to calculate the density of states for only two sites. The crystallographic parameter is quite constant all these compounds and is about 7.2 Å. Table I gives the type, the number and the distance of the neighbours of the different types

Table I. — Type, number and distance of the neighbours in  $RM_2$  compounds.

Atoms	Neighbourg	Number of	Distance	
Atoms	neighbours	neighbours	a	
R	R	4	$\sqrt{12}/8$	
R	Μ	12	$\sqrt{11}/8$	
Μ	Μ	6	$\sqrt{8/8}$	
Μ	R	6	$\sqrt{11}/8$	

of atoms. For the atomic levels, we take the values given by Herman and Skillman [19] in the configuration  $3d^{n+1} 4s^1$  for the transition metals. The 5d atomic levels increase little across the rare-earth series. Since this variation is very small (~ 10%), we will neglect it in a first approximation and take for the values of the atomic level of every rare-earth that of yttrium : -0.4088 Ryd. We have to consider three types of hopping integrals depending on whether the two neighbouring sites are occupied by two M atoms, two R atoms or one M atom and one R atom. We use for the first, the values given by Desjonqueres [17] corrected by a  $d^{-5}$  law for the inter-atomic distance d. For the second, assuming the same band width for all the rare-earths ([20] for example), we take the values deduced from the band calculations on hexagonal Gd [21] corrected in the same way. The mixed hopping integrals R-M are estimated, following Shiba [22], as the geometrical averages of the parameters relative to the pure metals.

	$\Delta E^0$ Ryd.	$\beta_{MM}$ Ryd.	$\beta_{\rm RR}$ Ryd.	$\beta_{\rm MR}$ Ryd.	z <sub>M</sub>	z <sub>R</sub>	Z <sub>av.</sub>
RFe <sub>2</sub>	0.55	$dd\sigma = -0.062 3dd\pi = 0.029 5dd\delta = -0.003 8$	$dd\sigma = -0.143$ $dd\pi = 0.071$ $dd\delta = 0$	$dd\sigma = -0.066$ $dd\pi = 0.028$ $dd\delta = 0$	7	1.7	5.23
RCo <sub>2</sub>	0.63	$dd\sigma = -0.046$ $dd\pi = 0.0207$ $dd\delta = -0.0026$	$dd\sigma = -0.143$ $dd\pi = 0.071$ $dd\delta = 0$	$dd\sigma = -0.061 5$ $dd\pi = 0.029$ $dd\delta = 0$	8.3	1.7	6.1
RNi <sub>2</sub>	0.71	$dd\sigma = -0.0375$ $dd\pi = 0.0168$ $dd\delta = -0.00207$	$dd\sigma = -0.143$ $dd\pi = 0.071$ $dd\delta = 0$	$dd\sigma = -0.055$ $dd\pi = 0.026$ $dd\delta = 0$	9.4	1.7	0.83

Table II. — Values of the difference  $\Delta E^0$  between the atomic levels R and M ( $\Delta E^0 = E_R^0 - E_M^0$ ), of the different overlap integrals and the number of d electrons introduced by the different atoms in RM<sub>2</sub> compounds.

Finally, we assume that each atom of iron, cobalt and nickel introduces 7, 8.3 and 9.4 d electrons as in the pure metal. Johansson's [23], Duthie and Pettifor's [24] results indicate that one must assign to each rare-earth between 1.5 and 2.5 electrons of d character. We will assume an average number of 1.7 d electrons per atom. Table II gives the values of the different parameters used in a band calculation for the RM<sub>2</sub> compounds.

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2.2 DENSITY OF STATES OF YTTRIUM COMPOUNDS  $YFe_2$ . — For U = 4 eV, the self consistent calculation of the density of states gives 1/3 electron for the charge transfer per atom of iron. The atom with the lower atomic level receives electrons. The local paramagnetic density of states in Fe  $(n_{\rm Ee}(E))$  correct to the 16th moment is given in figure 1a; the zero of energy is taken at the middle of the atomic levels of Fe and Y. The Fermi level is  $E_{\rm F} = -0.117$  Ryd. This corresponds to a high density of states, and the Stoner criterion is satisfied :  $Un_{Fe}(E_F) = 1.4$ . The local density of states in Y is very flat over a wide range around the Fermi level. We can therefore neglect the magnetization of the 4d electrons for yttrium. The magnetic moment of iron deduced from the Stoner conditions is 1.48  $\mu_{\rm B}$ , in good agreement with the experimental values of 1.45  $\mu_{\rm B}$ . The values  $E_{\rm F\uparrow}$  and  $E_{\rm F\downarrow}$  of the Fermi level of the up and down spin bands are indicated in the same figure. It is worth noting that YFe<sub>2</sub> exhibits weak ferromagnetism.

YNi<sub>2</sub>. — For U = 4 eV, the self consistent calculation gives a charge transfer per atom of nickel of the same order. The local density of states in Ni  $(n_{\text{Ni}}(E))$  correct to the 16th moment is given in figure 1b, taking the zero of energy at the middle of the atomic levels of Y and Ni. The Fermi level is  $E_{\text{F}} = -0.031 \text{ Ryd}$ . The corresponding density of states is very small and Stoner criterion is not satisfied :  $Un_{\text{Ni}}(E_{\text{F}}) = 0.033$ . YNi<sub>2</sub> is Pauli paramagnetic.

<u>YCo<sub>2</sub></u>. — For U = 4 eV, the charge transfer is again 1/3 electron per atom of cobalt. The local density

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of states in Co  $(n_{Co}(E))$  correct to the 16th moment is given in figure 1c with the same convention for the energy origin. The Fermi level is  $E_{\rm F} = -0.0965$  Ryd.



Fig. 1. — (a) Local density of states at the Fe in YFe<sub>2</sub>. (b) Local density of states at the Ni in YNi<sub>2</sub>. (c) Local density of states at the Co in YCo<sub>2</sub>.

This corresponds to an intermediate density of states, and Stoner criterion is nearly satisfied :

$$Un_{\rm Co}(E_{\rm F})=0.85$$

Neither yttrium nor cobalt exhibits magnetic moments.  $YCo_2$  is Pauli paramagnetic.

<u>Conclusion</u>. — The densities of states of these three compounds look much alike. Roughly they originate from an overlap between the narrow 3d band of the transition metal (about 0.3 Ryd. wide) with high densities of states, and the wider 4d band of yttrium (about 0.5 Ryd. wide) with low densities of states. The Fermi level lies in the *flat* region of the band for YNi<sub>2</sub>, in the *high* region for YFe<sub>2</sub>, and in the *intermediate* region for YCo<sub>2</sub> which corresponds to a decreasing density of states. The value of the density of states (local in transition metal) at the Fermi level decreases from YFe<sub>2</sub> to YNi<sub>2</sub> through YCo<sub>2</sub>. Only YFe<sub>2</sub> satisfies Stoner's criterion and is ferromagnetic.  $Un_{Co}(E_F)$  is close to the critical value 1 in YCo<sub>2</sub>.

3. Electronic properties of yttrium compounds : effects of paramagnons. — The values of the electronic specific heat  $\gamma$  drawn from the calculations of densities of states are in good agreement with experimental results in YFe<sub>2</sub> and YNi<sub>2</sub> : respectively 6 and 6.5, 1.8 and 1.8 mJmole<sup>-1</sup> K<sup>-2</sup>. This is not the case for YCo<sub>2</sub> where the theoretical value is much smaller than the experimental one : we attribute this difference to the effects of paramagnons in the crystal. These effects are important as the Stoner criterion is nearly satisfied in YCo<sub>2</sub>. Two experimental results confirm this assumption. First, Muraoka's measurements [25] on the Y(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub> pseudo-binary alloys give a maximum of  $\gamma$  for x = 0.9(Fig. 2). Assuming a common density of states for Y(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub> and Y(Co<sub>1-x</sub>Ni<sub>x</sub>)<sub>2</sub>, our band cal-



Fig. 2. — Experimental variation of the electronic specific heat in  $Y(Fe_{1-x}Co_x)_2$ .

culations lead to a decrease of  $n(E_{\rm F})$  i.e.  $\gamma$  from YFe<sub>2</sub> to YNi<sub>2</sub> through YCo<sub>2</sub>. Taking into account paramagnons will give an increase in  $\gamma$  near to the critical concentration where magnetism appears. Our band calculation gives the critical value x = 0.85 in Y(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub> close to the experimental one. Measures of  $\gamma$  on Y(Co<sub>1-x</sub>Ni<sub>x</sub>)<sub>2</sub> would be of great interest since we do not expect any paramagnon effect. Another proof is given by the thermal variation of the susceptibility in YCo<sub>2</sub> and LuCo<sub>2</sub> [6], [7] (Fig. 3). While the susceptibility at zero temperature is directly proportional to  $R = |1 - Un(E_{\rm F})|^{-1}$ , the coefficient of the  $T^2$  term seems to be proportional to R as a classical Stoner theory would predict.



Fig. 3. — Thermal variation of the susceptibility in  $YCo_2$  and  $LuCo_2$ .

4. Electronic structure and magnetic properties of the rare-earth compounds at zero temperature. — We use in the description of the intermetallic compounds between a rare-earth and a transition metal, a model similar to that of RKKY and De Gennes for the rare-earth metals [26], [27], [28]. We consider the compound as a periodic arrangement of 4f impurities (rare-earth atoms) embedded in the sea of conduction electrons formed by the 3d and 4s electrons of the transition metal, and the 5d and 6s electrons of the rare-earth. Because of the strong similarity of yttrium to the other rare-earths, the conduction band in these compounds is the same as in yttrium compounds (cf. § 2).

The effect of the additional d-f interaction between f and d electrons spins is only to split the up and down spin bands.

4.1 BAND SPLITTING DUE TO THE d-f INTERACTION. — The magnetic rare-earth compounds differ from  $YM_2$  by the additional «d-f» interaction of the Ruderman and Kittel type [26]. If the crystal is formed of 4f impurities localized at  $\mathbf{R}_n$  with spin  $\mathbf{S}_n$ , every conduction electron with the spin  $\mathbf{s}(\mathbf{r})$  interacts with the others by the Hamiltonian :

$$v = -\sum_{n} \Gamma(\mathbf{r} - \mathbf{R}_{n}) \mathbf{s}(\mathbf{r}) \cdot \mathbf{S}_{n}$$
(1)

where  $\Gamma(\mathbf{r} - \mathbf{R}_n)$  is the exchange constant.

Within a Hartree-Fock approximation, the effect of the d-f interaction is to split the up and down spin bands. The total splitting of the bands due to the d-d, d-f interactions and to an applied magnetic field is

$$Um + 2 \mu_{\rm B} B_{\rm a} + \Gamma(g-1) \langle J_z \rangle \tag{2}$$

where  $(g-1) \langle J_z \rangle$  is the average value of the spin of the rare-earth atoms projected on an z axis and  $\Gamma$  a negative effective exchange constant which does not depend much on the rare-earth.

The d-f interaction and the application of a magnetic field play similar roles. One can interpret the d-f interaction within the molecular field approximation. If we call  $B_E$  the molecular field created inside the crystal by the rare-earth atoms, and  $\lambda$  the molecular field coefficient, we have :

$$\Gamma(g-1) \langle J_z \rangle = 2 \,\mu_{\rm B} \,B_{\rm E} \tag{3}$$

$$B_{\rm E} = \lambda \langle M_{\rm R} \rangle = \lambda g \mu_{\rm B} \langle J_z \rangle \tag{4}$$

where  $\langle M_{\rm R} \rangle$  is the average magnetic moment of a rare-earth atom. One can deduce the relation between the phenomenologic molecular field coefficient  $\lambda$  and the more microscopic constant  $\Gamma$ :

$$\Gamma = 2 \frac{g\mu_{\rm B}^2}{g-1} \lambda .$$
 (5)

The total splitting between the up and down spin bands can be written :  $(Um + 2 \mu_B B_T)$  where  $B_T$  is the field on the M atoms, coming from both the applied field and the molecular field created by the rare-earth atoms. We have the following conditions :

$$\int_{E_{1}}^{E_{1}} n(E) dE + \int_{E_{2}}^{E_{2}} n(E) dE = N$$

$$\int_{E_{1}}^{E_{1}} n(E) dE - \int_{E_{2}}^{E_{2}} n(E) dE = m$$

$$(E_{1} - E_{2}) = Um + 2 \mu_{B} B_{T}$$
(6)

where N is the number of d electrons per orbital and per atom and m is the average magnetic moment per orbital and per atom in Bohr magnetons.

4.2 RFe<sub>2</sub> AND RNi<sub>2</sub> COMPOUNDS. — All the RFe<sub>2</sub> compounds have the same electronic structure as YFe<sub>2</sub> (cf. Fig. 1*a*). Neglecting the 5d magnetization of the rare-earth, the conditions (6) allow us to determine the variation of the magnetization  $M_{\rm Fe}$  per atom of iron as a function of  $J_z$  of the rare-earth for temperature and field equal to zero. This variation is represented in figure 4. Taking  $\Gamma$  equal to  $10^{-2}$  eV [11], one notes that the iron moment changes little with alloyed rare-earth : it is 1.48  $\mu_{\rm B}$  in YFe<sub>2</sub> and LuFe<sub>2</sub>, and reaches only 1.6  $\mu_{\rm B}$  in GdFe<sub>2</sub>. The



Fig. 4. — Variation of the iron magnetization as a function of  $\Gamma(g-1) J_z$  in YFe<sub>2</sub>.

value of saturation is never reached; the  $RFe_2$  compounds exhibit *weak ferromagnetism*. These results agree with experiments on the  $RFe_2$  compounds [2]. Generally, the iron magnetization varies little with the magnetic field whether it results from the application of an external magnetic field, or from the molecular field created by the rare-earth atoms.

The  $RNi_2$  compounds have the same electronic structures as  $YNi_2$  (cf. Fig. 1*b*). The density of states is very flat over a wide region around the Fermi level so that the nickel magnetization is practically equal to zero whatever the rare-earth. This corresponds to one of the important experimental results obtained on the RNi<sub>2</sub> compounds [29].

4.3 RCo<sub>2</sub> COMPOUNDS. — The density of states of YCo<sub>2</sub> around  $E_{\rm F}$  displayed in figure 5*a* leads to the magnetization curve shown in figure 5*b*. The interpretation is as follows. The solution of the conditions (6) corresponds to an extremum of the free energy of the system and is

stable if 
$$\frac{U}{\frac{1}{2 n\uparrow(E_{\rm F})} + \frac{1}{2 n\downarrow(E_{\rm F})}} < 1$$

(then the susceptibility is positive) and

unstable if 
$$\frac{U}{\frac{1}{2 n \uparrow (E_{\rm F})} + \frac{1}{2 n \downarrow (E_{\rm F})}} > 1$$
  
(the susceptibility is negative).

In our case,  $Un(E_{\rm F})$  is lower than one at zero field and  $\frac{U}{\frac{1}{2 n\uparrow(E_{\rm F})} + \frac{1}{2 n\downarrow(E_{\rm F})}}$  increases first to a value

greater than one before decreasing as the splitting develops. This explains the shape of the curve and is related to the decreasing density of states at the Fermi level. Applying Maxwell's theorem, the system goes from state (1) to state (3) for a critical value  $B_T$ 



Fig. 5. — Variation of the cobalt magnetization with  $B_{\rm T}$  (b) for the YCo<sub>2</sub> density of states represented in (a).

which is such as to equalize the two hatched areas in figure 5b. This corresponds to the collective electrons metamagnetism of Wohlfarth and Rhodes [1]. Here, the critical field is nearly 100 T. The cobalt is magnetic only if the exchange field created by the rare-earth is large enough. This is realized for any magnetic rare-earth and agrees quite well with experimental results [30].

5. Effect of temperature and order of the transition. — All the previous results have been obtained at zero temperature (cf. conditions (6)). We now study the effect of temperature on these compounds and deduce the order of the magnetic transitions. We then study the behaviour in magnetic field of the compounds which exhibit a first order transition.

5.1 RFe<sub>2</sub> AND RNi<sub>2</sub> COMPOUNDS. — The curve  $M_{\rm Fe} = f(B_{\rm T})$  changes with temperature as shown in figure 6 (where  $M_{\rm Fe}$  is the iron magnetization per atom). Without the crystalline field effects, the rareearth magnetization is  $gJ\mu_{\rm B}$  per atom. The internal field  $B_{\rm T}$  seen by d electrons is due to the rare-earth moments and can be written in the molecular field approximation :

$$B_{\rm T} = g J \mu_{\rm B} \,\lambda_{\rm RFe} \,\mathfrak{B}_J \left(\frac{2 \,g J \mu_{\rm B} \,\lambda_{\rm RFe} \,M_{\rm Fe}}{kT}\right) \qquad (7)$$

where  $\lambda_{RFe}$  is the molecular field coefficient.

The corresponding variation of the internal field  $B_T$  created by the rare-earth atoms as a function of the iron magnetization is also shown in figure 6. At each temperature, the iron magnetization is given by the ordinate of the intersection of the two curves. The transition is second order and occurs when the two curves are tangent at the origin. Using the relation (6), the transition temperature is :

$$k\theta_{\rm c} = \frac{\Gamma^2(g-1)^2 J(J+1)}{6 \,\mu_{\rm B}^2} \,\chi(\theta_{\rm c}) \,. \tag{8}$$

In our model,  $\chi$  is the paramagnetic susceptibility



Fig. 6. — Discussion on the transition temperatures in  $RFe_2$ .

of  $YFe_2$ . Experimentally, this susceptibility obeys to a Curie-Weiss law :

$$\chi(T) = \frac{C}{T - \theta_0} \tag{9}$$

where C and  $\theta_0$  are respectively the Curie constant and temperature of YFe<sub>2</sub> ( $\theta_0 = 542$  K). In order to test the theory, we calculate from equations (8) and (9) the values of the Curie constant which permit a fit to the experimental ordering temperatures of different RFe<sub>2</sub> compounds [31]. Table III shows that C does not change much and is close to the experimental Curie constant [32] of YFe<sub>2</sub> (2  $\mu_B$  KT<sup>-1</sup> at<sup>-1</sup>).

For the RNi<sub>2</sub> compounds, the magnetic transitions are always second order. The Curie temperatures are given by relation (8) where  $\chi$  is the YNi<sub>2</sub> susceptibility which is constant with temperature. Table III gives the theoretical values of the susceptibility  $\chi$  which fit the experimental Curie temperatures of the RNi<sub>2</sub> compounds [31]. We note that this susceptibility is close to the experimental value for YNi<sub>2</sub> [3], [4] (1.25  $\mu_{\rm B}$  T<sup>-1</sup> at<sup>-1</sup>).

5.2  $RCo_2$  compounds. — We distinguish in this section the problem of  $RCo_2$  with a heavy and with a light rare-earth. The first generally exhibit first order transition except particular cases (GdCo<sub>2</sub>, TbCo<sub>2</sub>), the second have always second order transition.

 $RCo_2$  with a heavy rare-earth. — For  $RCo_2$  with a heavy rare-earth, the magnetization curve (Fig. 5) becomes distorted with temperature. We assume in the following that the point  $(B_{crit}, M_{crit})$  $(B_{crit} \approx 100 \text{ T} \text{ and } M_{crit} \approx 1 \mu_B)$  remains on the curve at each temperature. This hypothesis stems from the constancy of the cobalt magnetization and of the critical field for all these compounds. At each temperature, the cobalt magnetization is given by the ordinate of the intersection of this curve with the

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	RFe <sub>2</sub>	RFe <sub>2</sub>	RNi <sub>2</sub>	RNi <sub>2</sub>
R	$\theta_{\rm c} \exp.$ in K	$C \mu_{\rm B}  {\rm KT}^{-1}  {\rm at}^{-1}$	$\theta_{\rm c}$ exp. in K	$\chi 10^{-3} \mu_{\rm B}  {\rm T}^{-1}  {\rm at}^{-1}$
	_			
Sm	688	3.4	21	1.3
Gd	782	1.9	85	1.5
Tb	705	1.8	45	1.2
Dy	638	1.5	30	1.2
Ho	614	1.6	22	1.4
Er	596	2.1	21	2.2

Table III. — Transition temperatures of RFe<sub>2</sub> and RNi<sub>2</sub>.

corresponding Brillouin curve. One can then define three temperatures (Fig. 7) :

— the second order transition temperature  $\theta_c$  for which the two curves are tangent at the origin. It is defined by relation (8),

— the first order transition temperature  $T_c$  for which the Brillouin curve goes through the critical point  $(B_{crit}, M_{crit})$ ,

— the temperature  $T_0$  for which the tangent at the origin of the Brillouin curve goes through the critical point. One can assume equality of  $T_0$  and  $T_c$  to first order.



Fig. 7. — Discussion on the transition temperatures in  $RCo_2$ .

If  $\theta_c$  is larger than  $T_c$ , the magnetization develops continuously when the temperature decreases. The transition is second order. Conversely, if  $\theta_c$  is lower than  $T_c$ , the transition is first order. In order to know the order of the transition, we have to compare the temperatures  $\theta_c$  and  $T_c$ , that is to say, to a first approximation  $\theta_c$  and  $T_0$ .  $T_0$  is defined as follows :

$$kT_0 = \frac{\Gamma^2(g-1)^2 J(J+1)}{6 \,\mu_{\rm B}^2} \,\frac{M_{\rm crit}}{B_{\rm crit}}\,.$$
 (10)

Comparing the temperatures  $\theta_c$  and  $T_0$  amounts to comparing  $\chi$  and  $M_{crit}/B_{crit}$ . As long as the susceptibility is lower than the critical value

$$\chi_{\rm crit} = M_{\rm crit}/B_{\rm crit}\,,$$

the transition is first order. It becomes second order when  $\chi$  becomes larger than the critical value  $\chi_{crit}$ .

Experimentally, the paramagnetic susceptibility of  $YCo_2$  exhibits a broad maximum near to 250 K and reaches this critical value near 200 K

$$(\chi_{\rm crit} = 0.007 \ \mu_{\rm B} \ {\rm T}^{-1} \ {\rm at}^{-1})$$
.

Thus, we find that as long as the Curie temperature is lower than 200 K (DyCo<sub>2</sub>, HoCo<sub>2</sub>, ErCo<sub>2</sub>), the transition is first order. It becomes second order when transition temperatures are larger than 200 K, i.e. for GdCo<sub>2</sub> and TbCo<sub>2</sub>. The second order transition temperatures  $\theta_c$  of these two compounds deduced from equation (8) are respectively 350 and 230 K : these values agree with the experimental values [31] of 404 K and 230 K. For DyCo<sub>2</sub>, HoCo<sub>2</sub> and ErCo<sub>2</sub>,  $T_c$  is given by :

$$B_{\rm crit} = \frac{\Gamma(g-1)J}{2\,\mu_{\rm B}}\,\mathfrak{B}_J\left(\frac{\Gamma(g-1)J}{\mu_{\rm B}}\,\frac{M_{\rm crit}}{kT_{\rm c}}\right).$$
 (11)

As  $(T_0 - T_c)$  is small, we can expand the Brillouin function to third order and get :

$$\frac{\Delta T}{T_0} = \frac{T_0 - T_c}{T_0} = \frac{3 \,\mu_{\rm B}^2 \,B_{\rm crit}^2}{20 \,\Gamma^2} \,\frac{(2 \,J+1)^4 - 1}{(g-1)^2 \,J^3 (J+1)^3}\,.$$
(12)

The theoretical values of  $T_0$ ,  $\Delta T = T_0 - T_c$  and  $T_c$  for DyCo<sub>2</sub>, HoCo<sub>2</sub> and ErCo<sub>2</sub> are given in table IV. They are in good agreement with the experimental ordering temperatures [31].

Table IV. — Transition temperatures of the  $RCo_2$  compounds with heavy rare-earths.

RCo <sub>2</sub>	$T_0$ in K	$\Delta T$ in K	T <sub>c theor.</sub> in K	$T_{a exp}$ in K
		—		
DyCo <sub>2</sub>	148	10	138	135
HoCo <sub>2</sub>	94	10	84	77
ErCo <sub>2</sub>	53	10	43	33

Behaviour of the  $RCo_2$  compounds which exhibit a first order transition (DyCo<sub>2</sub>, HoCo<sub>2</sub>, ErCo<sub>2</sub>) in magnetic field. — For temperatures higher than the transition temperature, a magnetic field  $B_a$  must be applied to make cobalt magnetic in  $DyCo_2$ , HoCo<sub>2</sub> and ErCo<sub>2</sub>. Givord [9] has shown that the value of this field increases linearly with temperature; the corresponding slope increases from ErCo<sub>2</sub> to HoCo<sub>2</sub>, and from HoCo<sub>2</sub> to DyCo<sub>2</sub>. Theoretically, the transition occurs when the Brillouin curve goes through the critical point ( $B_{crit}$ ,  $M_{crit}$ ) :

$$B_{\rm crit} = \frac{\Gamma(g-1)J}{2\,\mu_{\rm B}} \times \\ \times \mathcal{B}_J \left( \frac{\Gamma(g-1)J}{\mu_{\rm B}} \frac{M_{\rm crit}}{kT} + \frac{gJ\mu_{\rm B}B_{\rm a}}{kT} \right). \quad (13)$$

Expansion of the Brillouin function to first order gives :

$$\frac{T - T_{\rm c}}{B_{\rm a}} = \frac{\Gamma}{6 \, k B_{\rm crit}} \, g(g - 1) \, J(J + 1) \,. \tag{14}$$

The magnetic field  $B_a$  increases linearly with temperature. g(g - 1) J(J + 1) increases in value from Er to Dy so the slope of the straight line  $T = f(B_a)$ increases from Er to Dy. Theoretical values of these slopes are given in table V as well as the experimental. Good agreement is obtained.

Table V. — Slopes of the straight lines  $T = f(B_a)$  for DyCo<sub>2</sub>, HoCo<sub>2</sub> and ErCo<sub>2</sub>.

$$\begin{array}{ccc} \text{RCo}_{2} & \left(\frac{T-T_{c}}{B_{a}}\right)_{\text{theor}} (\text{in KT}^{-1}) & \left(\frac{T-T_{c}}{B_{a}}\right)_{\text{exp.}} (\text{in KT}^{-1}) \\ \hline \\ \hline \\ \text{DyCo}_{2} & 8.2 & 11 \\ \text{HoCo}_{2} & 6.4 & 4 \\ \text{ErCo}_{2} & 4.3 & 2 \end{array}$$

 $RCo_2$  with a light rare-earth. — The  $RCo_2$ compounds with a light rare-earth exhibit second order transition for temperatures lower than 200 K. We give a different explanation than Bloch et al. [12]. As the Stoner criterion is nearly satisfied in YCo<sub>2</sub>, the RCo<sub>2</sub> serie is very sensitive to small change in the density of states. The slight increase of the 5d atomic level across the rare-earth series [19] leads probably to values of  $n(E_{\rm F})$  slightly larger in the first part of the serie. This is confirmed by the experimental decrease of the electronic specific heat  $\gamma$ across the rare-earth serie [33], [10], [25]. This increase of  $n(E_{\rm F})$  would permit the paramagnetic susceptibility to become larger than the critical value  $\chi_{crit}$ and give a second order transition. Transition temperatures can be calculated from the relation (8). Table VI gives the values of  $\chi(\theta_c)$  corresponding to the experimental Curie temperatures [31]. We note that the values found are always larger than the critical value  $(\chi_{crit} = 0.007 \ \mu_B T^{-1} at^{-1})$ ; furthermore, the paramagnetic susceptibility effectively decreases across the rare-earth serie.

Table VI. — Transition temperatures of the  $RCo_2$  compounds with light rare-earths.

RCo <sub>2</sub>	$\theta_{c exp.}$ in K	$\chi(\theta_{\rm c}) \ \mu_{\rm B} \ {\rm T}^{-1} \ {\rm at}^{-1}$
PrCo <sub>2</sub>	45	0.019
$NdCo_2$	99	0.018
$SmCo_2$	208	0.015

6. Conclusions. — Generally speaking, the band structure of the  $RM_2$  compounds results from an overlap between the narrow 3d band of the transition metal with strong density of states, and the larger 5d(4d) band of rare-earth (yttrium) with low density of states. Three cases can then occur :

If the 3d band is not completely filled ( $RFe_2$  compounds) : the Stoner criterion is satisfied, and the transition metal atoms are magnetic.

If the 3d band is completely filled  $(RNi_2 compounds)$ : the Stoner criterion is not satisfied, and the transition metal atoms are never magnetic.

Finally if the 3d band is nearly filled ( $RCo_2$  compounds), the Stoner criterion is nearly satisfied, and the properties are peculiar.  $YCo_2$  is not magnetic; but if yttrium is replaced by another rare-earth, the molecular field created by the rare-earth atoms moves the spin up and spin down Fermi levels, and leads to Wohlfarth and Rhodes metamagnetism. This property is related to the position of the Fermi level in a *transition region* characterized by a decreasing density of states. Such a phenomenon could be found every time there is an overlap between two d bands of different widths for example in compounds between two transition metals.

In the paper, we have also shown that the model of an exchange effective field acting on d electrons permits a satisfactory explanation of the magnetic properties of the three series RM<sub>2</sub> as a function of temperature and applied magnetic field. The position of the Fermi level for YCo<sub>2</sub> in a decrease of the density of states leads to important asymmetric effects when alloying and moving the Fermi level. This would not be obtained if the Fermi level was lying in a minimum. In addition to the asymmetric variation of  $\gamma$  in Y(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub> and Y(Co<sub>1-x</sub>Ni<sub>x</sub>)<sub>2</sub> seen above, we predict important asymmetric effects related to the introduction of impurities in these alloys. The effect of an impurity in YCo<sub>2</sub> must depend very much upon its character. Any impurity decreasing the number of cobalt electrons, moves the Fermi level to lower energies and increases the paramagnetic susceptibility. The cobalt atoms of  $YCo_2$  can even become magnetic, depending upon impurity concentration (A, Fe...). Experimentally, there is an increase of the YCo<sub>2</sub> paramagnetic susceptibility on the addition of aluminium impurities [34]; the compound becomes magnetic for iron concentrations larger than 10 %. Conversely, any impurity adding electrons Nº 8

to cobalt atoms, decreases the paramagnetic susceptibility of the compound. Whatever the impurity concentration, the compound remains paramagnetic. It would be interesting to study the experimental effects of such impurities (Ni, Cu probably). This model also allows us to understand, why the variation of the RCo<sub>2</sub> Curie temperature with a heavy rare-earth (HoCo<sub>2</sub> for example) depends upon the nature of the added impurity [35]. Recent experiments on the electrical resistivities of (Ho, Y) Co<sub>2</sub> [36] also confirm our result on the position of the Fermi level.

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