

MAGNETIC PROPERTIES AND ELECTRONIC STRUCTURE OF
RARE-EARTH-TRANSITION METAL INTERMETALLIC COMPOUNDS

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ABSTRACT

A model for the electronic structure of the $R_x M_y$ intermetallic compounds is proposed in which the s electrons are spread over the crystal and the d states are localized on the transition metal sites. We distinguish between two cases: 1) magnetism driven by the localized f moments (e.g. $GdCo_2$), and 2) magnetism sustained by the d band (e.g. $LuFe_2$). These two situations are discussed in terms of an effective s - d coupling and an s - f exchange; the transition metal magnetic moment in case 2) is calculated using a simple model. The rare-earth hyperfine fields and isomer shifts, as well as the total paramagnetic susceptibility of the compound are also considered. Finally, the effects of V_{sd} hybridization are studied as they provide a mechanism for the effective s - d coupling.

1. INTRODUCTION

The magnetic properties of the $R_x M_y$ intermetallic compounds where R is a rare-earth and M is a transition metal have been investigated experimentally using a number of techniques (Taylor 1971)¹. In the present work we will make use of the magnetic hyperfine field data, isomer shifts and information on the presence of magnetic order to suggest a model for the electronic structure of these compounds; some general features of this model were given in an earlier publication (Gomes 1972)².

We will use a simple band consisting of s and d electrons, with a sharp f level, the d band being formed of 5d states from the rare-earth metal and nd states from the transition metal. The s electrons are spread out through the entire crystal and have 6s-ns character ($n = 4,5,6$). The degree of localization of the d electrons on the M sites, however, varies from 3d, to 4d, and 5d transition metals. When M is a 3d metal the energy difference between the 3d electrons and the rare-earth 5d electrons is so large that the d electrons are well localized on the M site; as we change to 4d or 5d transition elements the density of d electrons on the lanthanide site tends to increase (this is discussed in more detail in section 4). On the basis of this reasoning we will altogether neglect the density of d electrons on the R sites, when considering compounds with 3d transition metals.

The magnetic moment of the rare-earth 4f shell and the d magnetic moment associated to the transition metal are antiparallel when R is a heavy rare-earth, and parallel when R is in the first half of the lanthanide series; since $J = L + S$ for the heavy rare-earths and $J=L-S$ for the light rare-earths, it follows that the spins of the f and d elec-

trons are always antiparallel. The d moments attributed to the transition metals in the compounds are generally smaller than the moments in the pure metals, but in some cases may have comparable values.

Let us compare initially the magnetic behaviour of intermetallic compounds containing iron ($M=Fe$) with those formed with cobalt. In Fig. 1 the magnetic ordering temperatures of several $R_x Co_y$ compounds (Taylor 1971)¹ are drawn against the rare-earth de Gennes factor. One notes that for lower cobalt concentrations (less than 67%) the curves pass through the origin (which corresponds to zero magnetic moment at the rare-earth site) thus showing that in the absence of rare-earth moment some Co systems cannot remain magnetic. For large concentrations of cobalt, however, magnetic order is sustained irrespective of the lanthanide moment. A different behaviour is found in the Fe intermetallic compounds; now the systems with 67% Fe remain magnetic even with zero lanthanide moment (as in $LuFe_2$) (Fig. 2) showing that in this case the interaction between d electrons is the main mechanism underlying the onset of magnetic order.

We will study the two possible cases of magnetic $R_x M_y$ intermetallic compounds: the intermetallic systems where the magnetic order results primarily from the effect of the localized f moments, typified by the RCo_2 (Section 2) and the compounds, represented by the RFe_2 , which become magnetic essentially as a result of interelectronic repulsion (similarly to the pure transition metals). In Section 4 the observed trends in the isomer shifts and the rare-earth excess hyperfine fields in the RM_2 compounds are shown to be in accordance with the model; expressions for the paramagnetic susceptibility of the compounds are derived in Section 5.

Finally, an attempt to justify the antiparallel coupling of s and d spins through s-d mixing (invoked in Sections 2 and 3) is given in Appendix A.

2. MAGNETISM DRIVEN BY THE f MOMENTS

We will consider intermetallic compounds formed with a 3d transition metal with moderate rare-earth concentration, like the RCo_2 series. In such a system, as stated above we regard the density of d electrons on the R site negligible. The exchange field due to the spin S of the 4f shell acting on the s band is obtained from:

$$-g_e \mu_B \vec{s} \cdot \vec{H}_{\text{exch}} = -J_{sf} \vec{s} \cdot \langle \vec{S} \rangle \quad (2-1)$$

which implies:

$$\vec{H}_{\text{exch}} = \frac{J_{sf} \langle \vec{S} \rangle}{g_e \mu_B} \quad (2-2)$$

The average s conduction electron magnetization on the rare-earth site is

$$\vec{m}_R^s = \chi_R^s \vec{H}_{\text{exch}} = \frac{J_{sf} \chi_R^s \langle \vec{S} \rangle}{g_e \mu_B} \quad (2-3)$$

which is parallel to the rare-earth spin (we expect $J_{sf} > 0$ since d-states are absent on the rare-earth site) (Gomes et al. 1972a). The s magnetization on the transition metal site will in general be different from that over R, but it is reasonable to find a proportionality between the s susceptibilities at the two sites, i.e.

$$\chi_M^s = \Gamma \chi_R^s \quad (2-4)$$

where Γ is a parameter to be determined. The magnetization at an M site is then

$$\vec{m}_M^S = \chi_M^S H_{\text{exch}} = \frac{\Gamma J_{sf} \chi_R^S \langle \vec{S} \rangle}{g_e \mu_B} \quad (2-5)$$

again parallel to the rare-earth magnetization. To calculate the magnetization of the d band we consider the s- and d-magnetizations coupled through s-d mixing, this mixing being described phenomenologically by a Hamiltonian of the form (Long and Turner 1970⁴, Gomes et al. 1972a³) $U \vec{S}^s \cdot \vec{S}^d$. We take that $U > 0$, i.e. the mixing couples the s and d spins antiparallel; this assumption is given a physical justification in Appendix A. Therefore

$$-g_e \mu_B \vec{S}^d \cdot \vec{H}^{ds} = U \vec{S}^d \cdot \langle \vec{S}_M^s \rangle \quad (2-6)$$

and the molecular field H^{ds} acting on the d electrons is (using $m_M^S = g_e \mu_B \langle S_M^s \rangle$)

$$\vec{H}^{ds} = - \frac{U \langle \vec{S}^s \rangle}{g_e \mu_B} = - \frac{U \vec{m}_M^S}{g_e^2 \mu_B^2} \quad (2-7)$$

Using Eq. (2-5) one arrives at

$$\vec{H}^{ds} = - \frac{U \Gamma J_{sf} \chi_R^S \langle \vec{S} \rangle}{g_e^3 \mu_B^3} \quad (2-8)$$

From Eq. (2-8) one sees that the effective field acting on the d electrons is antiparallel to the rare-earth spin, the same occurring with the d magnetization, which is given by

$$\vec{m}^d = \chi^d \vec{H}^{ds} = - \frac{U \Gamma J_{sf} \chi_R^s \langle \vec{S} \rangle}{g_e^3 \mu_B^3} \chi^d \quad (2-9)$$

Assuming for χ^d a strong exchange-enhanced susceptibility one gets for the d-like magnetization:

$$\vec{m}^d = - \frac{\chi^d(0)}{1 - \lambda_{dd} \chi^d(0)} \frac{U \Gamma J_{sf} \chi_R^s \langle \vec{S} \rangle}{g_e^3 \mu_B^3} \quad (2-10)$$

The experimentally observed antiparallel alignment between \vec{m}^d and the rare-earth spin is embodied in the above equations.

An alternative approximate version of equation (2-8) which will be useful later on is obtained by introducing the s-d mixing coefficients α_{sd} and α_{ds} . With the mixing described by $U \vec{S}^d \cdot \vec{S}^s$, the coefficients α_{sd} and α_{ds} are related to the interaction constant U and the susceptibilities by (Gomes et al. 1972a)³

$$\alpha_{sd} = \frac{U \chi^s}{g_e^2 \mu_B^2} \quad (2-11a) \quad \text{and} \quad \alpha_{ds} = \frac{U \chi^d}{g_e^2 \mu_B^2} \quad (2-11b)$$

We re-write Eq. (2-8) as

$$g_e \mu_B \vec{H}^{ds} = - \Gamma J_{sf} \langle \vec{S} \rangle \frac{U \chi_R^s}{g_e^2 \mu_B^2} \quad (2-12)$$

Then

$$g_e \mu_B \vec{H}^{ds} = -\Gamma J_{sf} \langle \vec{S} \rangle \alpha_{sd} \quad (2-13)$$

The α_{sd} coefficient is known from the study of transition metals to be of the order of 0.1, so that one can easily estimate the order of magnitude of the molecular field acting on the d electrons.

3. MAGNETISM SUSTAINED BY THE d-BAND

The $R_x Fe_y$ compounds and the cobalt based systems with more than 67% Co order magnetically even when the rare-earth spin is zero; in these cases the Stoner criterion $(1 - \lambda_{dd} \chi^d(0)) < 0$ is satisfied by the d band. The magnetization of the d states is transferred via H^{sd} to the s band and then coupled through J_{sf} to the lanthanide spin S, again providing antiparallel alignment of the d and rare-earth spins. To compute the d-band magnetization in a system where the Stoner criterion is satisfied we cannot, of course, use Eq. (2-10). We start by writing the Hartree-Fock energies of the d electrons in the presence of the effective field H^{ds} (which results from s-d mixing and s-band polarization induced by the local moment). This field describes the effect of the local moment on the stabilization of self-sustained d magnetization. These equations are:

$$\epsilon_{k\sigma} = \epsilon_k + I_{eff} \langle n_{-\sigma}^d \rangle - g_e \mu_B \sigma H^{ds} \quad (3-1a)$$

$$\epsilon_{k-\sigma} = \epsilon_k + I_{eff} \langle n_{\sigma}^d \rangle + g_e \mu_B \sigma H^{ds} \quad (3-1b)$$

where I_{eff} describes the effective Coulomb + exchange effects; the number of electrons with spin up and spin down $\langle n_{+\sigma}^d \rangle$ and $\langle n_{-\sigma}^d \rangle$ satisfy the conditions:

$$\langle n_{+\sigma} \rangle + \langle n_{-\sigma} \rangle = n^d \quad (3-2a)$$

$$\langle n_{+\sigma} \rangle - \langle n_{-\sigma} \rangle = \frac{2m^d}{g_e \mu_B} \quad (3-2b)$$

In order to solve the simultaneous equations (3-1) and (3-2) one has to know the curve for the density of d states ($N(\epsilon)$). In the absence of band calculations for this system and also for simplicity reasons we take a model density of states consisting of two overlapping parabolae (Fig. 3). These parabolae have equal heights and the degree of overlap is a parameter we can vary. We choose the parameters such that the total number of states of each spin sub-band is 5 in order to take into account the degeneracy of the d bands. It should be emphasized that the details of the band structure are quite critical for this type of problem and in fact we find (see below) that the variation of d magnetic moment with $\langle S \rangle$ is strongly dependent on the band shape.

In the $R\text{Fe}_2$ intermetallic compounds the iron moments vary from approximately $1.5 \mu_B$ (in LuFe_2) to about $2 \mu_B$ in GdFe_2 (e.g. Taylor 1971)¹; this corresponds to a change in the spin of the rare-earth from zero to $7/2$. From equation (2-13) one sees that the effective magnetic field H^{ds} is directly connected to the s-f exchange integral, to the ratio of the s susceptibilities, to the α_{sd} coefficient, and to the rare-earth spin.

The α_{sd} coefficient is known from the study of transition metals to be of the order of 0.1; since for GdFe_2 $S = 7/2$ and the iron moment is $2 \mu_B$, one can derive the value of the product ΓJ_{sf} . The parameters of the model band containing seven d electrons are obtained in two steps:

a) by postulating that the iron moment for $S = 0$ is equal to $1.5 \mu_B$, the resulting value of I_{eff} should agree with the estimates calculated in the band theory of transition metals; and b) the value of J_{sf} should be of the same order of magnitude as derived by other methods. In the case of zero magnetic field one obtains from the moment ($1.5 \mu_B$) and the assumed number of d electrons (seven) that $n_{\uparrow} = 4.25$ and $n_{\downarrow} = 2.75$. Using these numbers one gets the position of the Fermi level and the value of I_{eff} (from the energy splitting = $I_{eff} m^d$). For different values of the overlap (parameter α in Fig. 3) one gets values of I_{eff} which are of the same magnitude as those obtained by Wakoh and Yamashita (1966)⁵ for iron metal. The next step is then solving equations (3-1) and (3-2) self-consistently, using the value adopted for I_{eff} . The results of the calculation are shown in Fig. 4 where we have plotted the iron magnetic moment as a function of the magnetic energy $g_e \mu_B H^{ds}$. The sensitivity of the results for the overlap of the two parabolae is easily seen; it turns out that the larger the overlap of the two parabolic humps, the larger is the effect of the magnetic field. This is associated to the fact that the Fermi level lies in the overlap region of the \uparrow spin band, so that for small overlaps the density of states at the Fermi level on the \uparrow spin band is small, and consequently the effect of the field is also small. Now using equation (2-13) and the value of the field H_0^{ds} for which $m^d = 2$ (as deduced from Fig.4) one has:

$$\Gamma J_{sf} = \frac{g_e \mu_B H_0^{ds}}{0.35}$$

from which one may derive the value of ΓJ_{sf} ; the usual values of J_{sf} are of the order of 10^{-2} .

It remains to discuss the expected order of magnitude for the parameter Γ consistent with the present model for the intermetallic compounds. At the rare-earth site one expects to have a rather large local s density of states at the Fermi level as compared to the s density at the iron site, since one should accommodate 3 s-like electrons. On the transition metal site, on the other hand, almost all density of state is of d character, reducing in consequence the s contribution. One expects then

$\Gamma = \frac{n^S_M}{n^S_R} < 1$. These arguments of order of magnitude exclude the small overlaps ($\alpha > 0.5$) since one of these quantities Γ or J_{sf} would be larger than expected. For $\alpha < 0.5$ reasonable values of ΓJ_{sf} can be obtained. If one takes $\alpha = 0.4$ and assumes $J_{sf} \cong 0.08$ one gets $\Gamma = 5/8 < 1$.

Then, this crude model shows that for reasonable values of the parameters (in particular the overlap of the parabolae should provide significant d density of states) one can fit the observed variation of the iron magnetic moment with the rare earth spin. It should be emphasized that a theoretical density of states curve as obtained in a band calculation would be very important to check the results of this model.

4. HYPERFINE FIELDS AND ISOMER SHIFTS IN THE RM_2

We shall now proceed to discuss some nuclear hyperfine field and isomer shift data in the light of the present model for the RM_2 compounds. The magnetic hyperfine fields at the rare-earth nuclei in the RFe_2 inter-

metallic compounds are several hundred kilooersteds higher than the same fields in the free ions (e.g. Bleaney 1972)⁶; the value of this excess field in GdFe_2 is about 800 kOe (Gegenwarth et al. 1967)⁷.

The total hyperfine field at the rare-earth nuclei in the RM_2 compounds is a sum of two contributions: H_0 arising from an orbital term and polarization of the core electrons, and H_1 , the effect of the interaction with the polarized conduction electrons (s- and d-like). According to the model of section 2, in the intermetallic compounds of the form RFe_2 the term H_1 will arise¹ for s electrons only (Gomes 1972)²; the s electron hf field is given by

$$H = A(Z) m_R^{S^*} \quad (4-1)$$

where $A(Z) \approx 4 \times 10^3 \text{ kOe}/\mu_B$ for gadolinium (Campbell 1969)⁹. We cannot compute H with any reasonable accuracy, but we can verify that for a field of 800 kOe, the associated s magnetization on the rare-earth site is $0.2 \mu_B$, which is a value of the right order of magnitude. One therefore expects, from this approximate picture, hf fields in the RFe_2 intermetallic compounds higher than the free ion fields by several hundred kOe. The situation in the pure rare-earth metals is quite different; in these metals the magnetism is driven by the localized f moments, and consequently one can further split H_1 into two parts: one due to the ion's own spin, and the other due to the spins of the neighbouring ions, (both acting on conduction electrons of s and d character). It turns out that these two

¹ A similar idea has been independently suggested by Eagles (1972, private communication)⁸.

conduction electron polarization contributions are of the same order of magnitude, but have opposite signs, so that they partly cancel out, leaving a total hf field in the metal comparable to the free ion value (Hüfner and Wernick 1968)¹⁰.

The hf fields at the iron nuclei in the RFe_2 intermetallic compounds arise from the core polarization induced by the d electrons, and contact interaction with the s electrons: since the s magnetization m_M^s is antiparallel to the d magnetization m^d the two field terms have the same (negative) sign. As the s and d polarizations are modified by the rare-earth spins, (see Section 2) the iron hf fields are dependent on S. The experimentally observed dependence is very roughly linear, the fields increasing in absolute value with the rare-earth spin (e.g. Guimarães and Bunbury 1972)¹¹.

The rare-earth isomer shifts in the RM_2 , M being a 3d metal, measure the s electron densities at the nucleus, the shielding by the d electrons being negligible. When instead of a 3d metal M is a 4d or 5d transition metal, the energy difference between the 5d states of the rare-earth and the nd states on M decreases and the d density on the rare-earth sites increases (Gomes et al. 1972b)¹². Consequently the shielding of the s electrons by the d electrons increases as we go from 3d to 4d and then to 5d transition metals; this in turn decreases the effective s electron density at the rare-earth nucleus. This explains the systematic variation of the RM_2 isomer shifts measured with ^{161}Dy nuclei (Nowik et al. 1966)¹³ and also the shifts in the dipositive europium intermetallic compounds (Atzmony et al. 1967)¹⁴.

When one goes from $GdFe_2$ to $GdRh_2$ and then to $GdPt_2$ the Gd hyperfine fields change from +430 kOe to -170 kOe (Bleaney 1972)⁶, the number of

d states at the rare-earth site increases, and one tends towards the situation found in pure gadolinium metal, where the magnetism is driven by localized f moments.

5. SUSCEPTIBILITY IN THE PARAMAGNETIC PHASE

We now derive expressions for the susceptibility in the paramagnetic phase appropriate to intermetallic systems like RCo_2 , where the magnetism is driven by a localized f moment. We follow the main lines of the method used by Bloch and Lemaire (1970), but we take into account the details of the model discussed in part 2. We start defining the individual magnetizations existing at the two sites, namely the rare-earth site and the transition metal site: the magnetizations are m_R^S and m^f at the rare-earth site and m_M^S and m^d at the transition metal site. We introduce the molecular field coefficients λ_{ff} and λ_{fs} describing the coupling between f moments and f and s electrons. It should be emphasized that within the picture adopted here the d-state density is zero on the rare-earth site, and therefore the molecular field coefficient λ_{fd} is taken equal to zero. The d-states of the transition metal couple to the s-states through s-d mixing (described phenomenologically by the parameters α_{sd} and α_{ds}) and so can be coupled indirectly to the f moment. Finally intra-atomic Coulomb interactions acting within d-states and giving rise to exchange enhancement effects are included through a molecular field coefficient λ_{dd} . In this approximation the rare-earth site magnetizations are given by

$$m^f = \frac{C_f}{T} (H + \lambda_{ff} m^f + \lambda_{fs} m_R^S) \quad (5-1a)$$

$$m_R^S = \chi_R^S (H + \lambda_{fs} m^f) \quad (5-1b)$$

At the transition metal sites one has

$$m_M^s = \tilde{\chi}_M^s H - \alpha_{sd} m^d \quad (5-1c)$$

$$m^d = \chi^d(0) (H + \lambda_{dd} m^d) - \alpha_{ds} m_M^s \quad (5-1d)$$

In equations (5-1a) and (5-1b) C_f is the Curie constant of the rare-earth ion and χ_R^s is s-band susceptibility at the rare-earth site. One should note that the s-band susceptibility is in general not the same at the rare-earth and transition metal sites; we describe this geometric change through the relation

$$\chi_M^s = \Gamma \chi_R^s$$

In equation (5-1d) $\chi^d(0)$ is the Pauli susceptibility of the d-electrons, the exchange effects being included in the λ_{dd} coefficients. Finally $\tilde{\chi}_M^s$ in equation (5-1c) is the s-band susceptibility at the transition metal site in absence of s-d mixing effects, but in the presence of the localized f moments. It describes the fact that the s electrons carry the magnetization induced by the localized spin over to the transition metal sites, since there is no direct exchange interaction between f and d electrons. $\tilde{\chi}_M^s$ is given by

$$\tilde{\chi}_M^s = \Gamma \tilde{\chi}_R^s \quad (5-2)$$

Where $\tilde{\chi}_R^s$ is the total susceptibility (including exchange interactions with the localized spin) at the rare-earth site, the geometric factor Γ taking into account the difference between sites. The susceptibility $\tilde{\chi}_R^s$ is ob-

tained directly from equations (5-1a) and (5-1b). Now we solve explicitly equations(5-1) for the magnetizations involved; from equations (5-1b) and (5-2) one gets:

$$m^f = \frac{C_f (1 + \lambda_{fs} \chi_R^s)}{T - \theta} H \quad (5-3)$$

Where the paramagnetic Curie temperature θ is given by:

$$\theta = C_f (\lambda_{ff} + \lambda_{fs} \chi_R^s) \quad (5-4)$$

The magnetization of the s states at the rare-earth is

$$m_R^s = \chi_R^s \left\{ 1 + \frac{\lambda_{fs} C_f (1 + \lambda_{fs} \chi_R^s)}{T - \theta} \right\} H \quad (5-5)$$

Equations (5-3), (5-4) and (5-5) are solved for the magnetizations at the rare-earth; using equation (5-2) one obtains for the susceptibility $\tilde{\chi}_M^s$

$$\tilde{\chi}_M^s = \Gamma \chi_R^s + \Gamma \frac{C_f \lambda_{fs} \chi_R^s (1 + \lambda_{fs} \chi_R^s)}{T - \theta} \quad (5-6)$$

One sees that the susceptibility at the transition metal site in the absence of s-d mixing is the sum of the s-band value ($\Gamma \chi_R^s$) and the spin polarization contribution. Now we solve for the s and d magnetizations at the transition metal site; one gets from (5-1c) and (5-1d)

$$m^d = \frac{\chi^d(0) - \alpha_{ds} \tilde{\chi}_M^s}{1 - \lambda_{dd} \chi^d(0) - \alpha_{ds} \alpha_{sd}} H \quad (5-7)$$

and

$$m_M^s = \left\{ \tilde{\chi}_M^s - \frac{\alpha_{sd} \chi^d(0) - \alpha_{sd} \alpha_{ds} \tilde{\chi}_M^s}{1 - \lambda_{dd} \chi^d(0) - \alpha_{ds} \alpha_{sd}} \right\} H \quad (5-8)$$

The total susceptibility is defined as

$$\chi = \frac{1}{H} (m^f + m_R^s + 2m^d + 2m_M^s) \quad (5-9)$$

The factor 2 appears since we have two transition metals per formula unit. Using the expressions for the individual magnetization (Eqs. (5-5), (5-7) and (5-8)) we have, for the total susceptibility:

$$\chi = \chi_b + \frac{C_f (1 + \lambda_{fs} \chi_R^s)^2}{T - \theta} \left\{ 1 + 2 \frac{\lambda_{fs} \chi_M^s}{1 + \lambda_{fs} \chi_R^s} \times \frac{1 - \lambda_{dd} \chi^d(0) - \alpha_{ds}}{1 - \lambda_{dd} \chi^d(0) - \alpha_{sd} \alpha_{ds}} \right\} \quad (5-10)$$

With the band susceptibility χ_b defined as

$$\chi_b = \chi_R^s + \frac{2(1 - \alpha_{sd}) \chi^d(0)}{1 - \lambda_{dd} \chi^d(0) - \alpha_{ds} \alpha_{sd}} + 2\chi_M^s \frac{1 - \lambda_{dd} \chi^d(0) - \alpha_{ds}}{1 - \lambda_{dd} \chi^d(0) - \alpha_{ds} \alpha_{sd}} \quad (5-11)$$

Equations (5-11) shows the three contributions to the band susceptibility, namely the part due to the rare-earth site (first term), the exchange enhanced d-band susceptibility reduced by a factor $(1 - \alpha_{sd})$, and the s contribution corresponding to the transition metal site. In the absence of s-d mixing the last term reduces to $2\chi_M^s$ which is the pure s-band suscep-

tibility, and a pure exchange-enhanced susceptibility for the d states. The expression (5-11) is appropriate to describe the susceptibility of a system like LuCo_2 , which has no localized magnetic moment. In Eq. (5-10) the band and localized spin contributions are clearly separated. We now re-write the expression for χ in order to compare it to the result of Bloch and Lemaire (1970); let us introduce the susceptibility

$$\chi_M^{sd} = 2\chi_M^s \frac{1 - \lambda_{dd} \chi^d(0) - \alpha_{ds}}{1 - \lambda_{dd} \chi^d(0) - \alpha_{ds} \alpha_{sd}} \quad (5-12)$$

which is the s-like contribution to the susceptibility at the transition metal, and the reduced susceptibility

$$\frac{\chi_M^s}{\chi_b} = \frac{\chi_M^{sd}}{\chi_b} \quad (5-13)$$

The effective Curie constant \tilde{C}_f is defined as

$$\tilde{C}_f = C_f (1 + \lambda_{fs} \chi_R^s)^2 \quad (5-14)$$

Using these definitions one gets for χ (Eq. (5-10)):

$$\chi = \chi_b + \frac{\tilde{C}_f}{T - \theta} \left\{ 1 + \frac{\lambda_{fs} \chi_M^{sd}}{1 + \lambda_{fs} \chi_R^s} \right\} \quad (5-15)$$

This expression can be re-written in a way formally identical to the result of Bloch and Lemaire (1970):

$$\chi = \frac{\tilde{C}_f + \chi_b (T - E \tilde{C}_f)}{T - \theta} \quad (5-16)$$

With the quantity E defined as

$$E = \frac{\lambda_{ff} - \lambda_{fs} \bar{\chi}_M^{sd} + \lambda_{fs}^2 \chi_R^s - \lambda_{fs}^2 \chi_R^s \bar{\chi}_M^{sd}}{(1 + \lambda_{fs} \chi_R^s)^2} \quad (5-17)$$

or equivalently

$$E = \frac{\lambda_{ff} + \lambda_{fs}^2 \chi_R^s - \lambda_{fs} \bar{\chi}_M^{sd} (1 + \lambda_{fs} \chi_R^s)}{(1 + \lambda_{fs} \chi_R^s)^2} \quad (5-18)$$

Since the expression given above for the total susceptibility (Eq. 5-16) is formally equivalent to that derived by Bloch and Lemaire, it can be used equally well to fit the experimental data. Our derivation takes into account the details of the band structure of the intermetallic compounds; we recall that Bloch and Lemaire (1970) discussed a simplified picture consisting of a single exchange-enhanced band and a collection of localized f moments. Furthermore, in the expression for E (Eq. 5-17 or 5-18) one can see that an eventual temperature dependence of this parameter would be associated to the temperature dependence of $\chi^d(0)$.

Appendix A. EFFECT OF s-d HYBRIDIZATION ON THE POLARIZATION OF THE s BAND

The purpose of this Appendix is to discuss how an already magnetized d band can transfer its magnetization through s-d mixing to the s electrons. We formulate the problem in the following way: firstly we consider a non-hybridized d band, which through Coulomb interaction among its electrons exhibits a magnetic moment. The Coulomb repulsion is described within a Hartree-Fock-Stoner approach, the spin up and spin down bands are split in energy, the splitting being given by $I m^d$: I is the Coulomb repulsion and m^d the d magnetic moment (Fig.3). Now one superposes non-magnetic s-like band (of essentially plane wave character) and the s-d mixing is switched on. The problem now is to compute the hybridized bands in this system, or more specifically, to evaluate the occupation numbers for s-like states and consequently obtain the s magnetic moments. In order to carry out this program we have to introduce some approximations to make the calculation feasible. We follow essentially the same lines of Kishore and Joshi (1970)¹⁶ in their work about the influence of s-d mixing on the ferromagnetic instabilities in transition metals; to clarify the main approximations involved let us write down the Hamiltonian for the situation described above. In second quantization form it can be written as

$$\mathcal{H} = \sum_k \epsilon_k^s c_{k\sigma}^+ c_{k\sigma} + \sum_k \epsilon_{k\sigma}^d d_{k\sigma}^+ d_{k\sigma} + \sum_k v_k^{sd} (c_{k\sigma}^+ d_{k\sigma} + d_{k\sigma}^+ c_{k\sigma}) \quad (\text{A-1})$$

The spin dependence of the d band in Eq. (A-1) accounts for the fact that the d band is magnetized (see Fig. 5), so that Hartree-Fock corrections are already incorporated into the Hamiltonian. The last term of (A-1)

describes s-d mixing, and it is expected to provide the polarization of the s band. Although exactly soluble, the problem of diagonalizing this equation involves a difficulty in the calculation of the density of states of the hybridized bands, which is connected to the k-dependence of the V_{sd} matrix element. Kishore and Joshi (1970)¹⁶ introduced the simplification of taking a constant matrix element, thus obtaining analytical expressions for the density of states. In the present work we intend to go one step further in this approximation, by taking two values of V_{sd} , one for the spin up and the other for the spin down sub-bands; the values used are the averages of V_k^{sd} in the corresponding regions of overlap of the s and d sub-bands (see below).

Following Hodges et al. (1966)¹⁷, the matrix element V_k^{sd} may be approximately written as

$$V_k^{sd} \sim \int j_2(kr) V(r) \phi(r) r^2 dr \approx V j_2(k\beta) \quad (\text{A-2})$$

Where β is the value of r corresponding to the peak of $\phi_d(r)$. Using the asymptotic expansion of the Bessel function $j_2(k\beta)$ for free electron s states:

$$V_{sd} \approx V \frac{k^2 \beta^2}{15} = \frac{2m\beta^2}{15} V \epsilon_k^s \quad (\text{A-3})$$

The k dependence of V_k^{sd} is then approximately described by Eq. (A-3). Now we average this matrix element over the range of energy values where s and d states overlap. This seems reasonable since the mixing occurs mainly in these regions. As a consequence of the initial assumption of

split bands and of the energy dependence of the mixing matrix element, the highest energy spin sub-band will be more strongly admixed into the s band. We therefore replace the Hamiltonian (Eq. A-1) by:

$$\mathcal{H} = \sum_k \epsilon_k^s c_{k\sigma}^\dagger c_{k\sigma} + \sum_k \epsilon_k^d d_{k\sigma} + \sum_{k,\sigma} V_{sd}^\sigma (c_{k\sigma}^\dagger d_{k\sigma} + d_{k\sigma}^\dagger c_{k\sigma}) \quad (\text{A-4})$$

With the averaged matrix elements given by:

$$\bar{V}_{sd}^\sigma = \frac{\delta d}{\delta s} \frac{2m\beta^2 v}{15} (A_\sigma + \frac{\delta d}{2}) \quad (\text{A-5})$$

Where δ_s and δ_d are respectively the widths of the s and d bands and A_σ is the spin dependent position of the bottom of the d band. Comparing equations (A-3) and (A-5) one sees that averaged matrix element is equal to the ratio of the widths of d and s bands times the value of the mixing at the middle of the d-band. The ratio $\delta d/\delta s$ appears to account for the fact that s and d states hybridize only at the regions of overlap. The rest of the calculation beyond this point follows strictly Kishore and Joshi (1970)¹⁶. We recall here the main steps of their calculation; a more detailed discussion of this part of the present work will be given elsewhere (Lopes et al. 1972, to be published)¹⁸.

The simplest way to solve Eq. (A-4) and obtain the density of states is by the introduction of the Green functions $\langle\langle c_{k\sigma}; c_{k'\sigma}^\dagger \rangle\rangle_\omega$ and $\langle\langle d_{k\sigma}; d_{k'\sigma}^\dagger \rangle\rangle_\omega$ for s and d electrons respectively, since from these functions the density of states is easily obtained. A straightforward calculatu

ion shows the s and d propagators to be:

$$G_{k\sigma}^{ss}(\omega) = \frac{1}{2\pi} \frac{(\omega - \epsilon_{k\sigma}^d)}{(\omega - \epsilon_k^s)(\omega - \epsilon_{k\sigma}^d) - |V_{sd}^\sigma|^2} \quad (\text{A-6a})$$

and

$$G_{k\sigma}^{dd}(\omega) = \frac{1}{2\pi} \frac{(\omega - \epsilon_k^s)}{(\omega - \epsilon_k^s)(\omega - \epsilon_{k\sigma}^d) - |V_{sd}^\sigma|^2} \quad (\text{A-6b})$$

The poles of the propagators give the familiar second order equation

$$(\omega - \epsilon_k^s)(\omega - \epsilon_{k\sigma}^d) - |V_{sd}^\sigma|^2 = 0 \quad (\text{A-7})$$

which provide the dispersion relation for the two hybridized bands. Equations (A-6) and (A-7) are general in the sense that the s and d dispersion relations ϵ_k^s and ϵ_k^d have arbitrary k dependence. Again we follow Kishore and Joshi and introduce the approximation of homothetic bands defined by:

$$\epsilon_k^s = \epsilon_k \quad (\text{A-8a})$$

$$\epsilon_{k\sigma}^d = A\epsilon_k + A_\sigma \quad (\text{A-8b})$$

A_σ being the bottom of the σ spin d sub-band. This corresponds to bands with same k-dependence but having different "effective masses". Using (A-8) one obtains a narrow d band overlapping a broad s-like band, which is the

usual picture one has of a transition metal. It follows from Kishore and Joshi (1970)¹⁶ and the use of (A-8) that the densities of states are given by analytical expressions:

$$\rho_s^\sigma(\omega) = \frac{1}{A} \sum_p \left| \frac{\omega - A_\sigma - A g_\sigma^p(\omega)}{g_\sigma^+(\omega) - g_\sigma(\omega)} \right| N(g_\sigma^p(\omega)) \quad (\text{A-9a})$$

$$\rho_s^\sigma(\omega) = \frac{1}{A} \sum_p \left| \frac{\omega - g_\sigma^p(\omega)}{g_\sigma^+(\omega) - g_\sigma^-(\omega)} \right| N(g_\sigma^p(\omega)) \quad (\text{A-9b})$$

where $N(\omega)$ is the density of states associated to the dispersion relation and the functions $g_\sigma^p(\omega)$ are

$$g_\sigma^p(\omega) = \frac{1}{2A} \left\{ (A+1) - A_\sigma + p \left[((1-A)\omega - A_\sigma)^2 + 4A|V_{sd}^\sigma|^2 \right]^{1/2} \right\} \quad (\text{A-10})$$

From Equations (A-9a), (A-9b), and (A-10), which involve only $A, A_\sigma, |V_{sd}^\sigma|^2$ as parameters and a given shape of the density of states $N(\omega)$ we derive the occupation numbers $\langle n_\sigma^s \rangle$ and $\langle n_\sigma^d \rangle$ through integration up to the Fermi level.

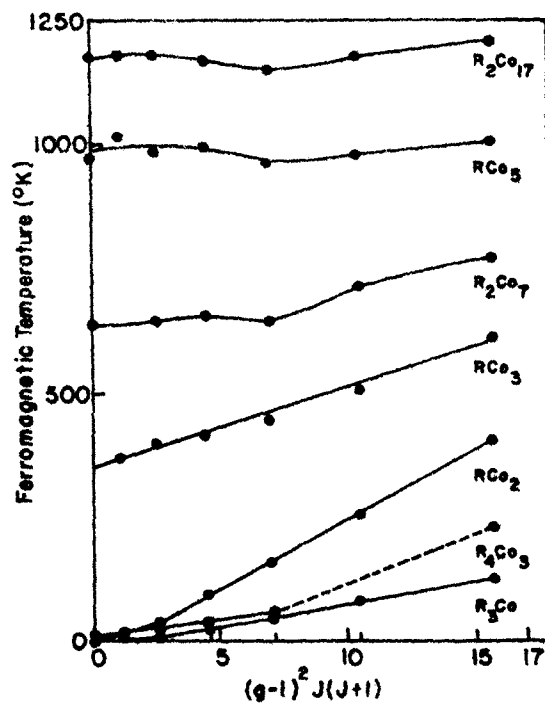
The results of these calculations are shown in Figs. 6a and 6b, where we plot the s and d magnetic moments for some values of the s-d mixing parameter as a function of the Fermi energy. The most important results revealed by these calculations are: a) the s polarization can be

negative (i.e. opposite to the d magnetization), and b) the s polarization changes sign approximately at the maximum of the d band magnetization curve. The reason for this change in sign can be easily understood: due to the higher energy of the \downarrow spin band, the s - d mixing associated to \downarrow spins is larger than the corresponding mixing for \uparrow spins. Consequently the \downarrow spin band lies lower in energy than the \uparrow spin band, but with a smaller density of states (Fig. 6a). Then for values of the Fermi level ϵ_F close to the bottom of the bands a negative spin polarization is obtained. Now, when ϵ_F increases, the rate of variation of the number of occupied \uparrow states is larger than the corresponding value for \downarrow states (Fig. 6b) and this depends on the fact that the \uparrow spin density of states is larger than the \downarrow density of states. Therefore at a certain energy ϵ_F^C the sign is reversed; this effect was verified to exist for parabolic and square shapes of the density of states.

* * *

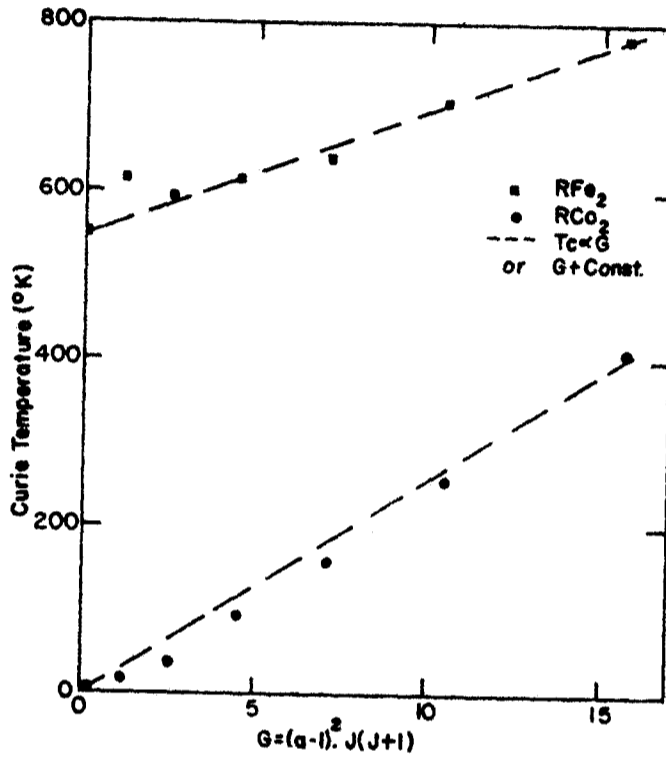
ACKNOWLEDGEMENTS

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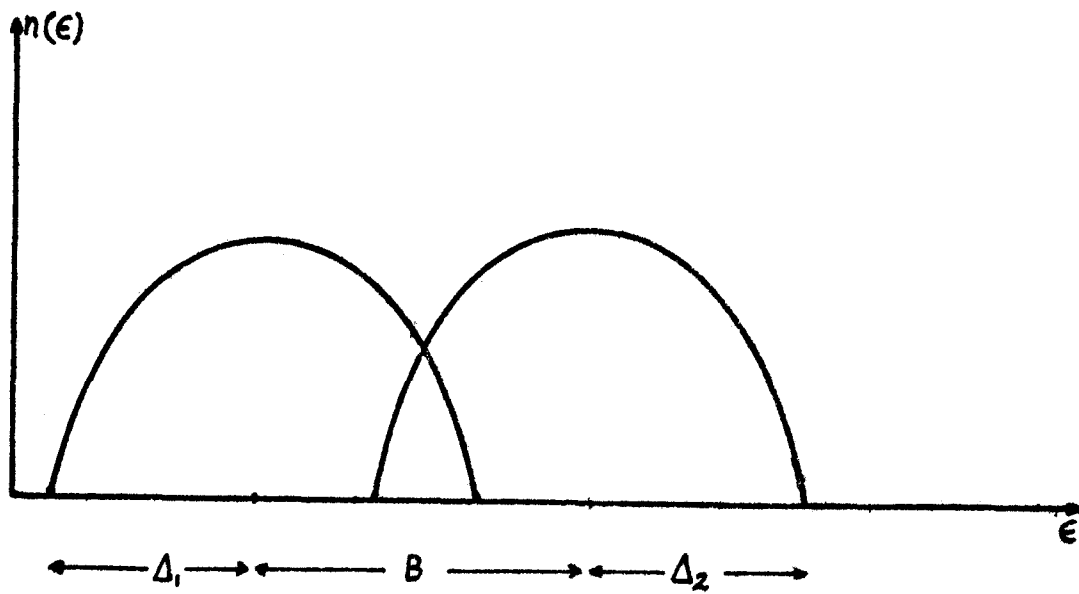
Magnetic transition temperatures of several rare-earth-cobalt intermetallic compounds plotted against rare-earth de Gennes factor (from Taylor 1971).

FIG. 1



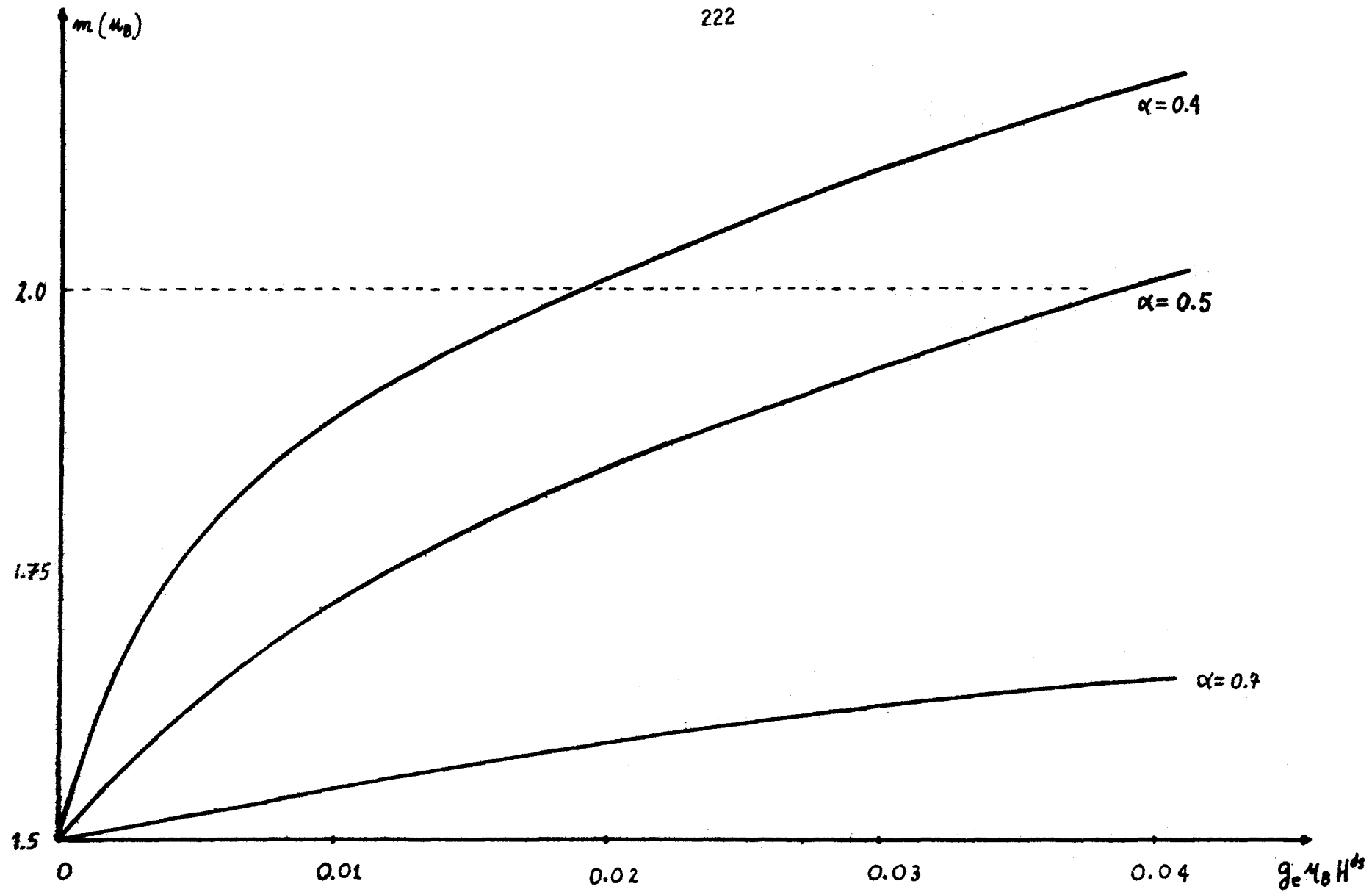
Magnetic ordering temperatures of several RFe_2 and RCo_2 intermetallic compounds versus rare-earth de Gennes factor (from Taylor 1971). Note that for $J = 0$ the compound containing iron has a Curie temperature of over $500^\circ K$, whereas the corresponding cobalt compound does not order magnetically.

FIG. 2



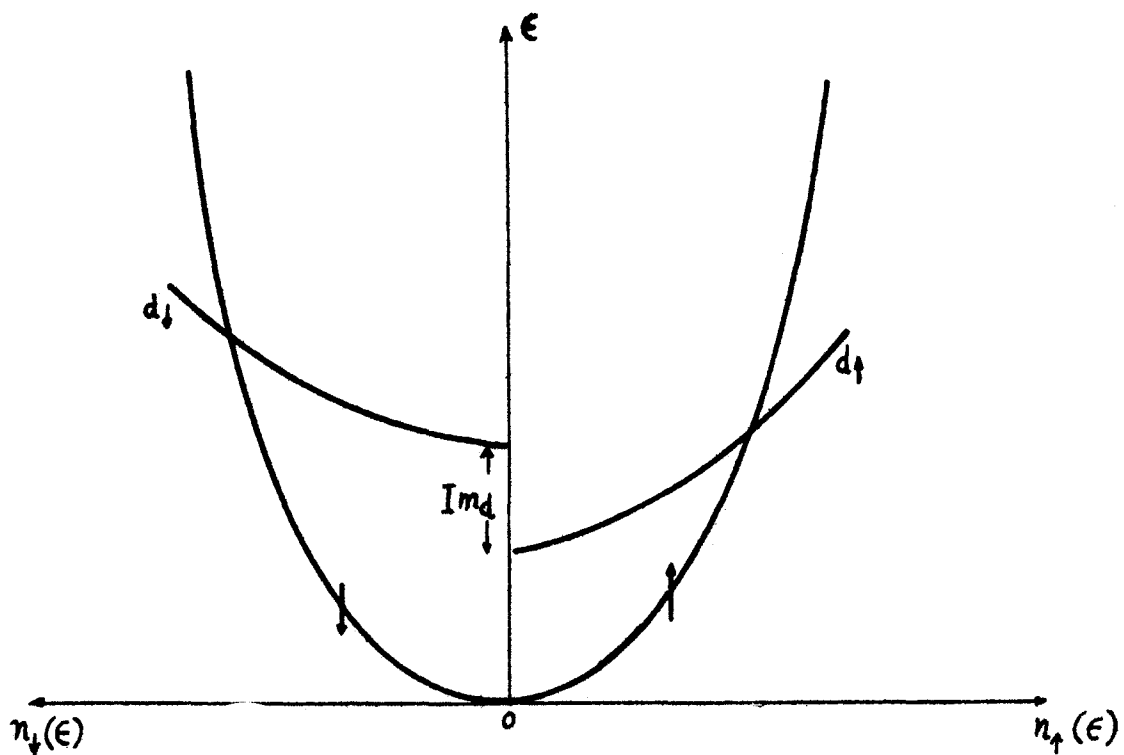
Model d-density of states used to solve equations 3-1a and 3-1b; this band is a sum of two parabolae of equal heights and different widths. The parameter α ($B = \Delta_1 + \alpha \Delta_2$) describes the degree of overlap of the two parabolae. The results of the calculation are shown in Fig. 4.

FIG. 3



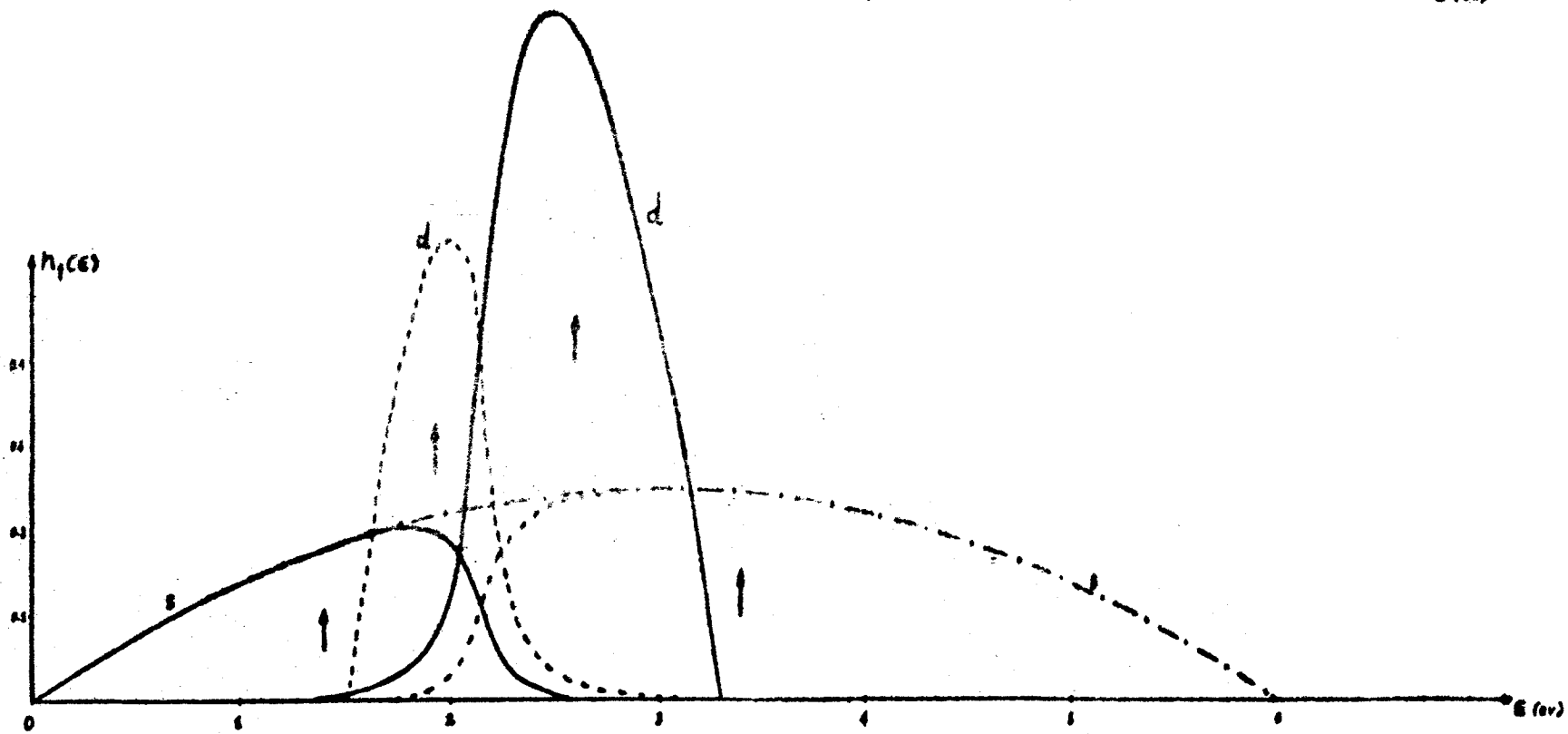
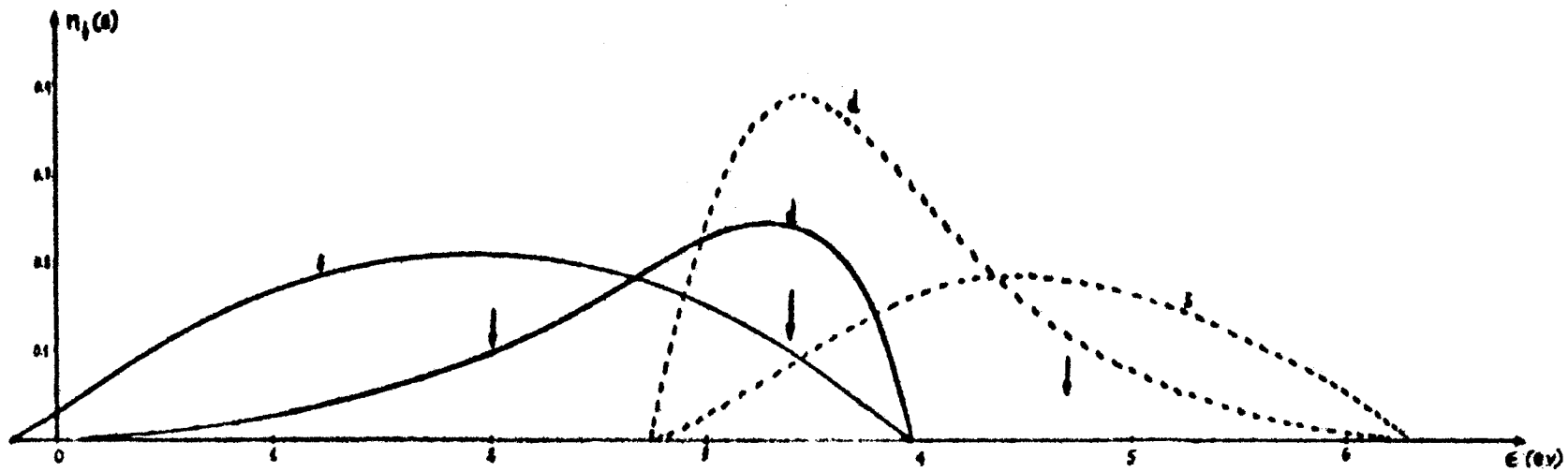
Magnetic moment of the d band (Fig. 3) as a function of the effective magnetic interaction $g_e \mu_B H^{ds}$, for different values of α .

FIG. 4



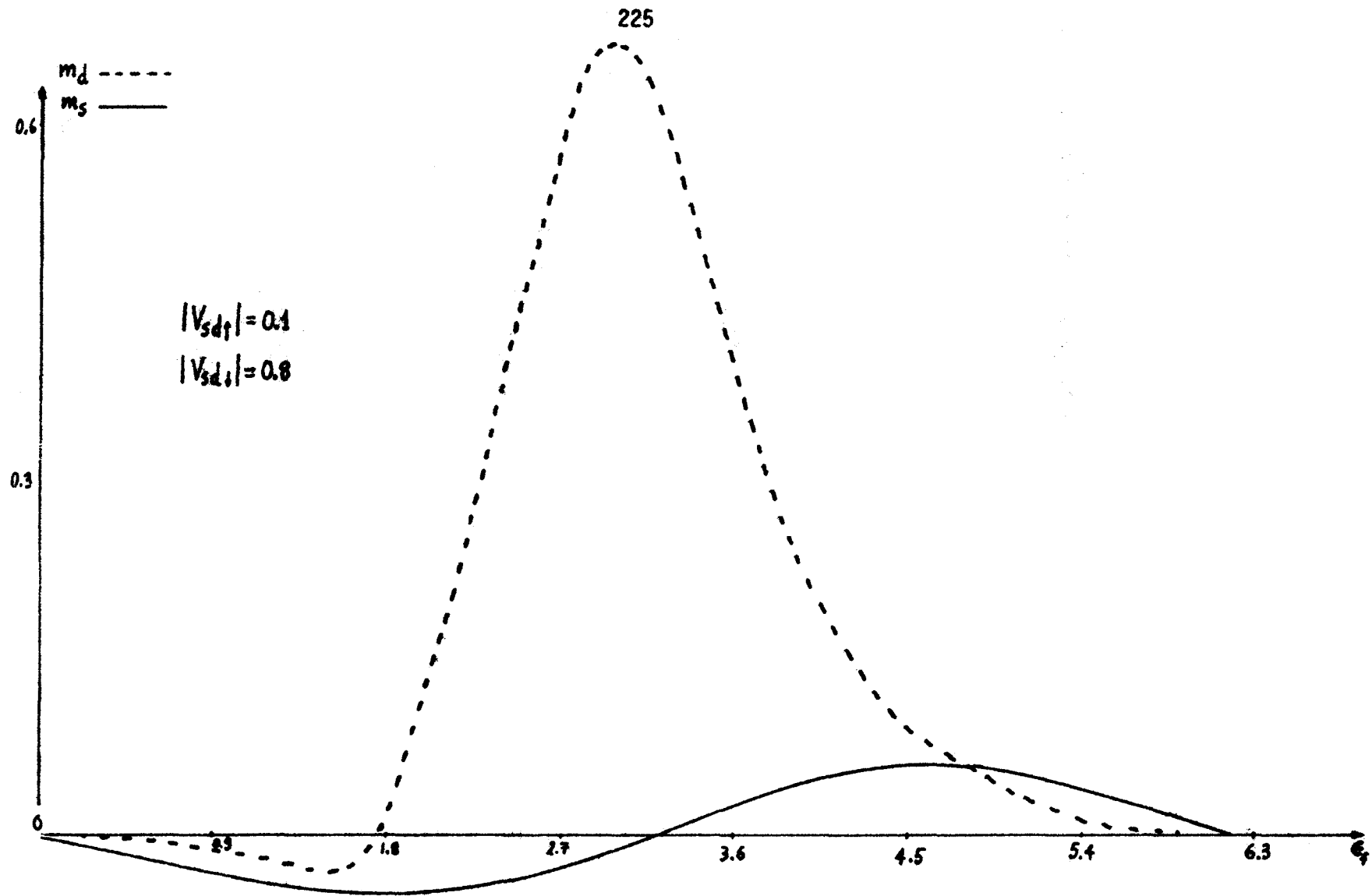
Representation of a magnetized d band before the s-d mixing (which eventually polarizes the s band) is switched on.

FIG. 5



Density of states of the hybridized bands, for up and down spin states
 $(|v_{sd\downarrow}| > |v_{sd\uparrow}|)$.

FIG. 6a



Magnetic moments of the s and d bands as a function of the Fermi energy, for a pair of potentials $V_{sd↑}$ and $V_{sd↓}$ (from Lopes et al. 1972, to be published). It can be seen that, depending on ϵ_F , m^d and m^s can be either parallel or antiparallel.

FIG. 6b

REFERENCES

1. Taylor, K.N.R., 1971, Adv. Phys. 20, 551.
2. Gomes, A.A., 1972, Phys. Letters, 39A, 139.
3. Gomes, A.A., Guimarães, A.P., and Iannarella, L., 1972, J.Phys.C, 5, L99.
4. Long, P.D., and Turner, R.E., 1970, J.Phys.C, Metal Phys. Suppl., 4, S127.
5. Wakoh, S., and Yamashita, J., 1966, J. Phys.Soc. Japan, 21, 1712.
6. Bleaney, B., 1972, Magnetic Properties of Rare Earth Metals, Ed. R. J. Elliott (London: Plenum Press), pg. 383.
7. Gegenwarth, R.E., Budnick, J.I., Skalski, S., and Wernick, J.H., 1967, Phys. Rev. Letters, 18, 9.
8. Eagles, D.M., 1972, private communication.
9. Campbell, I.A., 1969, J. Phys. C, 2, 1338.
10. Hufner, S., and Wernick, J.H., 1968, Phys.Rev., 173, 448.
11. Guimarães, A.P., and Bunbury, D.St.P., 1972, Notas de Física, 18, 307, and to be published.
12. Gomes, A.A., Guimarães, A.P., and Danon, J., 1972, Communication to the Conference on Mössbauer Spectroscopy, Israel.
13. Nowik, I., Ofer, S., and Wernick, J.H., 1966, Phys. Letters, 20, 232.
14. Atzmony, U., Bauminger, E.R., Nowik, I., Ofer, S., and Wernick, J.H., 1967, Phys.Rev., 156, 262.
15. Bloch, D., and Lemaire, R., 1970, Phys. Rev. B, 2, 2648.

16. Kishore, R., and Joshi, S.K., 1970, Phys. Rev. B, 2, 1411.
17. Hodges., L., Ehrenreich, H., and Laing, N.D., 1966, Phys.Rev., 152, 505.
18. Lopes, L.C., Continentino, M.A., and Gomes, A.A., 1972, to be published.

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