UvA-DARE (Digital Academic Repository)

Magnetic Polarization in Ramirez-Falicov Model of Valency Change Transitions - Application to Cerium

de Châtel, P.F.; Grimberg, A.J.T.

Publication date

1974

Document Version

Final published version

Published in

Physical Review. B, Condensed Matter

[Link to publication](#)

Citation for published version (APA):

de Châtel, P. F., & Grimberg, A. J. T. (1974). Magnetic Polarization in Ramirez-Falicov Model of Valency Change Transitions - Application to Cerium. *Physical Review. B, Condensed Matter*, 10(10), 4112-4120.

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)

Magnetic polarization in the Ramírez-Falicov model of valency change transitions: Application to cerium*

P. F. de Châtel and A. J. T. Grimberg†

*Natuurkundig Laboratorium van de Universiteit van Amsterdam,
Valckenierstraat 65, Amsterdam, The Netherlands*

(Received 20 May 1974)

The Ramírez-Falicov model of the α - γ phase transition of cerium is extended, allowing for a field-induced or spontaneous splitting of the bands and of the sixfold degenerate $4f$ level. The effect of presently available magnetic fields on the α - γ transition temperature in cerium is found to be negligible. With higher values (not appropriate to cerium) for the conduction-electron- f -electron exchange parameter, the model shows first- and second-order transitions to a ferromagnetic γ phase. The resulting phase diagrams are discussed in terms of the magnetization behavior expected from a system described by the model.

I. INTRODUCTION

Pauling¹ and Zachariasen² pointed out a long time ago that the α - γ transition in cerium, which is accompanied by a 15% volume change without structural change, can be qualitatively understood in terms of the promotion of conduction electrons on to localized $4f$ states. Ramírez and Falicov³ (RF) have proposed a microscopic model, which is capable of quantitatively describing such an electronic transition.

The investigation to be described in the present paper was aimed at the implications of the RF theory regarding the influence of magnetic field on the transition. In order to calculate the response to a magnetic field, we had to introduce exchange into the RF model. For certain values of the exchange parameters we found that the model produces very interesting ferromagnetic transitions which, although not relevant to cerium, seemed worth investigating.

In this section we will give a brief summary of the RF model, making use of some of the more recent results of Kiwi and Ramírez⁴ (KR). In Sec. II we introduce the exchange interaction and determine the conditions of equilibrium in the presence of an external magnetic field. Section III is devoted to cerium, and leads to the conclusion that the RF theory does not predict any spectacular effects of presently available magnetic fields on the α - γ transition. We present the results of some numerical calculations on the model for exchange-parameter values leading to a variety of magnetic transitions in Sec. IV, and summarize our results in Sec. V.

The essential features of the RF model are represented in Fig. 1. A hybridized s - d conduction band of width W , and a sixfold degenerate $4f$ state on each cerium ion are the basic ingredients. The

conduction band is supposed to be able to accommodate 12 electrons, and to have a constant density of states, whose value (per cerium atom, including spin degeneracy) is

$$D = 12/W. \quad (1.1)$$

In the ground state of α -cerium the number of conduction electrons, $n_{+1/2} + n_{-1/2}$, where

$$n_s = \frac{1}{2} \int_0^W D n_s(\epsilon) d\epsilon, \quad (1.2)$$

$n_s(\epsilon)$ being the occupation probability of spin- s conduction electrons, is exactly 4, and the empty $4f$ state lies an energy E above the Fermi energy.

The most important interaction in the model is that between two f electrons on the same atom. The Coulomb energy associated with a doubly occupied f state is supposed to be much larger than any other energy parameter in the model, and, therefore, only the $4f^0$ and $4f^1$ configurations are allowed. Projecting out all states involving $4f^2$, $4f^3$, etc. configurations amounts to taking into account exactly intra-atomic correlations if the Coulomb energy is infinitely large, but leads to the peculiar situation that the intra-atomic Coulomb energy never explicitly enters the theory.

The interaction between conduction electrons and $4f$ electrons does explicitly enter the theory. It is characterized by the energy G , which is the amount by which all conduction-electron energies are raised if all cerium ions in the lattice are converted from the $4f^0$ configuration to the $4f^1$ configuration.³

As was pointed out by Alascio *et al.*,⁵ it is the entropy associated with the sixfold degeneracy of the $4f^1$ configuration that drives the α - γ transition. In the limit where the Fermi energy is much larger than $k_B T$, the f -state occupation probability can be written⁴

$$n_f = \left\{ \frac{1}{18} \exp[(E - \rho n_f)/k_B T] + 1 \right\}^{-1}, \quad (1.3)$$

where k_B is the Boltzman constant,

$$\rho = 2G - (1/D), \quad (1.4)$$

and the factor $\frac{1}{18}$ arises from the sixfold degeneracy. Equation (1.3) has one or three solutions, and the α - γ transition occurs at the temperature $T_{\alpha\gamma}$ where one of the three solutions is $n_f = \frac{1}{2}$. The other two solutions then, which correspond to the α and γ phases, and will be denoted by $n_\alpha(T_{\alpha\gamma})$ and $n_\gamma(T_{\alpha\gamma})$ respectively, satisfy the sum rule

$$n_\alpha(T_{\alpha\gamma}) + n_\gamma(T_{\alpha\gamma}) = 1. \quad (1.5)$$

These are the results of Kivi and Ramírez,⁴ who used them to express the characteristics of the phase diagram in terms of the parameters D , E , and G defined above and the spin degeneracy $q = 6$. In terms of these, the α - γ transition temperature is

$$T_{\alpha\gamma} = (E - \frac{1}{2}\rho)/k_B \ln q, \quad (1.6)$$

and the critical temperature is

$$T_c = \frac{1}{4}\rho/k_B. \quad (1.7)$$

These results can be used to determine the interaction parameter G and the pressure dependence of the f -electron energy E on the basis of the experimentally observed phase diagram.

II. EQUILIBRIUM CONDITIONS FOR NONVANISHING MAGNETIZATION

In the presence of a magnetic field H , the conduction electrons acquire an imbalance between spin-up and spin-down occupation numbers, and the $J = \frac{5}{2}$ level of $4f^1$ -configuration cerium ions splits up into six nondegenerate levels characterized by $J_M = -\frac{5}{2}, -\frac{3}{2}, \dots, +\frac{5}{2}$. A new set of parameters has to be introduced to account for the unequal numbers of $4f^1$ cerium ions in the various J_M states. We denote by p_M the probability of a given $4f^1$ cerium ion being in the $J_M = M$ state; with this definition the number of such ions is $Nn_f p_M$. Obviously,

$$\sum_M p_M = 1, \quad (2.1)$$

where $\sum_M$ indicates summation over half-integers between $-\frac{5}{2}$ and $+\frac{5}{2}$.

Due to the magnetic polarization, it is not possible to describe the f -electron-conduction-electron interaction by a single parameter G ; to distinguish between the interaction of parallel-spin and anti-parallel-spin pairs the Coulomb (U) and exchange (K) integrals have to be introduced. The interaction energy of a $4f^1$ cerium ion in the $J_M = M$ state with the conduction electrons is

$$\sum_s \alpha_{Ms} [(U - K)n_s + Un_{-s}],$$

where $\sum_s$ stands for summation over $s = -\frac{1}{2}, +\frac{1}{2}$ and α_{Ms} is the Clebsch-Gordan coefficient squared, giving the weight of the spin- s component in the $J_M = M$ state. The wave function of this state can be written

$$|J = \frac{5}{2}, J_M = M\rangle = \sum_s (-2s) \left(\frac{7 - 4Ms}{14} \right)^{1/2} \times |L = 3, L_M = M - s; S = \frac{1}{2}, S_M = s\rangle,$$

hence

$$\alpha_{Ms} = \frac{1}{14}(7 - 4Ms). \quad (2.2)$$

The total energy of interaction between f electrons and conduction electrons can be split into a direct and an exchange part as

$$E_{fc} = Nn_f \sum_M p_M \left((U - \frac{1}{2}K) \sum_s n_s + \frac{2}{7}KM \sum_s sn_s \right). \quad (2.3)$$

Using the conservation of the total number of particles,

$$n_{\text{tot}} = \sum_s n_s + n_f = 4, \quad (2.4)$$

Eq. (2.3) can be written

$$E_{fc} = N(U - \frac{1}{2}K)(4n_f - n_f^2) + \frac{2}{7}Kn_f \left(\sum_M Mp_M \right) \left(\sum_s sn_s \right). \quad (2.5)$$

In order to be able to explain the experimentally found enhancement of the initial susceptibility⁶ at low temperatures, we also have to introduce the conduction-electron-conduction-electron Coulomb (V) and exchange (J) integrals. Using Eq. (2.4), we can write the total conduction-conduction-electron interaction as

$$E_{cc} = 8(V - J) - \frac{1}{2}(V - \frac{1}{2}J)(8n_f - n_f^2) - J \left(\sum_s sn_s \right)^2. \quad (2.6)$$

The entropy can be calculated from the general expression for N atoms having m possible states each:

$$S = k_B \left(N \ln N - \sum_{i=1}^m n_i \ln n_i \right),$$

FIG. 1. Schematic representation of the Ramirez-Falicov model.

where n_i is the number of atoms in the i th state. In our case there are seven states: the $4f^0$ configuration and the six states within the $4f^1$ configuration. Accordingly, the entropy becomes

$$S = k_B \left(N \ln N - (1 - n_f) N \ln[(1 - n_f)N] - \sum_M N n_f p_M \ln(N n_f p_M) \right).$$

Breaking up the logarithms of products and using Eq. (2.1) we get

$$S = -k_B N \left(n_f \ln n_f + (1 - n_f) \ln(1 - n_f) + n_f \sum_M p_M \ln p_M \right). \quad (2.7)$$

Assuming, as Ramírez and Falicov³ did, that D , the density of conduction-band states is constant within the band of width W , the total free energy, dropping constant terms, becomes

$$\begin{aligned} \frac{1}{N} \mathcal{F} = & \frac{1}{2} D \sum_s \int_0^W [(\epsilon - s g_c \mu_B H) n_s(\epsilon) + k_B T K(n_s(\epsilon))] d\epsilon \\ & + n_f \left(E' - G n_f - g_f \mu_B H \sum_M M p_M \right) \\ & + k_B T \left(n_f \sum_M p_M \ln p_M + K(n_f) \right) \\ & + \frac{2}{7} K n_f \left(\sum_M M p_M \right) \left(\sum_s s n_s \right) - J \left(\sum_s s n_s \right)^2, \end{aligned} \quad (2.8)$$

where $g_c = 2$ and $g_f = g_{5/2} = \frac{7}{8}$ are the g factors appropriate to the conduction and f electrons, respectively; μ_B is the Bohr magneton; $K(n) = n \ln n + (1 - n) \times \ln(1 - n)$; $E' = E'' + 4[(U - \frac{1}{2}K) - (V - \frac{1}{2}J)]$, E'' being the energy of the $4f$ state in the absence of conduction electrons, and $G = U - \frac{1}{2}K + \frac{1}{2}(V - \frac{1}{2}J)$. It is clear that the meaning of the parameter G is the same here as in Ref. 3 and in Eq. (1.3).

The free energy (2.8) has to be minimized with respect to $n_s(\epsilon)$, n_f , and p_M , taking into account the subsidiary conditions (2.1) and (2.4), which are added, with Lagrange multipliers λ and ζ respectively, to $\mathcal{F}$. Introducing the f -electron and conduction-electron magnetizations

$$\sigma_f = n_f g_f \mu_B \sum_M M p_M, \quad (2.9)$$

$$\sigma_c = g_c \mu_B \sum_s s n_s, \quad (2.10)$$

the following results are found.

(i) Conduction electrons: the condition $\delta(\mathcal{F}/N - \zeta n_{\text{tot}})/\delta n_s(\epsilon) = 0$ results in

$$\ln \left(\frac{n_s(\epsilon)}{1 - n_s(\epsilon)} \right) = - \frac{\epsilon - s g_c \mu_B H_c - \zeta}{k_B T}, \quad (2.11)$$

where we have introduced the effective field felt by the conduction electrons

$$H_c = H - (K/6\mu_B^2)\sigma_f + (J/2\mu_B^2)\sigma_c. \quad (2.12)$$

Formally, Eq. (2.11) is equivalent with the Fermi distribution

$$n_s(\epsilon) = \{\exp[(\epsilon - s g_c \mu_B H_c - \zeta)/k_B T] + 1\}^{-1}, \quad (2.13)$$

in which the spectra of spin-up and spin-down electrons are shifted relative to each other by $g_c \mu_B H_c$. Assuming that

$$\zeta \pm \mu_B H_c, W - (\zeta \pm \mu_B H_c) \gg k_B T, \quad (2.14)$$

we can determine the dependence of ζ on n_f by substituting Eq. (2.13) into Eq. (1.2), making use of the identity $\int (e^x + 1)^{-1} dx = \ln[e^x/(e^x + 1)]$, and finally substituting these results into Eq. (2.4). The result,

$$\zeta = (4 - n_f)/D, \quad (2.15)$$

is seen to be consistent with our starting assumption (2.14). Using Eq. (1.1) and noting that $0 \leq n_f \leq 1$, we find that $\frac{1}{4}W \leq \zeta \leq \frac{1}{3}W$ (in all cases treated in the present paper $\mu_B H_c \ll W$).

The distribution functions (2.13) are formally identical with the ones arising in the Stoner-Wohlfarth theory of band magnetism,⁷ and we shall take over some of the results derived there. Our assumption that the density of states is constant is crucial at this point. With an energy dependent density of states the fact that ζ strongly depends on n_s [cf. Eqs. (2.4) and (2.15)] would lead to a situation different from the one treated in the Stoner-Wohlfarth theory. Under the assumptions (2.14) it can be shown⁷ that the conduction-electron magnetization is proportional to H_c ; it is given in terms of the unenhanced Pauli susceptibility of the conduction band as $\sigma_c = D \mu_B^2 H_c$. Substituting Eq. (2.12) for H_c , we find

$$\sigma_c = [D \mu_B^2 / (1 - \frac{1}{2}JD)] [H - (K/6\mu_B^2)\sigma_f]. \quad (2.16)$$

We recognize in the first factor the exchange-enhanced Pauli susceptibility, and in the second one an effective field, which is reduced with respect to the external field by the antiferromagnetic interaction of conduction electrons with the $4f$ electrons.

(ii) $4f$ electrons: the condition $\partial(\mathcal{F}/N - \zeta n_{\text{tot}})/\partial n_f = 0$ results in

$$\begin{aligned} \ln[n_f/(1 - n_f)] = & - \left(E' - 2G n_f \right. \\ & \left. - g_f \mu_B H_f \sum_M M p_M - \zeta \right) / k_B T \\ & - \sum_M p_M \ln p_M, \end{aligned} \quad (2.17)$$

where the effective field for $4f$ electrons is defined as

$$H_f = H - (K/6\mu_B^2)\sigma_c. \quad (2.18)$$

Using Eq. (2.16), σ_c can be eliminated:

$$H_f = \left(1 - \frac{\frac{1}{2}KD}{1 - \frac{1}{2}JD}\right) H + \frac{D}{1 - \frac{1}{2}JD} \left(\frac{K}{6\mu_B}\right)^2 \sigma_f. \quad (2.19)$$

This result is very suggestive. We see that the external field is effectively reduced by the antiferromagnetic coupling K between $4f$ and conduction electrons, but the same coupling, in second order, makes a positive contribution (proportional to the f -electron magnetization) to the effective field.

This second term indicates a ferromagnetic interaction between $4f$ electrons, which is mediated by the conduction electrons.

(iii) Polarization of the $4f$ electrons: the condition $\partial(\mathcal{F}/N - \lambda \sum_M p_M)/\partial p_M = 0$ results in

$$\ln p_M = \frac{Mg_f \mu_B H_f}{k_B T} + \frac{\lambda}{N n_f k_B T} - 1.$$

In order to eliminate λ , we impose the condition (2.1); we find

$$p_M = \exp(Mg_f \mu_B H_f / k_B T) / \sum_{M'} \exp(M'g_f \mu_B H_f / k_B T). \quad (2.20)$$

This is formally identical with the probabilities one finds for free ions in an effective field H_f . Consequently, $\sum_M M p_M$ is given by the Brillouin function⁸:

$$\sum_M M p_M = \frac{5}{2} B_{5/2}(X) = 3 \coth \frac{5}{2} X - \frac{1}{2} \coth \frac{1}{2} X; \quad (2.21)$$

$$X = \frac{g_f \mu_B H_f}{k_B T}.$$

Having found the nine equilibrium conditions given by Eqs. (2.13), (2.17) and (2.20), we now proceed to reduce the number of conditions. If we use in Eq. (2.17) the expression (2.19) for H_f and Eq. (2.15) for ξ , we have eliminated n_s from n_f . The six variables p_M can be replaced by σ_f with the use of Eq. (A3). Then, defining $E = E' - 4/D$ and using Eq. (1.4) the result for n_f becomes

$$n_f = \left[\frac{\sinh(\frac{1}{2} g_f \mu_B H_f / k_B T)}{\sinh(3 g_f \mu_B H_f / k_B T)} \exp\left(\frac{(E - \rho n_f)}{k_B T}\right) + 1 \right]^{-1}. \quad (2.22)$$

According to Eq. (2.19), H_f is a function of σ_f , which can be determined by combining Eqs. (2.9) and (2.21):

$$\sigma_f = \frac{5}{2} g_f \mu_B n_f B_{5/2}(\mu_B H_f / k_B T). \quad (2.23)$$

Although this seems to be a simple product of an occupation number and a Brillouin function, one must realize that n_f also depends on H_f . The dependence of H_f on σ_f itself is a familiar feature of molecular-field theories.

Thus, Eqs. (2.22) and (2.23) have to be solved simultaneously to find the probability of the occurrence of the $4f^1$ configuration and the f -electron magnetization as functions of the temperature, pressure, and magnetic field.

Taking $H=0$ and $K=0$, we recover the well known result of Kłwi and Ramírez,⁴ Eq. (1.3).

III. CERIUM

Having derived general expressions for the f -state occupation probability and magnetization, we wish to apply them to the case of cerium. In particular, we shall derive the shift in the α - γ transition temperature $T_{\alpha\gamma}$ due to an external magnetic field. As the magnetic field can reduce the energy of the $4f^1$ configuration by orienting the spin, and cannot influence the energy of the nonmagnetic $4f^0$ configuration, one can expect a stabilization of the γ -phase with respect to the α phase, that is, a lowering of $T_{\alpha\gamma}$. To find the magnitude of this effect, we have to introduce in our model the parameters appropriate to cerium.

The density of states at the Fermi energy is known from the measured coefficient γ of the electronic specific heat.⁹ Assuming a 50% enhancement due to electron-phonon and electron-electron interaction, we have

$$D(\epsilon_F) = 3\gamma/\pi^2 k_B^2 = 2.7 \text{ states/atom eV}. \quad (3.1)$$

In what follows we will take this as the constant value D of the density of states.

Two further parameters can be determined from the phase diagram using Eqs. (1.6) and (1.7). With the data of the experimentally established phase diagram we find

$$\rho = 0.2 \text{ eV}, \quad (3.2)$$

$$E(\text{eV}) = 0.117911 + 0.002045 P (\text{kbar}). \quad (3.3)$$

We can calculate the interaction parameter G from the definition (1.4) of ρ and Eq. (3.1):

$$G = \frac{1}{2}(\rho + 1/D) = 0.28 \text{ eV}. \quad (3.4)$$

In Sec. II we had to introduce several new interaction parameters in order to extend the Ramírez-Falicov model for the case of nonzero magnetic polarization. In our final result, Eqs. (2.22) and (2.23), we have absorbed two of the interaction parameters in ρ and E , whose values are already given in Eqs. (3.2) and (3.3), respectively. The exchange parameters, J and K , however, appear explicitly in the definition (2.19) of H_f , and their

values have to be established before we can apply our results to cerium. To this end, we will derive explicit formulas for the total magnetization in terms of J and K .

It can be readily shown by evaluating $\sigma_{\text{tot}} = -\partial\mathcal{F}/\partial H$ that the total magnetization is simply the sum of the conduction-electron magnetization (2.16) and the f -electron magnetization (2.23). Assuming that the exchange parameters are not large enough to bring about a spontaneous magnetization, in which case H_c and H_f as well as σ_c and σ_f vanish if $H \rightarrow 0$, we can expand the Brillouin function in Eq. (2.23) and express the low-field f -electron magnetization as

$$\sigma_f = \frac{15}{4} n_f (\mu_B^2 / k_B T) H_f, \quad (3.5)$$

where n_f is the f -state occupation probability for $H=0$ [given by Eq. (1.3)]. Substituting Eq. (2.19) for H_f and adding the conduction-electron magnetization (2.16), we can express the total magnetization as

$$\sigma_{\text{tot}} = \sigma_f + \sigma_c = D \mu_B^2 \frac{1 - \frac{5}{4} n_f (2K + 3J - 6/D) / k_B T}{1 - \frac{1}{2} J D - \frac{5}{84} n_f D K^2 / k_B T} H. \quad (3.6)$$

It is easily verified that in the limiting cases where the f -state occupation probability and the conduction-band density of states vanish, this expression reduces to the exchange-enhanced Pauli susceptibility and the Curie susceptibility, respectively.

As is seen from Eq. (2.22), in the low-temperature limit

$$n_f \xrightarrow{T \rightarrow 0} \exp\left\{\left[\frac{5}{2} g_f \mu_B H_f - (E - \rho n_f)\right] / k_B T\right\}, \quad (3.7)$$

i.e., n_f is exponentially small as long as $\frac{5}{2} g_f \mu_B H_f < E > 0.118$ eV, which will be the case for all presently available magnetic fields (the difference between H_f and H can be neglected in this case, because it is proportional with n_f itself). Therefore, the low-temperature susceptibility is dominated by the exchange-enhanced Pauli paramagnetic susceptibility of the conduction band. We can use the experimentally observed enhancement of the band susceptibility to determine the conduction-electron-conduction-electron exchange parameter J . With the D value of Eq. (3.1) and the measured low-temperature susceptibility,⁶ $\chi = 6.2 \times 10^{-4}$ emu/mole, the enhancement factor $S = (1 - \frac{1}{2} J D)^{-1}$ is found to be equal to 7.1, which gives $J = 0.635$ eV.

It is more difficult to estimate the value of conduction-electron- f -electron exchange parameter K . However, we can give an upper bound to K on the basis of the experimental observation that γ -cerium never becomes ferromagnetic. It is clear from Eq. (2.19) that Eq. (2.23) can have solutions with nonzero σ_f even if $H=0$. A sufficient condi-

tion for this to occur is that the free energy decrease upon the appearance of an infinitesimal magnetization. This will be the case, if the coefficient of the lowest-order (quadratic) term in the power series expansion of the free energy as a function of magnetization is negative. We presented this expansion in the Appendix. According to Eq. (A5) the quadratic term changes sign at the temperature

$$T_{\text{Curie}} = \frac{5}{2} n_f (T_{\text{Curie}}) S D \left(\frac{1}{6} K\right)^2 (g_f / k_B). \quad (3.8)$$

Thus, if at higher temperatures the material is paramagnetic, at $T = T_{\text{Curie}}$ there will be a transition to the ferromagnetic phase. For given values of the interaction parameters J and K we can define the highest possible Curie temperature by putting $n_f(T_{\text{Curie}}) = 1$:

$$T_{\text{Curie}}^{\text{max}} = \frac{5}{2} S D \left(\frac{1}{6} K\right)^2 (g_f / k_B). \quad (3.9)$$

As γ -cerium is not stable under 100 K, we can only assert that $T_{\text{Curie}} < 100$ K. At atmospheric pressure the value of n_f in the γ phase just above $T_{\alpha\gamma}$ being practically 1, we can estimate K by requiring that $T_{\text{Curie}}^{\text{max}} < 100$ K, which leads to $K < 0.08$ eV.

Having derived values for D , J , and K , we can proceed to estimate the change of $T_{\alpha\gamma}$ as a function of magnetic field. To this end, we have to compare the energy difference between the γ and α phases in zero external field at a temperature T slightly below $T_{\alpha\gamma}$ [$\Delta\mathcal{F}_0(T)$] on the one hand, and the same difference at $T_{\alpha\gamma}$ in a finite magnetic field [$\Delta\mathcal{F}_H(T_{\alpha\gamma})$] on the other hand. Defining $n_\alpha(T)$ and $n_\gamma(T)$ as the occupation probabilities at the corresponding minima of the free energy at a given temperature T (Fig. 3), $\Delta\mathcal{F}_0$ can be found from Eq. (A4); retaining only first-order terms in $T_{\alpha\gamma} - T$:

$$\Delta\mathcal{F}_0(T) = [n_\gamma(T_{\alpha\gamma}) - n_\alpha(T_{\alpha\gamma})] k_B (T_{\alpha\gamma} - T) \ln 6. \quad (3.10)$$

Expanding the free energy at $T_{\alpha\gamma}$ as a function of H as $\mathcal{F}_H(T_{\alpha\gamma}) = \mathcal{F}_0(T_{\alpha\gamma}) - \frac{1}{2} (\partial\sigma_{\text{tot}} / \partial H) H^2$, and using Eq. (3.6), we find with $C = \frac{5}{84} S D K^2$ the following expression for $\Delta\mathcal{F}_H(T_{\alpha\gamma})$:

$$\Delta\mathcal{F}_H(T_{\alpha\gamma}) = [n_\alpha(T_{\alpha\gamma}) - n_\gamma(T_{\alpha\gamma})] \left(\frac{\frac{1}{2} S D \mu_B^2}{k_B T_{\alpha\gamma}} \right) \times \frac{C / k_B T_{\alpha\gamma} + \frac{5}{4} [(6/D) - 2K - 3J]}{1 - C / k_B T_{\alpha\gamma} + (C / k_B T_{\alpha\gamma})^2 n_\alpha(T_{\alpha\gamma}) n_\gamma(T_{\alpha\gamma})} H^2. \quad (3.11)$$

Here we have used the identity (1.5), which will also enable us to give the maximum and minimum values of $\Delta\mathcal{F}_H(T_{\alpha\gamma})$. Both phases at $T_{\alpha\gamma}$ being paramagnetic, the denominator in Eq. (3.11) must be positive. Substituting for $n_\alpha(T_{\alpha\gamma}) n_\gamma(T_{\alpha\gamma})$ the

lowest and highest values compatible with Eq. (1.5), that is, 0 and $\frac{1}{4}$, we can deduce the maximum and minimum values, respectively, of $\Delta\mathcal{F}_H(T_{\alpha\gamma})$. We can find now the transition temperature in a magnetic field, $T_{\alpha\gamma}(H)$, by requiring that $\Delta\mathcal{F}_0(T_{\alpha\gamma}(H)) + \Delta\mathcal{F}_H(T_{\alpha\gamma}) = 0$. Substituting the given values of D , K , and J and any value between 100 and 580 K for $T_{\alpha\gamma}$, we find that $T_{\alpha\gamma}(H) < T_{\alpha\gamma}$: the magnetic field lowers the α - γ transition temperature as expected on the basis of the arguments presented at the beginning of this section. However, the effect is very small: taking $H = 1$ T for the magnetic field, $T_{\alpha\gamma} - T_{\alpha\gamma}(H)$ is found to be less than 0.2 K. Clearly, we are not predicting any spectacular effect, and although $T_{\alpha\gamma} - T_{\alpha\gamma}(H)$ is proportional with H^2 , it would be very hard to detect the lowering of $T_{\alpha\gamma}$ in presently available magnetic fields.

IV. FERROMAGNETIC PHASES

In the present section we will investigate the properties of our model in the case when one takes a higher value than 0.08 eV for the conduction-electron- f -electron exchange parameter K . We shall take $K = 0.25$ and 0.20 eV, which, according to Eq. (3.9), corresponds to $T_{\text{Curie}}^{\text{max}} = 829$ and 529 K, respectively, and therefore should give ferromagnetism in the γ phase. As pointed out in the preceding section, with such a choice of the interaction parameter the model is certainly not relevant to cerium. However, the ferromagnetic transitions to be discussed have some very interesting features, which might be of use in understanding other, related systems. In fact, Robinson and Erdős¹⁰ recently developed a very similar model to explain the antiferromagnetic transitions in some actinide compounds, and there is no reason why similar ferromagnetic systems should not exist.

In order to understand the qualitative features of the phase diagram appropriate to our model, let us consider the free energy in the absence of an external field at $T = 0$. Whether or not there is a spontaneous magnetization σ_f of the f electrons, we can visualize a competition between the energy necessary to localize an electron from the conduction band into the f state with energy E and the interaction energy (G and a term proportional to $K^2\sigma_f^2$) gained by localization. Therefore, if K is sufficiently large, there is a value of E [i.e., there is a certain pressure $P_{\text{Curie}}(0)$], below which localization onto ferromagnetically aligned f states occurs, and above which the paramagnetic state with no f electrons is stable. The value of E at which the transition takes place can be found by requiring that the free energies (in this case, $T = 0$, equal to the internal energies) of the ferromagnetic and

paramagnetic phases be equal. This condition results in

$$E(P_{\text{Curie}}(0)) = \frac{1}{2}\rho + \frac{1}{72}\left(\frac{5}{2}\right)^2 g_f^2 S K^2 D.$$

If we want to repeat the same argument for a finite temperature, in order to determine $P_{\text{Curie}}(T)$, we have to take into account the way the entropy of both phases changes. Clearly, with increasing temperature the entropy of the ferromagnetic γ (FM γ) phase rises faster than that of the paramagnetic α (PM α) phase, because of the greater number of microstates in the former case. Therefore, the free energy of the FM γ phase diminishes faster, and $P_{\text{Curie}}(T)$ increases with increasing temperature. This implies that, raising the temperature from $T = 0$ at a pressure just above $P_{\text{Curie}}(0)$, there will be a temperature at which a transition from the PM α to the FM γ phase takes place. Since in the PM α phase $n_f \ll 1$, whereas in the FM γ phase $n_f \approx 1$, this is a first-order transition.

As the temperature is raised further, thermal motion lowers the magnetization, and the total ferromagnetic interaction energy becomes smaller. Therefore, there are electrons falling back from the f states into the conduction band. On the other hand, the mechanism responsible for the α - γ transition leads to an increase of the f -state occupation probability. The balance between these two mechanisms determines the equilibrium state at any temperature. In the PM γ phase only the latter mechanism plays a role. Thus, the difference between the f -state occupation probabilities in the ferro- and paramagnetic γ phases becomes smaller with increasing temperature. This process will proceed until either the spontaneous magnetization σ_f dwindles away, at which point the f -state occupation probabilities of the two phases become equal (i.e., a second-order phase transition takes place), or the free energy of the FM γ phase becomes higher than that of the PM γ phase at a finite value of σ_f (i.e., a first-order transition takes place).

Figure 2 shows the phase diagram for two values of the exchange parameter K . For $K = 0.2$ eV (dash-dotted curve) the transition from the PM γ phase to the FM γ is always of second order; for 8.5 kbar $< P < 14.6$ kbar there is a first-order transition to the PM α phase as the temperature is further lowered. For $K = 0.25$ eV (full curve) the PM γ -FM γ transition is of second order up to 19 kbar, for 19 kbar $< P < 20.5$ kbar this becomes a first-order transition. The dashed curve beyond 19 kbar represents T_{Curie} as given by Eq. (3.8), in this case the only physical significance of T_{Curie} lies in determining the range of possible supercooling under the first order transition temperature. Below T_{Curie} the PM γ phase cannot exist,

not even as a metastable phase.

The behavior of the free energy, f -state occupation probability, and f -electron magnetization for $K=0.25$ eV at the pressures indicated in Fig. 2 is shown in Figs. 3 and 4. In some cases the free energy appears to be a double-valued function of n_f , but this is, of course, not the case. The full curves represent the free energy for $\sigma_f=0$; the broken curves correspond to the equilibrium magnetization, that is, they give the free energy after minimalization with respect to σ_f ; for the n_f values where the equilibrium magnetization is zero, there is only one curve.

Figure 3(b) corresponds to the "degenerate" case when the width of the FM γ range in the phase diagram has just disappeared at $P=P_4$. At $T=600$ K the free energies of the ferromagnetic and paramagnetic phases are equal, but both at higher and lower temperatures the paramagnetic phase corresponds to the absolute minimum of the free energy.

Figure 3(a) represents in our view the most interesting case. Between 650 and 600 K the free-energy minimum corresponding to the FM γ phase sinks below the one corresponding to PM γ : at $T=630$ K the occupation probability n_f changes discontinuously, and a finite magnetization corresponding to about 40% of the maximum possible magnetization of the γ phase, appears [Fig. 4(a)]. As the temperature is further lowered, the lowest free-energy minimum corresponding to the PM α phase appears to become the absolute minimum at $T=510$ K. Here the magnetization disappears, and n_f falls to its α -phase value, which tends to zero at even lower temperatures.

FIG. 2. Phase diagrams for models involving exchange parameters K not appropriate to cerium. The pressures P_1 – P_4 refer to Figs. 3 and 4.

The free-energy curve corresponding to $P=P_3$ and $T=600$ K [Fig. 3(b)] illustrates a feature of the first-order transitions, which can be used to derive at least a sufficient (if not necessary) condition for the occurrence of a first-order transition. A second order transition is defined by $[\partial \mathcal{F} / \partial (\sigma_f^2)]_{\sigma_f=0} = 0$ in combination with $\partial \mathcal{F} / \partial n_f = 0$ and $\partial^2 \mathcal{F} / \partial n_f^2 > 0$. This means that at T_{Curie} the magnetic branch of the free-energy curve splits off exactly in the minimum of the nonmagnetic curve, that is, at $n_f(T_{\text{Curie}})$. However, if the ferromagnetic branch starts off with a downward curvature, there will be a lower lying minimum at a higher n_f value, indicating that a first order transition has already taken place at a higher temperature. Mathematically, this can be expressed by stating that there is no second-order transition at T_{Curie} if

$$\frac{\partial^2 \mathcal{F}}{\partial n_f^2} - \frac{[\partial^2 \mathcal{F} / \partial n_f \partial (\sigma_f^2)]^2}{\partial^2 \mathcal{F} / \partial (\sigma_f^2)^2} < 0. \quad (4.1)$$

Using Eq. (A5), this condition becomes

$$\rho > k_B T_{\text{Curie}} \left(\left(1 - \frac{1225}{518} \right) \frac{1}{n_f(T_{\text{Curie}})} + \frac{1}{1 - n_f(T_{\text{Curie}})} \right). \quad (4.2)$$

FIG. 3. Free energy as a function of f -state occupation probability for two pressures indicated in Fig. 2 and various temperatures. The full line corresponds to $\sigma_f=0$ and the broken line to the equilibrium magnetization, when that is not zero.

The value of ρ is thus smaller than this expression along the PM γ -FM γ transition line for $K=0.2$ eV in Fig. 2, and along the line for $K=0.25$ eV up to the point where the broken curve branches off, at which point the two sides of (4.2) are equal, the right-hand side becoming smaller along the broken line.

V. CONCLUSION

We have studied the Ramírez-Falicov model of the α - γ phase transition in cerium allowing for a field induced or spontaneous splitting of the bands and of the sixfold degenerate $4f$ level. We found the effect of presently available magnetic fields on the transition temperature $T_{\alpha\gamma}$ in cerium to be small and of little experimental interest. Taking higher values (not appropriate to cerium) for the exchange parameter, we find a wealth of magnetic transitions of first and second order. The possibility of a valency change transition leading to magnetization curves such as shown in Fig. 4 is an interesting feature of the model and may turn out to be of practical interest in the analysis of experimental results. It is especially noteworthy that in a case like the one represented in Fig. 4 the nonmagnetic valency change transition is not observable, because the magnetic transition curve has fully enveloped the α - γ transition line. Under such circumstances it is by no means straightforward to identify the valency change transition on the basis of the observed magnetic behavior.

APPENDIX

In this appendix we shall rewrite the free energy (2.8) in terms of the f -electron magnetization σ_f (eliminating the conduction-electron magnetization) and derive a power series expansion for the free energy.

In the first term of Eq. (2.8) $K(n_s(\epsilon))$ is expressed, using Eq. (2.11) as:

$$\begin{aligned} K(n_s(\epsilon)) &= k_B T (n_s(\epsilon) \ln \{n_s(\epsilon)/[1-n_s(\epsilon)]\} \\ &\quad + \ln[1-n_s(\epsilon)]) = -(\epsilon - sg_c \mu_B H_c - \zeta) n_s(\epsilon) \\ &\quad + k_B T \ln[1-n_s(\epsilon)]. \end{aligned} \quad (A1)$$

Therefore we require the integral $\int_0^W \ln[1-n_s(\epsilon)] d\epsilon$, which can be evaluated by introducing the integration variable $z = 1-n_s(\epsilon)$ and using Eq. (2.11) and the identity $\int_0^1 \ln(z)/(1-z) dz = -\pi^2/6$; we obtain assuming that $\zeta, W - \zeta \gg k_B T$:

$$\begin{aligned} \int_0^W \ln[1-n_s(\epsilon)] d\epsilon &= -k_B T \{2[(s\mu_B H_c + \frac{1}{2}\zeta)/k_B T]^2 + \pi^2/6\} \\ &= k_B T \{\frac{1}{2}[(sg_c \mu_B H_c + \zeta)/k_B T]^2 + \pi^2/6\}. \end{aligned} \quad (A2)$$

In the third term of Eq. (2.8) $\sum_M p_M \ln(p_M)$ can be evaluated using Eq. (2.20):

$$\begin{aligned} \sum_M p_M \ln(p_M) &= \frac{g_f \mu_B H_f}{k_B T} \sum_M M p_M - \ln \sum_M \exp \frac{M g_f \mu_B H_f}{k_B T} \\ &= \frac{g_f \mu_B H_f}{k_B T} M p_M + \ln \frac{\sinh(\frac{1}{2} g_f \mu_B H_f / k_B T)}{\sinh(3 g_f \mu_B H_f / k_B T)}. \end{aligned} \quad (A3)$$

Using Eqs. (2.9), (2.10), (2.12), (2.15), (2.16), and (2.19), defining $E = E' - 4/D$ and $\rho = 2G - 1/D$, after substituting Eqs. (A1)–(A3) into (2.8) and dropping constant terms, we find the free energy as a function of P (through E), T , n_f , and H :

$$\begin{aligned} \frac{1}{N} \mathcal{F} &= -(\pi^2/6) D (k_B T)^2 - \frac{\frac{1}{2} D}{1 - \frac{1}{2} J D} (\mu_B H)^2 + n_f (E - \frac{1}{2} \rho n_f) \\ &\quad + \frac{\frac{1}{2} D}{1 - \frac{1}{2} J D} \left(\frac{K}{6 \mu_B} \right)^2 \sigma_f^2 \\ &\quad + k_B T n_f \ln \frac{\sinh(\frac{1}{2} g_f \mu_B H_f / k_B T)}{\sinh(3 g_f \mu_B H_f / k_B T)} + K(n_f), \end{aligned} \quad (A4)$$

where $\sigma_f = \sigma_f(H)$. It is easily verified that $\mathcal{F}$ is an even function of H , as it should be, and that for $H=0$, $\sigma_f=0$ this expression reduces to the free energy given by Kiwi and Ramírez⁴ in their Eq. (2.22).

For constant p and T , and $H=0$, the free energy is a function of n_f and σ_f^2 and can be expanded around the value $\sigma_f^2=0$ and an arbitrary value $n_f=n_0$:

FIG. 4. Magnetization (full curve) and f -state occupation probability (broken curve) as functions of the temperature for three different pressures indicated in Fig. 2.

$$\begin{aligned} \frac{1}{N} \mathcal{F}(\sigma_f^2, n_f) = & \frac{1}{N} \mathcal{F}(0, n_0) + A \left(1 - 5n_0 \frac{g_f A}{k_B T} \right) \left(\frac{\sigma_f}{\mu_B} \right)^2 + \frac{1}{N} \frac{\partial \mathcal{F}}{\partial n_f} (n_f - n_0) + \frac{37}{6} n_0 A \left(\frac{g_f A}{k_B T} \right)^3 \left(\frac{\sigma_f}{\mu_B} \right)^4 \\ & - \frac{5g_f A^2}{k_B T} \left(\frac{\sigma_f}{\mu_B} \right)^2 (n_f - n_0) \\ & + \frac{1}{2} \left[k_B T \left(\frac{1}{n_0} + \frac{1}{1 - n_0} \right) - \rho \right] (n_f - n_0)^2, \end{aligned} \quad (\text{A5})$$

where

$$A = \left[\frac{1}{2} D / (1 - \frac{1}{2} J D) \right] \left(\frac{1}{6} K \right)^2.$$

*Partially sponsored by the Foundation for Fundamental Research of Matter (F.O.M.) of the Netherlands.

†Present address: Koninklijke/Shell Exploratie en Produktie Laboratorium, Volmerlaan 6, Rijswijk, The Netherlands.

¹L. Pauling, J. Chem. Phys. **18**, 145 (1950).

²W. H. Zachariasen, Phys. Rev. **76**, 301 (1949).

³R. Ramírez and L. M. Falicov, Phys. Rev. B **3**, 2425 (1972).

⁴M. Kiwi and R. Ramírez, Phys. Rev. B **6**, 3700 (1972).

⁵B. Alascio, A. Lopez, and C. F. E. Olmedo, J. Phys.

F **3**, 1324 (1973).

⁶A. J. T. Grimberg and C. J. Schinkel, Solid State Commun. **13**, 193 (1973).

⁷E. P. Wohlfarth, J. Appl. Phys. **39**, 1061 (1968).

⁸C. Kittel, *Introduction to Solid State Physics*, 4th ed. (Wiley, New York, 1971).

⁹N. T. Panousis and K. A. Gschneidner, Solid State Commun. **9**, 1779 (1970).

¹⁰J. M. Robinson and P. Erdős, Phys. Rev. B **8**, 4333 (1973).