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Effect of finite f level linewidth on the theory of the α–γ transition in Ce

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Abstract. We have extended the Ramirez–Falicov theory of the α–γ transition in Ce to include the effect of hybridization of the localized 4f states with the band. The physical properties of the α and γ phases are calculated using thermodynamic Green functions which are determined by a decoupling procedure that accounts for the highly correlated character of the f levels. The decoupling procedure is exact to second order in the hybridization parameter. We find satisfactory values for the noninteger valency, electronic specific heat and magnetic susceptibility of the α phase. A Curie law for the γ phase is also obtained.

1. Introduction

The properties of Ce metal have attracted much attention lately (King *et al* 1970, Franceschi and Olcese 1969, Maple and Wohlleben 1971, Coqblin and Blandin 1968, Ramirez and Falicov 1971). This is due on one hand to the fact that Ce is the only metal known to present a paramagnetic and a superconducting phase (MacPherson *et al* 1971), and on the other hand to the fact that the α–γ transition resembles in many respects the metal insulator transition in cromium doped vanadium sesquioxide (Rice and McWhan 1970).

Zachariasen (1949) and Pauling (1950) have suggested that the transition is connected with the promotion of an electron from the conduction band in the α phase to an f orbital in the γ phase.

Two mechanisms have been proposed for this promotion. Coqblin and Blandin (1968) have formulated a theory based on an extension of the Anderson–Friedel model including a strong spin–orbit interaction. This theory explains the existence of a critical point and the noninteger valencies found in α cerium (Gschneidner and Smoluchowski 1963). By adjusting the value of the intra-atomic Coulomb repulsion, Coqblin (1971) was able to correlate the measurements of specific heat and magnetic susceptibility in this face.

This model is based on a Hartree–Fock approximation which neglects correlation between localized 4f electrons, whereas from the experimental values of the magnetic susceptibility of the γ phase one can extract a Landrú *g* value close to that of ionic Ce^{3+} indicating highly correlated 4f electrons. Furthermore, the Hartree–Fock scheme

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applied to the Green functions to obtain the thermodynamic properties does not allow for a correct description of the spin entropy in the γ phase.

An alternative mechanism has been proposed by Ramirez and Falicov (1971), who have formulated a theory based on the existence of highly correlated localized f states and itinerant conduction electron states derived from hybridized s and d bands. The spin entropy associated with the f levels plays a crucial role in enhancing the population of the localized states at high temperatures. The Coulomb repulsion between the band states and localized states provides a feedback mechanism which makes a first order transition possible. By assuming a linear dependence of the parameters on the pressure they were able to reproduce the main features of the phase diagram, including the existence of the critical point. This theory, in its present form does not account for the nonintegral valency, the weak temperature dependence of the susceptibility, and the large electronic specific heat found in the α phase.

Recently, Kiwi and Ramirez (1972) have attempted to explain these anomalous properties by including the $J = \frac{7}{2}$ multiplet, which due to spin–orbit coupling lies in the free ion some 3000 K above the ground state. Their main results however are invalidated by a wrong assumption concerning the spectral density of the fourteen 4f levels. In appendix 3 we briefly discuss the effect of including the $J = \frac{7}{2}$ multiplet by using straightforward statistical mechanics arguments. This discussion, which can be extended to include the effect of crystal field splittings of the $J = \frac{5}{2}$ level, shows that in the limit of strong correlation and for zero linewidth, these splittings have negligible effect and cannot in any way account for the anomalous properties of α-Ce.

We present here a modified form of the Ramirez–Falicov theory, based on a Hamiltonian that includes s–f hybridization and which is able to improve these features.

2. The model Hamiltonian

For the purposes of our theory, one can view cerium metal in the γ phase as an array of Ce^{3+} ion cores (going to Ce^{4+} in the α phase) immersed in the sea of conduction electrons. Since the strongly paramagnetic phase occurs only at relatively high temperatures, one can argue (Schrieffer 1969) that the spin at each atomic site will see no net magnetic field arising from its neighbours. For this reason one can reduce the problem to that of an aggregate of one centre problems.

We will consider the Coulomb repulsion between localized and band states in the Hartree–Fock approximation from the outset. Within our decoupling scheme for the Green functions, the nondiagonal terms arising from the Coulomb repulsion can be shown to give rise to a renormalization of the hybridization parameter.

With these two basic assumptions the one centre problem can be described with an Anderson type Hamiltonian (Anderson 1961) as that used by Coqblin and Schrieffer (1969) for the theory of the Kondo effect in Ce alloys

$$\begin{aligned} H = \sum_{kJ'M} E_k c^{+}_{kJ'M} c_{kJ'M} + E_0 \sum_{M} b^{+}_{M} b_{M} + U \sideset{}{'}\sum_{MM'} b^{+}_{M} b_{M} b^{+}_{M'} b_{M'} \\ + \sum_{kM} (V_k c^{+}_{kJM} b_M + V^{*}_{k} b^{+}_{M} c_{kJM}) \qquad (2.1) \end{aligned}$$

where

$$E_k = \epsilon_k + G \sum_{M} \langle b^{+}_{M} b_{M} \rangle$$

are the energies of the band states corrected by the Coulomb repulsion with the localized states $G\Sigma_M\langle b^+_M b_M\rangle$; $c^+_{kJ'M}$ is a creation operator for an electron in a band state of energy E_k, total angular momentum J' and z component M; $E_0 = E_L + Gn_c$ is the renormalized energy of the localized state, E_L being the bare energy of the localized states and n_c the number of conduction electrons per atom. b^+_M creates an electron in the localized state with total angular momentum $J = \frac{5}{2}$ and z component M ($M = \frac{5}{2}, \frac{3}{2}, \ldots, -\frac{5}{2}$). U is the intra-atomic Coulomb integral and V_k the hybridization parameter between the localized f states and the band.

To obtain the free energy associated with the Hamiltonian (2.1) we use the Green functions technique (Zubarev 1960). The equations of motion for the relevant Green functions that arise from our model Hamiltonian are:

$$\omega\langle\langle b_M|b^+_M\rangle\rangle = \frac{1}{2\pi} + E_0\langle\langle b_M|b^+_M\rangle\rangle + U\sum_{M'}{}'\langle\langle b^+_{M'}b_{M'}b_M|b^+_M\rangle\rangle + \sum_k V^*_k\langle\langle c_{kJM}|b^+_M\rangle\rangle \tag{2.2}$$

$$\begin{aligned}\omega\langle\langle b^+_{M'}b_{M'}b_M|b^+_M\rangle\rangle = {}& \frac{\langle b^+_{M'}b_{M'}\rangle}{2\pi} + E_0\langle\langle b^+_{M'}b_{M'}b_M|b^+_M\rangle\rangle + U\sum_{M''}{}'\langle\langle b^+_{M''}b^+_{M'}b_{M'}b_M|b^+_M\rangle\rangle\\ &+\sum_k V^*_k\langle\langle b^+_{M'}b_{M'}c_{kJM}|b^+_M\rangle\rangle + \sum_k V^*_k\langle\langle b^+_{M'}c_{kJM'}b_M|b^+_M\rangle\rangle\\ &-\sum_k V_k\langle\langle c^+_{kJM'}b_{M'}b_M|b^+_M\rangle\rangle\end{aligned} \tag{2.3}$$

$$\omega\langle\langle c_{kJM}|b^+_M\rangle\rangle = E_k\langle\langle c_{kJM}|b^+_M\rangle\rangle + V_k\langle\langle b_M|b^+_M\rangle\rangle. \tag{2.4}$$

In the equations above, $\langle\langle A|B\rangle\rangle$ indicates the Fourier transform of the Green function as defined by Zubarev (1960).

One possibility of solving these equations is to obtain a closed set by means of some decoupling procedure. As pointed out above, if one uses a Hartree–Fock decoupling one cannot describe the spin entropy associated with the Ce^{3+} ions which is essential to the RF mechanism for the transition. For this reason we choose the decoupling procedure used by Hewson (1966) for the Anderson Hamiltonian, as modified by Hewson and Zuckerman (1966), which is exact for $V_k = 0$ and thus allows for highly correlated states in the $U \to \infty$ limit. In fact, since U is thought to be much larger than either the linewidth of kT (Ramirez and Falicov 1971) we shall in what follows consider only the limit $U \to \infty$.

Accordingly, we make the following approximations in equation (2.3):

$$\langle\langle b^+_{M'}b_{M'}c_{kJM}|b^+_M\rangle\rangle \simeq \frac{V_k}{\omega - E_k}\langle\langle b^+_{M'}b_{M'}b_M|b^+_M\rangle\rangle$$

$$\langle\langle b^+_{M'}c_{kJM'}b_M|b^+_M\rangle\rangle \simeq 0$$

$$\langle\langle c^+_{kJM'}b_{M'}b_M|b^+_M\rangle\rangle \simeq 0.$$

Furthermore, $\langle\langle b^+_{M''}b_{M''}b^+_{M'}b_{M'}b_M|b^+_M\rangle\rangle$ for $M'' \neq M'$ is related to the double occupation of the localized states at the same atom, which we assume cannot occur (Blandin *et al* 1967, Toulouse 1970), and thus we set

$$\langle\langle b^+_{M''}b_{M''}b^+_{M'}b_{M'}b_M|b^+_M\rangle\rangle \simeq \delta_{M'M''}\langle\langle b^+_{M'}b_{M'}b_M|b^+_M\rangle\rangle. \tag{2.5}$$

This last equation becomes exact for $U \to \infty$ if the Fermi energy remains near E_0.

From (2.4) one gets

$$\langle\langle c_{kJM}|b_M^+\rangle\rangle = \frac{V_k}{\omega - E_k}\langle\langle b_M|b_M^+\rangle\rangle. \tag{2.6}$$

Replacing (2.6) into (2.2) and (2.3), and using the approximations described above, we obtain

$$\langle\langle b_M|b_M^+\rangle\rangle = \frac{1}{2\pi}\frac{S_M}{\omega - E_0 - \Delta(\omega)} \tag{2.7}$$

where

$$S_M = 1 - \sum_{M'}{}' \langle b_{M'}^+ b_{M'}\rangle = 1 - \sum_{M'}{}' n_{M'} \tag{2.8}$$

and

$$\Delta(\omega) = \sum_k \frac{|V_k|^2}{\omega - E_k}. \tag{2.9}$$

Correlation functions are calculated from the Green functions through (Zubarev 1960)

$$\langle A(t)B(0)\rangle = \int_{-\infty}^{\infty} \mathrm{d}\omega\, \mathrm{e}^{-\mathrm{i}\omega t} f(\omega)\, \mathrm{i}(\langle\langle B|A\rangle\rangle_{\omega+\mathrm{i}0} - \langle\langle B|A\rangle\rangle_{\omega-\mathrm{i}0})$$

where $f(\omega) = \{\exp(\omega - \mu)/T + 1\}^{-1}$ is the Fermi function. This allows us to calculate the occupation of the f levels. One obtains

$$n_M = S_M \int_{-\infty}^{\infty} \mathrm{d}\omega\, f(\omega) \frac{1}{\pi}\frac{\Gamma}{(\omega - E_0)^2 + \Gamma^2} \tag{2.10}$$

where $\Gamma = -\operatorname{Im}\Delta(\omega + \mathrm{i}0)$, and we have included $\operatorname{Re}\Delta(\omega + \mathrm{i}0)$ in E_0. One can easily see that in the limit $\Gamma \to 0$ one obtains

$$n_M = S_M f(E_0) = \frac{S_M}{\exp(E_0 - \mu/T) + 1}. \tag{2.11}$$

In the absence of external fields all the n_Ms are equal. Calling n the total occupation of the six f sublevels (equal to $6n_M$) we obtain from (2.11)

$$n = \{\tfrac{1}{6}\exp(E_0 - \mu)/T + 1\}^{-1}. \tag{2.12}$$

For the case of Ce, we have to use the concept of aggregate we described above. This gives a relation between μ and n implied by the conservation of charge:

$$n_c + n = 4 \tag{2.13}$$

Using a step function for the Fermi distribution (Alascio *et al* 1972) of the conduction electrons and a constant density of states α, as in Ramirez and Falicov (1971) one can write

$$n_c = \int_{Gn}^{E_F} \mathrm{d}\epsilon\, \alpha = \alpha(E_F - Gn). \tag{2.14}$$

Replacing $E_F \simeq \mu = Gn + (4 - n)/\alpha$, and $E_0 = E_L + Gn_c = E_L + G(4 - n)$ in (2.12) one obtains

$$n = \{\tfrac{1}{6}\exp(E - 2Bn/T + 1\}^{-1} \tag{2.15}$$

where

$$E = E_L + 4(G - 1/\alpha) \tag{2.16}$$

and

$$B = G - \tfrac{1}{2}\alpha \tag{2.17}$$

in agreement with formula (3.4) of Alascio *et al* (1972).

3. The free energy

The free energy per atom of the aggregate in the limit $V_k = 0$ can be easily seen to coincide with that of the Ramirez–Falicov theory (Ramirez and Falicov 1971) as is shown in appendix 1. This shows how the free energy used by these authors can be obtained from the Hamiltonian (2.1) by the use of Green functions. Within the above mentioned approximation of using a step function for the distribution function of the conduction electrons we obtain (Alascio *et al* 1972):

$$F_0 = En - Bn^2 + T\{n\ln n + (1-n)\ln(1-n) - n\ln 6\}. \tag{3.1}$$

The correction to the thermodynamic quantities due to the hybridization part of the Hamiltonian can be obtained from the correction to the thermodynamic potential Ω given by (Kadanoff and Baym 1962).

$$\delta\Omega = \delta(F - \mu N) = \int_0^1 \mathrm{d}\lambda \langle H'\rangle_\lambda \tag{3.2}$$

where $\langle\ldots\rangle_\lambda$ is the thermal average taken with the Hamiltonian $H_\lambda = H_0 + \lambda H'$. In our case H' is the hybridization part.

In the absence of a magnetic field we get

$$\delta\Omega = 6\int_0^1 \frac{\mathrm{d}\lambda}{\lambda}\int_{-\infty}^{\infty} \mathrm{d}\omega\, f(\omega)\,\frac{1}{\pi}\,\frac{\lambda\Gamma(\omega - E_0)S}{(\omega - E_0)^2 + \lambda^2\Gamma^2} \tag{3.3}$$

where $S = 1 - \frac{5}{6}n$.

This expression when expanded to second order in the hybridization parameter V_k reduces to

$$\delta\Omega^{(2)} = \int_{-\infty}^{\infty} \mathrm{d}\omega\, f(\omega)\,\frac{6}{\pi}\,\frac{\Gamma S}{\omega - E_0}$$

which coincides with perturbation calculations, which are an extension of the result of Scalapino (1966) to a sixfold degenerate level (Olmedo *et al* 1973).

The equation determining the occupation of the f levels (2.10) does not coincide to second order in V_k with the result of the perturbation calculation. This is due to the fact that the Green function $\langle\langle b_M | b_M^+\rangle\rangle$ obtained by the decoupling scheme is not correct to second order. In the calculation of $\delta\Omega$ however this Green function enters only in zeroth order.

The expression for n correct to second order can be obtained from $\delta\Omega^{(2)}$ by using the relation $n = \partial\Omega/\partial E_0$.

In the limit $T \ll |E_F - E_0|$, this expression coincides with the result one obtains expanding (2.10) to second order in V_k. The result is

$$n = n^{(0)} + \frac{6\Gamma}{\pi} S^{(0)} \int_{-\infty}^{\infty} \mathrm{d}\omega\, f'(\omega) \frac{1}{\omega - E_0} \tag{3.4}$$

where $n^{(0)}$ is the occupation of the f levels calculated with zero width (2.15), and $S^{(0)} = 1 - \frac{5}{6}n^{(0)}$.

The perturbation procedure is not valid for E_0 near E_F and it is in this range that the decoupling procedure provides an interpolation method.

The procedure used in the appendix to evaluate the free energy for the $\Gamma = 0$ case, when applied to equation (2.10) provides an alternative expression for the free energy. This does not coincide at first sight with the correction calculated from (3.2). Explicit evaluation of (3.3) however requires integrating over λ including $S(\lambda)$, which would follow only after the selfconsistent equation (2.10) for $n(\lambda)$ has been solved. In spite of this complication, the decoupling procedure used has the merit of being the simplest interpolation method that reduces to the exact result for $\Gamma \to 0$.

4. The physical properties

The expressions given in the preceding paragraph for the free energy should allow us in principle to adjust the parameters entering the model so as to reproduce the phase diagram of Ce. The rather crude nature of the Ramirez–Falicov model itself and of the decoupling scheme used make it unjustified, to perform the complex numerical calculations involved in such a procedure.

For this reason, we have used only the selfconsistent equation to estimate the values of the parameters, guided by the $\Gamma = 0$ results (Alascio *et al* 1972). In what follows we take $\Gamma = 200$ K, in agreement with the values usually quoted (Coqblin and Blandin 1968, Gonçalves da Silva and Falicov 1972). We then find $E = 2011 + 39{\cdot}85p$ and $B = 1500$, where p is the pressure in kbar and E and B are given in degrees Kelvin.

4.1. Valencies

The valencies are determined by intersecting the function $n/(6 - 5n)$ with the result of integrating the right hand side of (2.10) (Coqblin and Blandin 1968)

$$\phi(n) = \tfrac{1}{2} + \frac{1}{\pi} \operatorname{Im} \psi\left(\frac{1}{2} + \frac{\Gamma}{2\pi T} + \mathrm{i}\frac{2Bn - E}{2\pi T}\right) \tag{4.1}$$

where Im indicates the imaginary part, ψ is the digamma function and

$$2Bn - E = E_F - E_0. \tag{4.2}$$

Equation (4.1) reduces for $T = 0$, to

$$\phi(n) = \tfrac{1}{2} + \frac{1}{\pi} \arctan \frac{2Bn - E}{\Gamma} \tag{4.3}$$

and for $\Gamma = 0$ to

$$\phi(n) = \tfrac{1}{2} + \tfrac{1}{2} \tanh \frac{2Bn - E}{2T}. \tag{4.4}$$

In figure 1 we show plots of $\phi(n)$ for $T = 0$ K, 116 K and 300 K, with the value of E corresponding to zero pressure. The curve for $T = 300$ K has only one intersection with $n/(6-5n)$ at a value of n near 1, thus it corresponds to the γ phase (valency 3·02). The curve for $T = 116$ K shows three intersections at $n \simeq 0{\cdot}99$, $n \simeq 0{\cdot}5$ and $n \simeq 0{\cdot}24$. We take this as the curve corresponding to the transition. Thus we calculate a change of valency from 3·01 in the γ phase to 3·76 in the α phase.

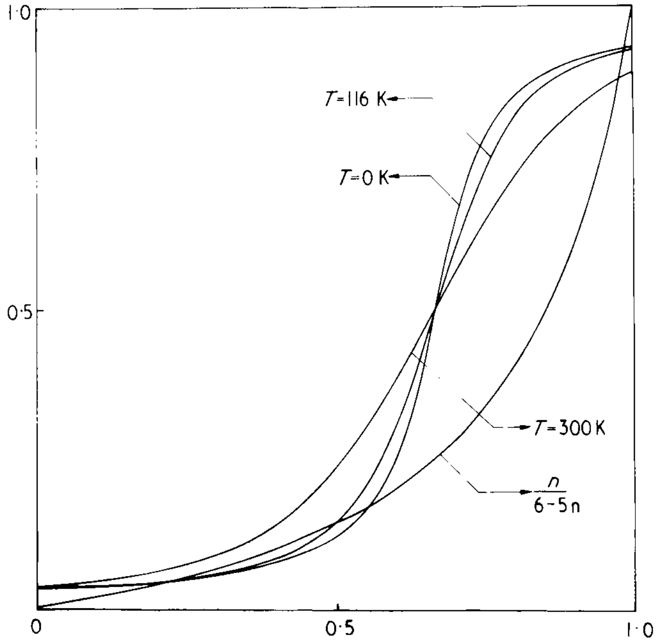

Figure 1. The function $\phi(n)$ plotted against n for different temperatures. Intersection with $n/(6-5n)$ gives the f level occupancy.

The curve for $T = 0$ also shows three intersections. We assume here that the stable phase is the α phase with a valency 3·77.

For $T \ll |E_0 - E_F|$ we can use the perturbation approximation to determine n. For $T = 0$ it follows that

$$n = n^{(0)} - \frac{6\Gamma}{\pi} S^{(0)} \frac{1}{E_F - E_0} \tag{4.5}$$

which can be used to give the valency of the α phase to sufficient accuracy.

Due to the increase in ionic radii induced by the occupancy of the f levels, we can correlate our determinations for n with the experimental values for the lattice constant a of Ce, as determined for instance by Franceschi and Olcese (1969). We assume a relation of the form

$$a = \alpha + \beta n \qquad (a \text{ in Å}). \tag{4.6}$$

According to Franceschi and Olcese, one has $a = 4{\cdot}65$ Å for the α' phase ($n = 0$) and $a = 5{\cdot}16$ Å ($n = 0{\cdot}955$) for the γ phase at $T = 300$ K. This gives $\alpha = 4{\cdot}65$ and $\beta = 0{\cdot}534$.

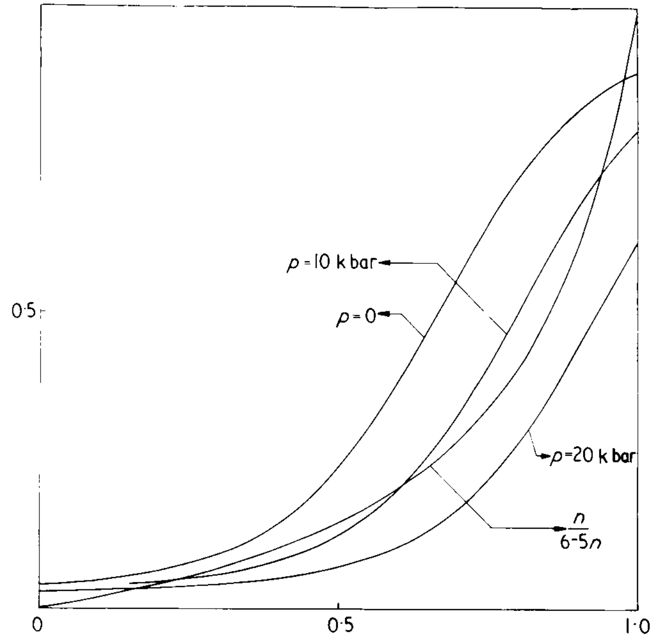

Figure 2. The function $\phi(n)$ plotted against n for $T = 300$ K and different pressures. The f level occupancy is determined by the intersection with the function $n/(6-5n)$.

Figure 2 is a graphical construction giving the f level occupancy n as the intersection of $n/(6-5n)$ with $\phi(n)$ as defined above, for different values of the pressure and $T = 300$ K.

In figure 3 we show a as a function of p as we obtain by solving the selfconsistent equation (2.10) and using (4.6). The experimental points by Franceschi and Olcese are also shown.

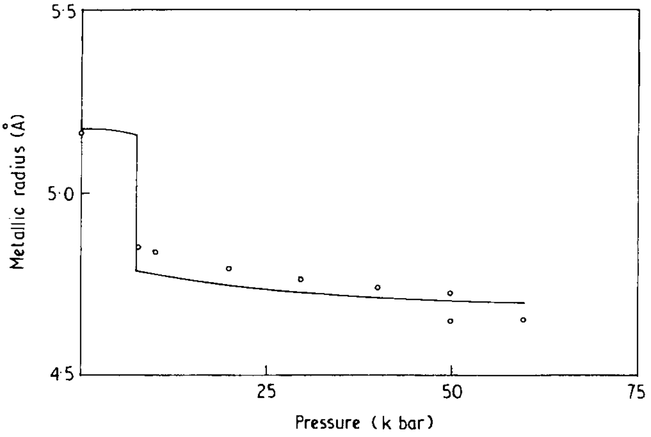

Figure 3. Lattice constant as a function of pressure. The solid line is the result of the present work; the points are from the experiments by Franceschi and Olcese (1969).

4.2. *Magnetic susceptibility*

In the presence of an external magnetic field the selfconsistent equation for the f levels occupancy is

$$n_M = S_M \int_{-\infty}^{\infty} \mathrm{d}\omega\, f(\omega) \frac{1}{\pi} \frac{\Gamma}{(\omega - E_M)^2 + \Gamma^2} \tag{4.7}$$

with $E_M = E_0 - M\mu H$, where $\mu = g\mu_B$ is the magnetic moment of the $J = \frac{5}{2}$ multiplet (Kittel 1971), $g = 0{\cdot}857$ is the Landé factor and H the external magnetic field.

To determine the contribution of the f electrons to the magnetic susceptibility we need to solve equations (4.7) to first order in H. To do this we write the solutions in the form

$$n_M = \tfrac{1}{6}n + M\delta \tag{4.8}$$

where δ is a quantity proportional to H. Substituting in (4.7) we get

$$\begin{aligned} \tfrac{1}{6}n + M\delta &= (S + M\delta) \int_{-\infty}^{\infty} \mathrm{d}\omega\, f(\omega) \left(\rho_L(\omega) - \frac{\partial \rho_L(\omega)}{\partial E_0} M\mu H \right) \\ &= \tfrac{1}{6}(S + M\delta) \left\{ \frac{n}{S} - \frac{\partial}{\partial E_0}\left(\frac{n}{S}\right) M\mu H \right\} \end{aligned} \tag{4.9}$$

with

$$\rho_L(\omega) = \frac{1}{\pi} \frac{\Gamma}{(\omega - E_0)^2 + \Gamma^2}$$

which implies

$$\delta = - \frac{S^2}{6(1 - n)} \frac{\partial}{\partial E_0}\left(\frac{n}{S}\right) \mu H. \tag{4.10}$$

The magnetic moment per atom will thus be

$$m = \mu \sum_{-J}^{J} M n_M = \mu\delta \sum_{-J}^{J} M^2 = \tfrac{1}{3}J(J + 1)(2J + 1)\mu\delta \tag{4.11}$$

and consequently we have for the susceptibility per atom

$$\chi_f = g^2\mu_B^2 \frac{J(J + 1)}{3} \frac{S^2}{1 - n} \left(- \frac{\partial}{\partial E_0} \frac{n}{S} \right). \tag{4.12}$$

For $\Gamma \ll T$, the selfconsistent equation in the absence of an external field reduces to

$$n = 6Sf(E_0)$$

so that

$$- \frac{\partial}{\partial E_0} \frac{n}{S} = \frac{1 - n}{S^2} \left(\frac{n}{T} \right)$$

and the susceptibility reduces to

$$\chi_f = g^2\mu_B^2 \frac{n(T)}{3T} J(J + 1). \tag{4.13a}$$

The condition $\Gamma \ll T$, is met in the γ phase at high temperature, in which case $n(T)$ is close to one, and thus (4.13a) gives the Curie type susceptibility which is experimentally found in these conditions.

The expression for χ_f, equation (4.12), can also be written as

$$\chi_f = g^2\mu_B^2 \frac{J(J+1)}{3} \frac{6S^2}{1-n} \int_{-\infty}^{\infty} d\omega\, f(\omega) \frac{\partial}{\partial\omega} \rho_L(\omega)$$

$$= g^2\mu_B^2 \frac{J(J+1)}{3} \frac{6S^2}{1-n} \int_{-\infty}^{\infty} d\omega \left(-\frac{\partial f(\omega)}{\partial\omega}\right) \rho_L(\omega)$$

so that for low temperatures ($T \ll \Gamma$) we have the result

$$\chi_f = g^2\mu_B^2 \frac{J(J+1)}{3} \frac{(2J+1)S^2}{1-n} \rho_L(E_F). \tag{4.13b}$$

The condition $T \ll \Gamma$ is met in the α phase; since n in this case is small and almost temperature independent, expression (4.13b) has the essential features of the low temperature susceptibility of the α phase.

We have numerically computed χ_f as given by (4.12) for $T = 300$ K and $\Gamma = 200$ K, as a function of pressure. When we add to this the (Pauli) susceptibility of the s electrons, which we estimate to be around $0{\cdot}88 \times 10^{-4}$ emu mol^{-1} (MacPherson *et al* 1971) we get a susceptibility for the α phase which varies from $2{\cdot}3 \times 10^{-4}$ emu mol^{-1} at $p = 10$ kbar to $1{\cdot}13 \times 10^{-4}$ emu mol^{-1} at $p = 45$ kbar.

These values are about half the values experimentally found (MacPherson *et al* 1971). One reason for the discrepancy lies in the possibility that the electrons in the band give a large contribution due to Stoner enhancement. Another possibility stems from the fact that the limit $U \to \infty$ overestimates the correlation effects of the f electrons. A third possibility which should not be ruled out is that the $J = \frac{7}{2}$ multiplet, although it lies some 3000 K above the $J = \frac{5}{2}$ level, because of its large p value ($p = 7{\cdot}94$ as compared to 2·54 for $J = \frac{5}{2}$ level (Kittel 1971)) makes a significant contribution to χ. Finally, although there is no experimental indication of magnetic ordering of any kind, it might be that our approximation of considering only the one centre problem is unjustified at low temperatures.

4.3. *Evaluation of specific heat*

To evaluate the specific heat we need the internal energy $U = \langle H \rangle$. From the Green functions obtained in § 2 we find

$$U = (6-5n) \int_{-\infty}^{\infty} d\omega\, \omega f(\omega)\, \rho_L(\omega - Gn_c) + \int_{-\infty}^{\infty} d\omega\, \omega f(\omega) \mathscr{D}(\omega - Gn) - Gnn_c. \tag{4.14}$$

Here $\mathscr{D}(\omega)$ is the density of states of the band; in writing (4.14) we explicitly indicated the presence of the Hartree–Fock self energies in each of the first two terms and have subtracted Gnn_c to avoid double counting the total Coulomb interaction energy. These terms are particularly important in evaluating the specific heat since the occupation numbers n and n_c are temperature dependent.

As usual, we evaluate the electronic specific heat at constant volume C_V for the system with a constant number of electrons. This last restriction implies $n + n_c = 4$; at low temperatures it is convenient to consider the quantity $U - 4E_F$ (Kittel 1971).

The specific heat is then evaluated through the steps indicated in appendix 2. The result can be expressed at low temperatures in the usual form

$$C_V = \gamma T \tag{4.15}$$

where

$$\gamma = \frac{\pi^2}{3}\left(\tilde{\rho}(E_\mathrm{F}) + \mathscr{D}(E_\mathrm{F}) + 5I\,\frac{\mathscr{D}(E_\mathrm{F})\bar{\rho}'(E_\mathrm{F}) - \bar{\rho}(E_\mathrm{F})\mathscr{D}'(E_\mathrm{F})}{\mathscr{D}(E_\mathrm{F}) + \bar{\rho}(E_\mathrm{F}) - 2G\mathscr{D}(E_\mathrm{F})\bar{\rho}(E_\mathrm{F})}\right) \tag{4.16}$$

with

$$\tilde{\rho}(\omega) = (6 - 5n)\rho(\omega) \qquad \bar{\rho}(\omega) = \tfrac{1}{6}(6 - 5n)^2\rho(\omega) = \tfrac{1}{6}(6 - 5n)\tilde{\rho}(\omega). \tag{4.17}$$

The prime indicates differentiation with respect to the argument: all functions are evaluated at the Fermi energy. The quantity I is defined by

$$I = \int_{-\infty}^{E_\mathrm{F}} \mathrm{d}\omega\,(E_\mathrm{F} - \omega)\rho(\omega - Gn_c). \tag{4.18}$$

Notice that in the α phase, where n is a small number, $\tilde{\rho}$ and $\bar{\rho}$ are very close to 6ρ.

Using the selfconsistent solution for n, which gives $n \sim 0{\cdot}2$, we have in fact $\tilde{\rho} \simeq 5\rho$ and $\bar{\rho} \simeq 4{\cdot}2\rho$.

The specific heat constant γ defined in (4.17) contains as was to be expected, the density of states at the Fermi level $\tilde{\rho} + \mathscr{D}$, plus an extra term which comes in because of the presence of the factors $(6 - 5n)$ in (4.14) which in turn originates in the high correlation implied by the $U \to \infty$ limit. It should be recalled here that the Hartree–Fock solution which is particularly unsuited in this limit, does not give rise to any anomalous term in the specific heat constant (Kjöllerström *et al* 1966). For the values of the parameters that we have been considering so far, the contribution from this term is about 30% that of the 'normal' term $\tilde{\rho} + \mathscr{D}$.

The specific heat constant that we obtain is $\gamma = 8{\cdot}6\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$ which is to be compared with the experimental values of 9·79 at $p = 0$ kbar (Panousis and Gschneidner 1970) and 11·3 at $p = 11{\cdot}3$ kbar (Phillips *et al* 1968).

In connection with this discrepancy it should be pointed out that ρ can vary between 0 and $1/\pi\Gamma$, and that the value of γ does depend rather critically on the distance $E_0 - E_\mathrm{F}$, from the maximum in ρ to the Fermi level.

5. Conclusions

In conclusion we show here that the anomalous properties of α-Ce can be easily accounted for through a simple extension of the Ramirez–Falicov theory. Anomalies of the same type are found in the collapsed phase (TmTe, SmTe, YbTe etc, Chatterjee *et al* 1972) of several compounds in which transitions of the same type occur. The present calculation opens the way to an interpretation of these anomalies in terms of highly correlated hybridized f or d states.

It should be noted, as we have already pointed out, that the main results, namely an intermediate valency and an enhancement of the specific heat and magnetic susceptibility, are qualitatively independent of the decoupling procedure used. When the condition $\Gamma \ll |E_\mathrm{F} - E_0|$ is met, perturbation theory can be successfully applied. The decoupling procedure, as indicated above, is the simplest approximation scheme that gives the right high temperature behaviour for the susceptibility and allows for a direct interpolation through the $\alpha - \gamma$ transition. When perturbation theory applies, one finds essentially the same results obtained in this paper, namely a strongly temperature dependent Curie type susceptibility when $E_0 < E_F$ (γ phase) (Scalapino 1966), and a weakly temperature dependent Pauli type susceptibility plus a linear term in T in the specific heat when $E_0 > E_F$ (α phase) (Olmedo *et al* 1973).

One can improve on our approximation of treating the short range Coulomb repulsion in the Hartree–Fock approximation by starting from the full Ramirez and Falicov Hamiltonian plus an hydridization term and devicing a decoupling scheme for the G part consistent with the one we have followed here. In this way one obtains quite similar results to those we have reported above, except for a renormalization of the mixing parameter $V_{k'}$ of order αG.

Appendix 1

We can calculate the contribution to the free energy from the localized states by using equation (2.12) and the formula

$$\begin{aligned} F_{\text{loc}} &= E_F n + \int_{E_0}^{\infty} n(E_0')\,\mathrm{d}E_0' \\ &= E_F n - T \ln\{1 + 6\exp(E_F - E_0)/T\}. \end{aligned} \tag{A1.1}$$

Using again equation (2.12) to eliminate E_F, yields

$$F_{\text{loc}} = E_0 n + T\{n \ln n + (1 - n)\ln(1 - n) - n \ln 6\}.$$

To obtain the total free energy, one should add to this expression the free energy of the band electrons: in our approximation of neglecting the entropy of this part of the system, this free energy reduces to:

$$E_{\text{band}} = \int_{Gn}^{E_F} \alpha\omega\,\mathrm{d}\omega = \frac{1}{2\alpha}(4 - n)^2 + Gn(4 - n).$$

The last term represents the Coulomb interaction.

When adding E_{band} to F_{loc} to obtain the total free energy, this term must be dropped to avoid counting it twice.

Appendix 2

As it was indicated in the text, the evaluation of the specific heat starts from the expression (4.14) for the internal energy per atom. At low temperatures it is convenient to consider the quantity $U - 4E_F$, which has the following low temperature expansion

$$\begin{aligned} U - 4E_F = (6 - 5n)&\left\{\int_{-\infty}^{\mu} \mathrm{d}\omega(\omega - E_F)\rho(\omega - Gn_c) + \tfrac{1}{6}\pi^2 T^2 \rho(E_F - Gn_c)\right\} \\ &+ \int_{-\infty}^{\mu} \mathrm{d}\omega(\omega - E_F)\mathscr{D}(\omega - Gn) + \tfrac{1}{6}\pi^2 \mathscr{D}(E_F - Gn) - Gnn_c. \end{aligned} \tag{A2.1}$$

The specific heat is given by $C_V = \partial U/\partial T$ which can be obtained from (A2.1). On differentiating (A2.1) the derivatives $\partial\mu/\partial T$ and $\partial n/\partial T$ come in. These are determined from the condition that the number of electrons be constant, $n + n_c = 4$. At low temperatures we obtain

$$\frac{\partial \mu}{\partial T} = -\frac{\pi^2}{3} T \frac{\mathscr{D}'(E_F) + \bar{\rho}'(E_F) - G(\bar{\rho}(E_F)\mathscr{D}'(E_F) + \bar{\rho}'(E_F)\mathscr{D}(E_F))}{\mathscr{D}(E_F) + \bar{\rho}(E_F) - 2G\mathscr{D}(E_F)\bar{\rho}(E_F)} \tag{A2.2}$$

and

$$\frac{\partial n}{\partial T} = \frac{\pi^2}{3} T \frac{\mathscr{D}(E_F)\bar{\rho}'(E_F) - \bar{\rho}(E_F)\mathscr{D}'(E_F)}{\mathscr{D}(E_F) + \rho(E_F) - 2G\mathscr{D}(E_F)\bar{\rho}(E_F)}. \tag{A2.3}$$

From (A2.1) we have

$$C_V = \frac{\pi^2}{3} T(\mathscr{D}(E_F) + \tilde{\rho}(E_F)) + 5I\frac{\partial n}{\partial T} + G\left\{n - n_c + (6 - 5n)\int_{-\infty}^{\mu} d\omega(\omega - E_F)\right.$$

$$\left. \times\ \rho'(\omega - Gn_c) - \int_{-\infty}^{\mu} d\omega(\omega - E_F)\mathscr{D}'(\omega - Gn)\right\}\frac{\partial n}{\partial T}. \tag{A2.4}$$

Since $\partial n/\partial T$ is of order T, we can neglect terms of order T^2 in n and n_c; to this approximation the factor multiplying G in (A2.4) vanishes and we have $C_V = \gamma T$ with γ as given in the text.

Appendix 3

Within a mean field theory, one can deal with the f electrons and the conduction electrons as independent entities, bearing in mind that the chemical potential is to be determined by keeping the total number of electrons constant, and that in writing the energy one should not count the interaction energy twice.

If one wants to deal with the fourteen 4f levels, which due to spin–orbit coupling split into a $J = \frac{5}{2}$ ground state with energy E and a $J = \frac{7}{2}$ excited state with energy E', in the limit of strong correlation (ie there can be no more than one electron occupying these levels), the simplest approach is to write the partition function for the f levels, which reads

$$Z_f = \sum_{\text{states}} \exp\{-\beta(E_s - \mu N_s)\}.$$

Thus, in our case we have

$$Z_f = 1 + 6\exp\{-(E - \mu)/T\} + 8\exp\{-(E' - \mu)/T\}. \tag{A3.1}$$

The highly correlated character of the f levels reflects itself on the fact that Z_f contains those terms corresponding to either zero or one particle.

Calling n_J the occupation probability of the $2J + 1$ degenerate sublevel we have from (A3.1)

$$n_J = \frac{2J + 1}{Z_f} \exp\left(-\frac{E_J - \mu}{T}\right) \tag{A3.2}$$

where E_J equals E or E' as the case may be.

The total occupation of the f levels thus reads

$$f = n_{5/2} + n_{7/2} = \frac{1}{Z_f}\left\{6\exp\left(-\frac{E - \mu}{T}\right) + 8\exp\left(-\frac{E' - \mu}{T}\right)\right\}. \tag{A3.3}$$

This expression reduces in the limit $E' \to \infty$, to the familiar expression of the Ramirez–Falieov theory; f can alternatively be written as

$$f = \left[\frac{1}{Q(T)}\exp\{(E-\mu)/T\} + 1\right]^{-1} \tag{A3.4}$$

where $Q(T) = 6 + 8\exp\{-(E'-E)/T\}$, is an effective degeneracy. If one assumes as in the Ramirez–Falicov theory that $E - \mu$ is a function of pressure, and keeps $E - E'$ fixed as was done by Kiwi and Ramirez (1972) expression (A3.4) will give a single transition as a function of pressure. The only difference with the Ramirez–Falicov theory lies in the appearance of the effective degeneracy $Q(T)$.

If one wants to deal with the effect of crystal field splitting on the $J = \frac{5}{2}$ level, since in a cubic field this will split into a doublet and quadruplet, one can use the foregoing argument by simply replacing the degeneracies 6 and 8 by 2 and 4.

Using the Green function technique one can calculate the spectral density of the 4f levels in the limit $U \to \infty$ and for zero linewidth; one obtains

$$\rho_J(\omega) = (2J+1)\left(1 - \frac{2J}{2J+1}n_J - n_{J'}\right)\delta(\omega - E_J). \tag{A3.5}$$

With this partial spectral density we obtain for n_J

$$n_J = \int_{-\infty}^{+\infty} \mathrm{d}\omega\, f(\omega)\rho_J(\omega) = \{(2J+1) - 2Jn_J - (2J+1)n_J\}f(E_J). \tag{A3.6}$$

Solving for n_J one can see that this coincides with (A3.2).

The total spectral density reads†

$$\rho(\omega) = 6(1 - \tfrac{5}{6}n_{5/2} - n_{7/2})\delta(\omega - E) + 8(1 - \tfrac{7}{8}n_{7/2} - n_{5/2})\delta(\omega - E'). \tag{A3.7}$$

Kiwi and Ramírez (1972) have taken as an *ansatz*

$$\rho(\omega) = \tfrac{6}{14}\delta(\omega - E) + \tfrac{8}{14}\delta(\omega - E') \tag{A3.8}$$

which obviously does not take due account of the correlation effects.

Thus, the conclusions at which they arrived starting from (A3.8), concerning the pressure dependence of the susceptibility, the intermediate valency for α-Ce, and the mechanism for the α–α′ transition are not valid.

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† It should not be surprising that this spectral density does not integrate to 14, since it does not contain the terms coming from those poles in the Green function which move away to infinity in the limit $U \to \infty$, and which are not relevant in the calculation of any thermodynamical property. In metallic Ce, E and E' are the renormalized energies of the localized states, which include the interaction with the band.

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