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VALENCE, ELECTRONIC SPECIFIC HEAT AND MAGNETIC SUSCEPTIBILITY OF ALPHA-CERIUM

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A sixfold degenerate Anderson Hamiltonian, which includes the Coulomb repulsion between localized and band states in the mean field approximation following Ramírez and Falicov, is treated in the limit of infinitely correlated $4f$ states and to second order in the mixing parameter. Assuming a line width $\Gamma \approx 0.02$eV we obtain at low temperatures and 11kbar, a valency of 3.76 and sizeable contributions from the $4f$ levels to the electronic specific heat and magnetic susceptibility of alpha Ce. Thus we show, that the highly correlated picture necessary to the explanation of the alpha–gamma transition by Ramírez and Falicov needs not to be abandoned in order to explain the anomalies in alpha Ce.

RECENTLY, Ramírez and Falicov (RF,[1] have proposed a model for the alpha–gamma phase transition in Ce which is based on the simultaneous existence of localized ioniclike $4f$ states and itinerant conduction band states. The short range part of the electron–electron interaction between localized and band states is the driving force for the transition. Assuming a linear variation with pressure of the $4f$ level distance to the Fermi level, the theory allows for a critical point.

Although the model allows for a description of the main properties of the alpha–gamma transformation, the low temperature phase does not have the actual properties of alpha-Cerium. In particular the model predicts the formation of tetravalent Ce ions at low enough temperatures, whereas experimental information indicates that there is an intermediate valency.[2] In concommitance with this, it is not surprising that the model predicts too low values for the electronic specific heat and for the magnetic susceptibility.

Quite recently, we have been able to extend the theory to include the effect of rare earths and Th addition cn the alpha–gamma transformation.[3] A bulk of experimental information on this effect[4–6] could thus be correlated with the RF theory, providing a strong argument in favor of this model.

As has been pointed out by RF,[1] a possible way to overcome the shortcomings cited above, is to include into the theory the effect of hybridization between $4f$ and conduction band states. We show in this work how a sixfold degenerate Anderson Hamiltonian,[7] which includes in the mean field approximation, the Coulomb repulsion[8] between localized and band states, when treated in the limit of infinitely correlated f states, and to second order in the mixing parameter, can account for the non-integer valency, and the enhancement in the low temperature specific heat and magnetic susceptibility of alpha-Ce. A more complete and detailed report, including the effect of the mixing term on the alpha–gamma phase transition will be published elsewhere.[9]

We consider Ce metal as an aggregate of single centers, one in each crystalline site. This approximation

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has been well justified in previous theories,[10] so we will not comment on it any further. Thus, we calculate the properties of the one impurity problem, and obtain macroscopic values multiplying by the number of atoms in the crystal. We start from the following model Hamiltonian,[7] which includes the Coulomb repulsion term in the mean field approximation from the outset:

$$H = H_0 + H_1$$

where

$$H_0 = \sum_{\mathbf{k},\sigma} \bar{\epsilon}_{k\sigma} C^+_{\mathbf{k}\sigma} C_{\mathbf{k}\sigma} + \sum_m \tilde{T}_m n_m + \frac{U}{2} \sum_{m \neq m'} n_m n_{m'}$$

$$H_1 = \sum_{\mathbf{k}\sigma m} (V^\sigma_{km} C^+_{\mathbf{k}\sigma} C_m + V^{*\sigma}_{km} C^+_m C_{\mathbf{k}\sigma})$$

with

$$\bar{\epsilon}_{k\sigma} = \epsilon_k + \mu_s \sigma H_z + G \sum_m \langle n_m \rangle = \bar{\epsilon}_k + \mu_s \sigma H_z$$

$$\tilde{T}_m = T_0 - \mu_f m H_z + G \sum_{\mathbf{k}\sigma} \langle n_{k\sigma} \rangle = \tilde{T}_0 - \mu_f m H_z$$

ϵ_k is the energy of a conduction electron, $C^+_{\mathbf{k}\sigma}$, $C_{k\sigma}$ are the usual creation and annihilation operators for electrons with wave vector **k** and spin σ; U is the interaatomic Coulomb interaction between two electrons in the $4f$ states, G is the Coulomb interaction parameter between localized and band electrons, T_0 is the energy of the $4f$ levels, $n_m = C^+_m C_n$ is the occupation number operator for the localized states with total angular momentum $J = 5/2$ and z component $m (m = -5/2, -3/2, \ldots 5/2)$; $\langle \quad \rangle$ denotes a mean value over the grand canonical ensemble; μ_s, μ_f are the magnetic moments of conduction and localized electrons respectively; $V^\sigma_{\mathbf{k}m} = V_k \langle km | \mathbf{k}\sigma \rangle$ is the hybridization matrix element between conduction and localized states,[11] H_z is an external magnetic field; energies are measured from the Fermi level. We have assumed here that the $J = 7/2$ multiplet is widely separated from the ground state $J = 5/2$. We also neglect multiplet splittings when there are two or more electrons on the impurity ($U \gg$ atomic exchange integrals).

Treating H_1 as a perturbation, the corrections to the free energy[12]

$$F = -k_B T \ln \mathrm{Tr}\, e^{-\beta H_0} \tag{2}$$

can be obtained by means of thermodynamic perturbation theory.[13]

In this paper, we are only concerned with the lowest order correction to the free energy: $F^{(2)}$, i.e. second order in H_1. From the well known expansion of the partition function

$$Z = \mathrm{Tr}\, e^{-\beta H_0} [1 + \sum_{n=1}^{\infty} \int_0^{\beta} d\lambda_1 \int_0^{\lambda_1} d\lambda_2 \ldots \int_0^{\lambda_{n-1}} d\lambda_2 \times H(\lambda_1) \times H(\lambda_2) \times \ldots \times H(\lambda_n)] \tag{3}$$

where

$$\beta = 1/k_B T \quad \text{and} \quad H_1(\lambda) = e^{\lambda H_0} H_1 e^{-\lambda H_0}$$

we obtain for $U \to \infty$

$$F^{(2)} = \sum_{\mathbf{k}m\sigma} | V^\sigma_{\mathbf{k}m} |^2 \left[\frac{n_{k\sigma} n_0}{\bar{\epsilon}_{k\sigma} - \tilde{T}_m} + \frac{(1 - n_{k\sigma}) n_m}{\tilde{T}_m - \bar{\epsilon}_{k\sigma}} \right] \tag{4}$$

with

$$n_0 = \frac{1}{Z_f}, \quad n_m = \frac{e^{-\beta \tilde{T}_m}}{Z_f}$$

and

$$Z_f = 1 + \sum_m \exp(-\beta \tilde{T}_m), \quad n_{k\sigma} = [\exp(\beta \bar{\epsilon}_k) + 1]^{-1} \tag{5}$$

The terms in parentheses in equation (4) are to be considered to zeroth order in V_k. Since in the RF theory the f level occupations n_m go to zero exponentially with T, we neglect in what follows the second term in parentheses in equation (4). To perform the integration over **k** we take a constant density of states ρ,[1,13] and we replace $| V_k |^2$ by an average V^2. In this way we obtain for the second order correction to the free energy at low temperatures

$$(T \ll \tilde{T}_m)$$

$$F^{(2)} = \rho \cdot V^2 \sum_m n_0 \left[\alpha_m^2 \ln \left| \frac{\tilde{T}_m}{W_h + \tilde{T}_m + \mu_s H} \right| + \beta_m^2 \ln \left| \frac{\tilde{T}_m}{W_h + \tilde{T}_m - \mu_s H} \right| \right] \tag{6}$$

where

$$\alpha_m = [(7 + 2m)/14]^{1/2} \quad \beta_m = [(7 - 2m)/14]^{1/2} \tag{7}$$

are Clebsch–Gordan coefficients and W_h is the distance from the bottom of the conduction band to the Fermi level; $W_h = 2.72\text{eV}$ in the RF theory.

If no magnetic field is present, $\tilde{T}_m = \tilde{T}_0$ and the correction to the $4f$ levels population is

$$n^{(2)} = \frac{\partial F^{(2)}}{\partial \tilde{T}_0} = \frac{(2J+1)}{\pi} \frac{\Gamma}{\tilde{T}_0} \cdot \frac{W_h}{(W_h + \tilde{T}_0)} \approx \quad (8)$$

$$\frac{(2J+1)}{\pi} \frac{\Gamma}{\tilde{T}_0} \quad (W_h \gg \tilde{T}_0)$$

where $\Gamma = \rho\, \pi V^2$ is the linewidth for these states. It has been pointed out that a reasonable value for the linewidth would be $\Gamma \approx 0.02$eV.[10,14] Since $\tilde{T}_0$ is almost an order of magnitude greater than Γ at $p \approx$ 11kbar, the perturbation expansion for low temperatures is well justified. Thus using for $\tilde{T}_0$ the form given in reference 3[15]

$$\tilde{T}_0 = 0.118 + 0.00366\,p \quad \text{(eV)} \tag{9}$$

for $p = 11$kbar, we have $\tilde{T}_0 = 0.158$eV so that $n^{(2)} \approx$ 0.24 and the valency $v = 4 - n = 3.76$.

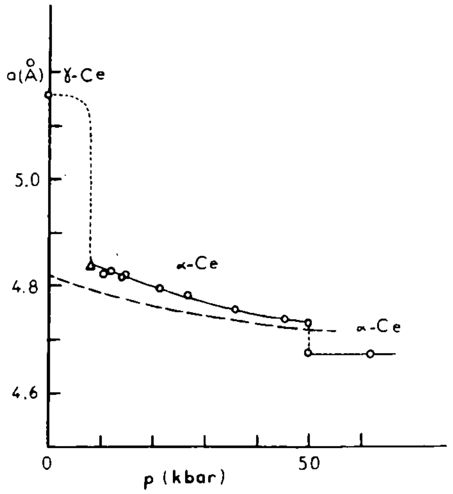

FIG. 1. Lattice parameter for alpha-Ce as a function of pressure. Full line: experimental values at room temperature after Franceschi and Olcese. Dashed line: second order perturbation theory results for $\Gamma \gg T$.

Because of the dependence of $\tilde{T}_0$ on pressure, the valency v will be a function of pressure too. To correlate this dependence with existing experimental data,[16] we assume[1] a linear relation between the lattice constant and the f level occupation

$$a = A + Bn \tag{11}$$

with $A = 4.65$Å and $B = 0.534$Å. Figure 1 is a plot of a as a function of pressure at low temperatures. The values of A and B have been chosen from the results of a finite temperature calculation.[9]

We can also calculate the electronic specific heat of the system. From equation (4), we obtain

$$\gamma_f = \frac{\pi^2}{3} k_b^2 \frac{n^{(2)}}{\tilde{T}_0} \tag{12}$$

where γ_f is the specific heat constant due to the $4f$ levels and k_b the Boltzmann constant. At $p = 11$kbar, from (12)

$$\gamma_f \approx 3.58 \text{ mJ/mole °K}^2$$

and as in RF theory[1]

$$\gamma_s \approx 3.53 \text{ mJ/mole °K}^2$$

we obtain

$$\gamma \approx 7.1 \text{ mJ/mole °K}^2$$

for the alpha phase. Phillips *et al.*[17] have measured at that pressure $\gamma_{exp} = 11.3$ mJ/mole °K^2. An extrapolation to $p = 0$kbar gives $\gamma = 10$ mJ/mole °K^2 which compares well with the value obtained by Panousis and Gschneidner, Jr.[10]

Finally, for the magnetic susceptibility in this approximation we obtain

$$\chi_f^{(2)} = -\left.\frac{\partial^2 F^{(2)}}{\partial H^2}\right|_{H=0} = \frac{\mu_b^2 g^2 J(J+1)}{3\tilde{T}_0} n^{(2)} \tag{13}$$

where μ_b is the Bohr magneton, g the Landé factor for $J = 5/2$ ($\mu_f = g\mu_b$). This expression formally resembles the Curie law result, but with $\tilde{T}_0$ in place of T. It is in fact temperature independent. At $p = 11$kbar, equation (13) gives

$$\chi_f^{(2)} \approx 1.06 \times 10^{-4} \text{ e.m.u./mole} \tag{14}$$

Since the magnetic susceptibility of tetravalent Ce has been estimated[2] $\chi \approx 1.2 \times 10^{-4}$ e.m.u./mole, we obtain for the alpha phase within the RF theory, to second order in the s–f hybridization and for low temperatures

$$\chi \approx 2.3 \times 10^{-4} \text{ e.m.u./mole} \tag{15}$$

which must be compared with the extrapolated value for low temperatures and $p = 10$kbar of about[19]

$$\chi_{exp} \approx 5.1 \times 10^{-4} \text{ e.m.u./mole.}$$

In conclusion, we show here by simple perturbation theory how the hybridization between localized and band states within the framework of RF theory, gives the clue to the understanding of anomalous properties of alpha-Ce without abandoning the highly correlated character of the $4f$ states.

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On a traité un Hamiltonien d'Anderson six fois dégéneré incluant la repulsion Coulombienne entre états localisés et des bandes selon l'approximation du champ moyen de Ramírez et Falicov, dans la limite des etats $4f$ infiniment corrélations au deuxième ordre dans le paramètre de mélange. En supposant une larguer $\Gamma \sim 0.02$eV on obtient a temperatures basses et 11 kbar, une valence de 3.76 et des contributions appréciables des niveaux $4f$ au chaleur specifique électronique et à la susceptibilité magnétique du Ce alpha. Donc, on a montré que l'image fortement corrélationné nécéssaire pour l'explication de la transition alpha–gamma selon Ramírez et Falicov ne doit pas être abandonnée pour expliquer les anomalies dans le Ce alpha.