CAE/1972/8

"ELECTRONIC PHASE TRANSITION IN $Ce_{1-x}La_x$ ALLOYS"

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October 1972
Bariloche - Argentina

ABSTRACT.

An extension of the Ramirez-Falicov theory of the alpha-gamma transition in Ce is given, which accounts for the effect of rare earths impurities, particularly La.

Experimental information on the effect of La addition on the α-γ transformation in Ce indicates that La as well as other trivalent rare earth impurities, lower the α-γ transition temperature at zero pressure by about 10 °K/at. % impurity; the transition pressure at room temperature increases by about 0.4kbar/at. % impurity.

This system has been theoretically studied recently by Ramirez an Kiwi[1] through an extension of the Ramirez-Falicov[2] theory (RF). The authors of Ref.1 are apparently unaware that Eq. (3) of their work gives a large discrepancy with the experimental values for the transition temperature of the alloys at zero pressure[3,4]. Numerical computation of Eq. (3) of Ref. 1 gives a decrease in the transition temperature of 3°K for 100% impurity and an initial slope of only 0.32°K/at. % impurity.

We wish to point out here that the assumptions of their derivation are inconsistent with the RF theory. In fact Eq. (1) of Ref. 1 is based on the idea that the values of E_{Ce} and E_{La} (distances fron the Fermi level to the 4f states in Ce and La) should not be modified significantly by dilute alloying since the s-d band, an and therefore the Fermi level, is independent of f-like atomic shells. This assumption contradicts the RF theory where in fact thermal excitation of electrons will convert some Ce^{4+} ions in the α phase into Ce^{3+} ions, which act as impurities. Within the mean field theory (MFT) these occupied f levels rise the energies of the band electrons due to the increase in Coulomb repulsion, G, thus diminishing E_{Ce}. It is this mechanism that makes a first order phase transition possible.

Furthermore, charge conservation implies that the total number of holes in the band below the Fermi level (n_h) must equal the number of electrons excited above the Fermi level (n_e), plus the number of localized electrons either in Ce (f_c) or in La (f_L) 4f states, i.e.

$$n_h = n_e + (1 - X)\, f_c + X\, f_L$$

where X is the impurity concentration. In making a particle-hole description one should also be aware of the change in Fermi energy produced by the fact that the impurity may contribute to the band a different number of electrons as the host does. Eq. (2) of Ref. 1 does not reflect these facts. The conclusions of Ref. 1 are invalidated by these major defects in their ansatz.

In order to extend the RF theory to describe CeLa alloys, we make the following assumptions:

a) When its 4f level is unoccupied, La as an impurity in α Ce, is equivalent to a Ce^{3+} ion.

b) La is trivalent at all interesting temperatures and pressure, and for all concentrations.

Assumption a) is based on the fact that band structure calculations in the rare earths[5] indicate that the general features of the s-d band do not change appreciably from one element to another of the same valency, and that the effect of one 4f localized electron less in La, is compensated by the defect in one nuclear charge.

As for b), it is a simplifying assumption justified by the lack of evidence that La impurities in Ce change valency at the α - γ transformation temperature or at any other temperature.

Using assumption a) we have the following expression for the free energy in the MFT approximation[6,7]

$$F = \int_0^W d\varepsilon\ D(\varepsilon)\left|\underline{\varepsilon\ n(\varepsilon) + T\ K(\varepsilon)}\right| + (1 - x)\ \Delta_c\ f_c$$
$$+ x\ \Delta_L\ f_L + G\left|\underline{(1 - x)\ f_c + x\ (f_L + 1)}\right| \cdot \int_0^W d\varepsilon\ D(\varepsilon)\ n(\varepsilon) \quad (1)$$
$$+ T\left\{\left|\underline{(1 - x)\ K_c + x\ K_L}\right| - \left|\underline{(1 - x)\ f_c + x\ f_L}\right|\ \ell n\ 6\right\}$$

where W is the total band width, $D(\varepsilon)$ the density of states function, $n(\varepsilon)$ the electron distribution function, $K = f \ln f + (1 - f) \ln (1 - f)$, Δ_c the energy of the Ce 4f level measured from the botton of the conduction band in α Ce, f_c the population of this level; Δ_L and f_L are the corresponding quantities for La. G is the Coulomb repulsion between localized and band electrons.

The expression above, should be minimized with respect to $n(\varepsilon)$, f_c and f_L subject to the constraint:

$$\int_0^W d\varepsilon \; n(\varepsilon) D(\varepsilon) + (1 - x) f_c + x f_L = 4 (1 - x) + 3 x \qquad (2)$$

When written in terms of particle-hole excitations, this equation does not coincide with Eq. (2) of Ref. 1. Our equation (2) expresses the fact that each Ce atom contributes four electrons, each La aton three, and these may be either in the band or localized. Following now the procedure described in Refs.6,8,9 and taking the same density of states for electrons as Rf, the condition for extremun with respect to f_c and f_L leads us to following relation:

$$\frac{f_L}{1 - f_L} = e^{- \Delta/T} \frac{f_c}{1 - f_c} \qquad (3)$$

where $\Delta = \Delta_L - \Delta_c$ is the distance from the La 4f level to the Ce 4f level. Assumption b) corresponds to taking $\Delta/T >> 1$ and therefore $f_L \sim 0$. Under this conditions the procedure of Refs. 6,9 gives the following expression for the transition temperature at zero pressure:

$$T = T_o - x L \qquad (4)$$

where $T_o \ln 6 = \Delta_c + 3 G - \frac{7W}{24}$ is the transition temperature at zero pressure for pure Ce, and $L = (G - W/24) / \ln 6$.

Equation (4) gives a decrease of the transition temperature of 6.47 °K/at. % impurity. The same expression holds for any trivalent impurity[6]. If the same pressure dependence of the parameters is assumed to hold for the alloy as for pure Ce, the transition line on the p-T diagram is determined by[6]:

$$T = T_o - x L + \theta p \qquad (5)$$

where θ = 23.7 °K/kbar. This gives an increase in the transition pressure of 0.3 kbar/at. % impurity.

As in Ref. 8 we obtain for the critical temperature:

$$T_c = T_c^o \quad (1 - x)$$

where T_c^o is the critical temperature for pure Ce.

It is worth mentioning that extrapolation of these results to dilute LaCe alloys, results in Ce being a magnetic impurity, with its 4f level lying about 950 °K below the Fermi level. Using the pressure dependence of the parameters indicated above, one sees that the 4f level will cross the Fermi energy at about 25 kbar. Although this value should not be taken too seriously, it compares well with the value quoted by Coqblin for LaCe alloys[11].

ACKNOWLEDGEMENTS

We would like to acknowledge discussions with F. de la Cruz and J.M. Cotignola.

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