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CONTENTS ON

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

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ABSTRACT

It is shown that the Ramirez-Falicov model for the α - γ transition in Ce, in its present form, fails to account for the experiments on $\text{Ce}_{1-x}\text{La}_x$. This result is in disagreement with a recent work by Ramirez and Kiwi published in this journal.

In a recently published paper in this journal ¹, Ramirez and Kiwi (RK) claim to have explained the effect of La addition on the α - γ transformation in Ce metal. We want to show here that the main conclusion at which they arrive is incorrect.

As is known, The Ramirez-Falicov model for pure Ce ², assumes a s-d band with a constant density of states and highly correlated ionic-like f levels with zero width. In α Ce the band contains four electrons per atom, and the f level which lies above the Fermi energy is empty. When electrons are thermally excited to the f level, the Coulomb repulsion between localized and band states pushes the band energies up, and since the f levels have an important contribution to the entropy due to the angular momentum degeneracy, the free energy can be lowered by completely occupying the f level and consequently moving up the band states, which now contain only three electrons per atom. The situation has been schematized in fig. 1.

On the basis of these ideas, it is clear how substitutional impurities which do not appreciably change the band structure but have different valency and different f level energies, can alter the transition temperature. A tetravalent impurity with a lower f level energy E_I will lower the trans-

tion temperature, and one with higher E_I will increase it. The latter is the case of alloying with Th.

If the impurity f level energy E_I lies well above or well below the Fermi energy, and due account is taken of the valency effects, one can explain⁵ the qualitative features of the effect of alloying³⁻⁴ with Pr, Dy, Lu, trivalent impurities, and Eu and Yb which are divalent in the α phase.

In ref. 1, La is assumed to be a trivalent impurity, which implies that the Fermi energy is depleted with respect to pure Ce. Since the authors indicate that $E_{La} > E_{Ce}$, the conclusion implicit in Eq. (3) that the transition temperature at constant pressure is lowered, cannot be understood.

To show that this is in fact so, we start from the following expression for the free energy per atom

$$F = \int_0^W d\epsilon D(\epsilon) [n(\epsilon) \epsilon + T K(\epsilon)] + (1-x) E_c f_c + x E_L f_L + G [(1-x) f_c + x f_L] \int_0^W d\epsilon D(\epsilon) n(\epsilon) + T [(1-x) K_c + x K_L] - T [(1-x) f_c + x f_L] \ln 6 \quad (1)$$

The notation is as in PK except that X stands for La concentration, C indicates cerium and L lanthanum.

This expression has to be minimized with respect to $n(\epsilon)$, f_c and f_L subject to the constraint

$$\int_0^W d\epsilon N(\epsilon) n(\epsilon) + (1-X) f_c + X f_L = 4(1-X) + 3X \quad (2)$$

It should be noticed that Eqs. (1) and (2) above differ from Eqs. (1) and (2) of ref.1 and this might be the reason for the wrong conclusion arrived at in that work. The Fermi energy is given by

$$\epsilon_F = \frac{W}{12} [4 - X - (1-X)f_c - Xf_L] + G(1-X)f_c + GXf_L \quad (3)$$

This expression gives the variation of ϵ_F with La concentration, which ranges from the value

$$\epsilon_F = \frac{W}{12} (4 - f_c) + G f_c \quad (4)$$

for pure Ce to

$$\epsilon_F = \frac{W}{12} (3 - f_L) + G f_L \quad (5)$$

for pure La, assuming the same band structure as va-

relation is important in view of the fact that in ref. 1 the results are extrapolated to interpret the behaviour of pure La, assuming that the Fermi energy is unchanged over the whole concentration range $0 \leq x \leq 1$.

Following the procedure outlined in refs. 5-6, we eliminate the conduction electrons using the condition (2) and neglect the band entropy term $K(\epsilon)$. This last approximation is justified in the constant density of states model since one is only interested in entropy changes and these are negligible if the band changes from four electrons per atom in the α phase to three in the γ phase. In this way one obtains F as a function of only f_c and f_L . Variation of this function with respect to f_c and f_L allows us to write the following relation between the occupation probabilities :

$$\frac{f_L}{1-f_L} = e^{-\Delta/T} \frac{f_c}{1-f_c} \quad (6)$$

In this form, one can finally write F as a function of f_c alone which has in general two minima and a maximum. The graphs of $F(f_c)$ have a similar form to those given in fig. 2 of ref.6. At the transition temperature, the two minima have the same height and the maximum occurs for $f_c = 1/2$.

Imposing the condition that the equation that determines f_c has the solution $f_c = 1/2$, we find that the

transition temperature is given by

$$T \ln 6 = E_0 - B + \chi [E_1 - B(2f_L^x - 1)] \quad (7)$$

where

$$E_0 = E_c + 4\left(G - \frac{W}{12}\right) = 1366 \text{ }^\circ\text{K}$$

$$E_1 = \frac{W}{12} - G = 2786 \text{ }^\circ\text{K}$$

$$B = G - \frac{W}{24} = 1160 \text{ }^\circ\text{K}$$

$$f_L^x = \frac{1}{e^{\Delta/T} + 1}$$

The main conclusion to be drawn from equation (7) is that there is no value of Δ that will make negative the factor multiplying χ . Therefore, the model predicts an increase in the transition temperature at constant pressure, or a decrease of the transition pressure at constant temperature, in contradiction to the results of refs. 3-4.

A possible way to improve the model to explain the $\text{Ce}_{1-x}\text{La}_x$ transition, as has been already pointed out in ref. 2, is to use a more realistic density of states for conduction electrons, which would make the Fermi energy to be less depleted by alloying. We have performed calculations using a parabolic density of states and have found that this is not enough to obtain at least qualita-

tive agreement with experiments. We believe that s-f hybridization² will help in this connection, because a finite line width of the f levels would encourage the transition. Work on the effect of s-f hybridization on the properties of the α phase and on the α - γ transformation is presently in progress, and will be the subject of a forthcoming paper.

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FIGURE CAPTION

Fig. 1 - Density of states for localized and band electrons used in the RE theory . The graph on the left depicts the situation in the α phase. $E_c + 4G$ is the renormalized energy of the localized state in the α phase at $T=0$. $E_c + 3G$ is the position of the f levels in the χ phase . The bottom of the band is shifted upwards by an amount G when the f level is occupied .

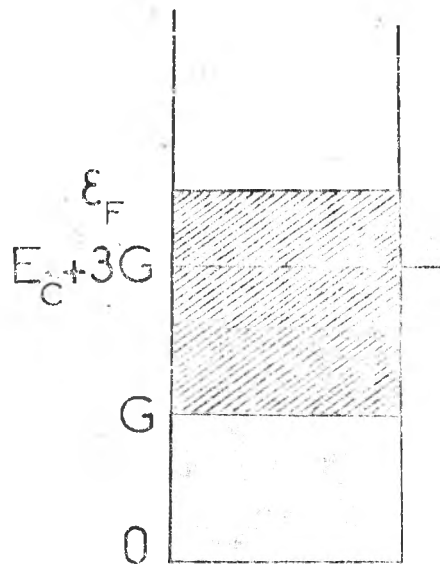
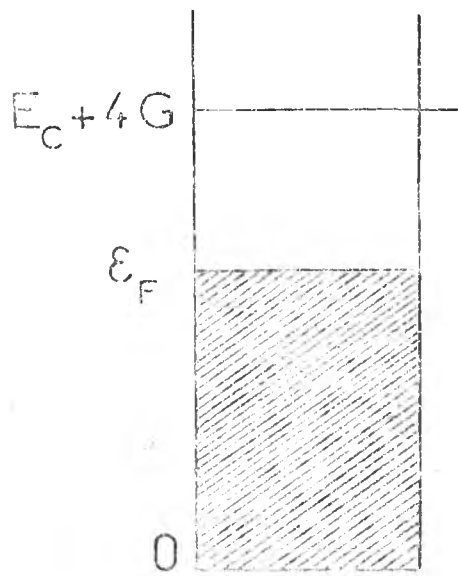


Fig.1