CAB/1971/8

EFFECT OF Th - IMPURITIES ON THE α - γ TRANSITION IN METALLIC Ce

B. Alascio and A. López

Centro Atómico Bariloche
Comisión Nacional de Energía Atómica
Instituto de Física "Dr. José A. Balseiro"
Universidad Nacional de Cuyo

*

San Carlos de Bariloche
Argentina

ABSTRACT

The model of Ramirez and Falicov for α - γ transition in Ce has been extended to the Ce-Th system. Convenient approximations give simple relations between transition temperatures and pressures and the parameters of the model. Comparison with experiments is made.

May, 1971

Recently Ramirez and Falicov (RF)[1], have proposed a model for the α - γ transition in Ce, based on a mechanism of promotion of electrons from an extended band to a set of localized f like states of energy Δ. Since this mechanism depends strongly on the number of localized states, one could get a good test of the model by replacing a few Ce atoms by atoms, as similar to Ce as possible which have their localized f states far enough from the Fermi energy as to be empty at all interesting temperatures. In this sense, one could think of La, Pr and Th and other rare earths as impurities. We have applied the RF model to the Ce-Th system and the results are reported herein. Since pure Th is non magnetic with the same number of conduction electrons as Ce, it seems justified to assume that the f level of Th in Ce lies far above the Fermi energy.

A great simplification of the calculations results when one notices that replacement of the Fermi distribution by a step function does not introduce appreciable error. We assume a constant density of states per atom α extended from zero to infinity.

Following RF (and calling n_L the population of the localized levels) we obtain for the free energy per atom

$$F(n_L) = c \left\{ E\, n_L - \frac{B}{2}\, n_L^2 + T \left[n_L \ln n_L + (1-n_L) \ln (1-n_L) - \ln 6 \right] + \text{const} \right\}$$

with $E = \Delta + 4G - \frac{4}{\alpha}$, $B = 2\,(1 - t)\left(G - \frac{1}{2\alpha} \right)$, where c and t are the Ce and Th concentration, G is the Coulomb repulsion between localized and band states, and T is the temperature. The n_L's for which F is an extremum satisfy $6 + \exp\left[(E - B n_L)\, T^{-1} \right] = 6/n_L$.

As discussed by RF the model allows for first order transitions and a critical point as observed in pure Ce[2]. The condition for a critical point

is that at the critical temperature $\left.\frac{dn_L}{dT}\right]_{T_c} = \infty$ which leads to: $n_L^2 - n_L + \frac{T_c}{B} = 0$. Careful analysis of $F(n_L)$ indicates that from the values that satisfy these equations only $n_L = 1/2$ corresponds to a true minimum of the free energy. So we get $B = 4T_c$ and for pure Ce, $B° = 4T_c° = 2316°K$. Again analysis of $F(n_L)$ shows that at the transition temperature T_T there is always a solution of the self consistent equation for $n_L = 1/2$. This implies that $T_T \ell n6 = E - B/2$. Assuming that E varies linearly with pressure $E(p) = E(o) + \theta p$, and adjusting T_T to the experimental curve for the p - T diagram of Ce, we get $\theta = 42{,}53°K/k$ bar

which is slightly at variance with formulae (3.5) of RF. Using the t dependence of B we obtain the following relations for the Ce-Th system: $T_c = (1-t)\, T_c°$, $p_c = p_c° - \rho\, t$, where $\rho\, \theta = T_c° (2 = \ell n6)$. From the above relations the model further predicts that T_T at zero pressure increases linearly with t. Experiments of ref (3) show an hysteresis effect (T_T increases with t for cooling and decreases for heating), so that comparison is not possible. Our formulae give a maximum concentration of Th, t = .38 above which there are no more first order transitions, which, considering the crudness of the model is in reasonable agreement with the results of ref. (3) (c f. Fig. 3).

Extension of the model to other impurities requires careful consideration of the position of the impurity f level relative to the Fermi level of Ce. We have performed similar calculations for La as an impurity. Since Ratto et al. (4) have argued that the f level of La lies not far above the Fermi level in pure La, one could not safely assume that when in Ce this f level would be far above the Fermi energy. In fact the results for Ce-La contradict the experimental results of ref. (5). After this work was

completed we received a preprint by Ramirez and Kiwi in which this model has been applied to Ce-La, with the same results.

REFERENCES

(1) R. Ramirez and L.M. Falicov, Phys. Rev. B, 3, 2425 (1971).

(2) A. Jayaraman, Phys. Rev. 137, A 179 (1965).

(3) K.A. Gshneidner, R.O. Elliot and R.R. McDonald, J. Phys. Chem. Solids 23, 1191 (1962).

(4) C.F. Ratto, B. Coqblin and E. Galleani D'Agliano, Adv. Phys. 18, 489 (1969).

(5) K.A. Gschneidner, R.O. Elliot and Mc Donald, J. Phys. Chem. Solids 23, 1201 (1962).