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## VOLUME COLLAPSE IN THE KONDO LATTICE

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The  $\alpha$ - $\gamma$  transition of Ce and its compounds are explained within a compressible Kondo lattice model where the variation of  $|J|/D$  with volume is taken into account. We show that, contrary to the valence change model, the Kondo contribution is sufficient to induce a first order transition at low temperature from a magnetic to a Kondo phase. The disappearance of magnetism is then related to an extremely high Kondo temperature. Applications to Ce and CeAl<sub>2</sub> cases are given.

**1. Introduction.** The transformation of elemental Ce from the high volume, local moment  $\gamma$  phase to the low volume, Pauli paramagnetic  $\alpha$  phase has been of interest for many years. Generally, the properties of cerium in intermetallic compounds can also be characterized as being  $\gamma$ -like or  $\alpha$ -like. The different models proposed to explain this, are based:

(i) either on the promotion of part of the 4f electron into the conduction band (the valence change model) [1],

(ii) or on the increase of the 4f band width, leading to a Mott transition [2],

(iii) or on the increase of the f level-d band hybridization [3].

Objections particularly to the first model have been made by photoemission, positron annihilation, Compton scattering experiments as well as by melting-point and cohesive energy arguments [4]. The photoemission results of Croft et al. [4] show that the pressure does not affect the position of the 4f level contrary to the valence change model, but that its effect is rather to increase the f-d resonance. Following this idea, we propose here a model of a "compressible Kondo lattice" where the parameter  $|J|/D$  ( $J$  being the Kondo exchange interaction and  $D$  the half-width of the conduction band) varies with the volume.

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The Kondo lattice is described by the effective hamiltonian of Lacroix and Cyrot [5]; it is obtained by the transformation of the Kondo exchange interaction into a fictitious d-f hybridization within a functional integration method:

$$H = \sum_{k\sigma} (\epsilon_k + \frac{1}{4} J m_{-\sigma}) c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{i\sigma} (E_0 + \frac{1}{4} J n_{-\sigma}) d_{i\sigma}^{\dagger} d_{i\sigma} + \frac{J}{2} \sum x_i (d_{i\uparrow}^{\dagger} c_{i\uparrow} + c_{i\downarrow}^{\dagger} d_{i\downarrow}) + \frac{J}{2} \sum y_i (d_{i\downarrow}^{\dagger} c_{i\downarrow} + c_{i\uparrow}^{\dagger} d_{i\uparrow}), \quad (1)$$

where  $c_{k\sigma}^{\dagger}$ ,  $d_{i\sigma}^{\dagger}$ ,  $\epsilon_k$  and  $E_0$  have the usual meaning;  $x_i$  and  $y_i$ , determined self-consistently, represent the fictitious d-f hybridization, and  $m_{\sigma} = \langle d_{\sigma}^{\dagger} d_{\sigma} \rangle$ ,  $n_{\sigma} = \langle c_{\sigma}^{\dagger} c_{\sigma} \rangle$ .

The phase diagram as a function of  $|J|/D$  is given in fig. 1. At zero temperature, there is a succession of

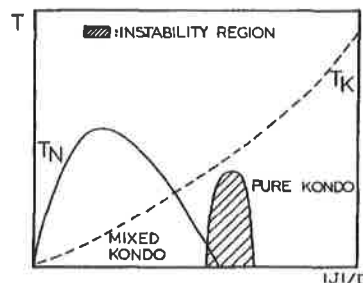


Fig. 1. Phase diagram of the Kondo lattice as a function of  $|J|/D$ .

two phases: the "mixed" Kondo phase where the magnetic moment is reduced by the Kondo effect, and the "pure" Kondo phase where the magnetic moment is zero. A volume decrease leads to an enhancement of the parameter  $|J|/D$  and then induces a transition from a mixed to a pure Kondo phase. The problem of the stability of the phases obtained theoretically remains to be solved. The free energy of the matrix will be considered phenomenologically by the introduction of a parameter, the bulk modulus. The purpose of this paper is to show that the Kondo contribution, added to the matrix energy, can create a thermodynamically unstable region, giving a first order transition at low temperature. The disappearance of magnetism in the  $\alpha$ -phase is then explained by an extremely high Kondo temperature.

2. *The equations of the isotherms at zero temperature.* The variation of  $|J|/D$  with the volume is taken as follows:

$$|J|/D = |J|/D|_0 \exp[-q(V - \tilde{V}_0)/\tilde{V}_0]. \quad (2)$$

$\tilde{V}_0$  and  $|J|/D|_0$  are the atomic volume and the value of  $|J|/D$  at normal pressure;  $q$  is a coefficient which can be deduced approximately from the Slater rules, usually  $q \approx 6-8$ .

The Kondo contribution to the free energy can be calculated at  $T=0$  from the densities of states  $\rho_c^{\sigma}(\omega)$  and  $\rho_d^{\sigma}(\omega)$  of the conduction and impurity electrons:

$$\Delta F = \sum_{\sigma} \int_0^{E_F} \omega [\rho_c^{\sigma}(\omega) + \rho_d^{\sigma}(\omega)] d\omega - \frac{Jx^2}{2} - \frac{J}{2} \sum_{\sigma} n_{\sigma} m_{-\sigma}. \quad (3)$$

The origin of the energy is taken for  $x=0$ ; we find, depending on whether the system is in the mixed or pure Kondo phase:

$$\Delta F_{\text{pure}} = -De^{2D/J},$$

$$\Delta F_{\text{mixed}} = D[-8(D/J)^2 e^{4D/J} - J^2/32D^2]. \quad (4)$$

The free enthalpy can easily be deduced by adding the energy of the matrix, i.e. of the normal system without Kondo or magnetic effects. If we note by  $V_0$  and  $Y$  the atomic volume and the bulk modulus of such a system, then

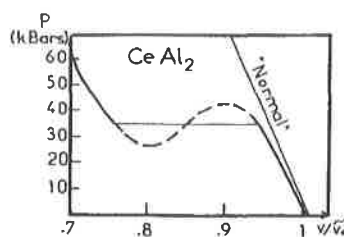


Fig. 2. Isotherm of  $\text{CeAl}_2$  at  $T=0$ .

$$G = \Delta F + \frac{1}{2} Y [(V - V_0)/V_0]^2 + PV. \quad (5)$$

The  $P-V$  isotherm is obtained by putting eq. (2) into  $\partial G/\partial V = 0$ .

### 3. Application to the cases of $\text{CeAl}_2$ and cerium

3.1. *CeAl<sub>2</sub>.* The isotherm obtained at zero temperature for  $\text{CeAl}_2$  is drawn in fig. 2 using the following values:  $B = Y/V_0 = 745 \text{ kbar}^{-1}$ ,  $\tilde{V}_0 = 521 \text{ \AA}^3$  for 8 formulae,  $V_0 = 523 \text{ \AA}^3$  for 8 formulae,  $D = 2.5 \text{ eV}$ ,  $|J|/D|_0 = 0.26$ ,  $q = 7$ . There is a first order transition at a critical pressure of 35 kbar as expected experimentally [6,7], with a volume collapse of the order of 18%. The instability region overlaps the magnetic transition line situated at  $V/\tilde{V}_0 = 0.92$  (see fig. 1). The Kondo temperature at ambient pressure is of the order of 1 K and the one at the beginning of the transition is 70 K. This last value agrees with the one given by Levine and Croft [8] in  $\text{Ce}_{1-x}\text{Sc}_x\text{Al}_2$ :  $T_K = 50 \text{ K}$  for  $x = 0.5$ , just before the transition.

3.2. *Cerium.* For:  $B = 240 \text{ kbar}$ ,  $\tilde{V}_0 = V_0 = 34 \text{ \AA}^3$ ,  $D = 0.4 \text{ eV}$ ,  $|J|/D|_0 = 0.4$ , and  $q = 7$ , the results are similar to the previous case with a critical pressure of -3 kbar, as can be expected from experimental results [9].

In summary, the pressure induces a transition from a mixed Kondo phase ( $\gamma$  type) to a pure Kondo phase of extremely high  $T_K$ . In both cases considered here, the Kondo temperature in the  $\alpha$  phase, i.e. after the transition, is particularly high, of the order of 1000 K (Ce) or 6000 K ( $\text{CeAl}_2$ ). This constitutes our description of the  $\alpha$ -phase: contrary to the valence change model, the disappearance of magnetism is related to

<sup>†1</sup> These values for  $\text{CeAl}_2$  if "normal" are extrapolated from those of  $\text{LaAl}_2$  and  $\text{PrAl}_2$ .

the passage to a phase of very high Kondo temperature.

4. *Bulk modulus.* The bulk modulus of the system at normal pressure is directly related to the second derivative of the free energy:

$$B' = -V_0 \partial^2 F / \partial V^2 = B + D(V_0 / \tilde{V}_0)(q^2 / \tilde{V}_0) \times \{-32(D/J)^2 e^{4D/J} [(1 + 2D/J)^2 + D/J] - J^2 / 8D^2\}. \quad (6)$$

The second term represents the Kondo contribution and is negative: the bulk modulus is always lower than it would be if the system was "normal".

In  $\text{CeAl}_2$ , for example, the Kondo contribution of  $-38$  kbar permits the bulk modulus to be lowered from 745 to 707 kbar, close to the experimental value of 710 kbar [10].

In conclusion, the model of a compressible Kondo lattice can provide a possible explanation of the phase diagram of cerium and its compounds. It appears that the Kondo contribution is sufficient to create a thermodynamically unstable region giving a first order transition at low temperature. The disappearance of magnetism in the  $\alpha$  phase is then explained by an extremely high Kondo temperature. The advantage of the model

is that it is consistent with photoemission experiments and leads to reasonable results. However, at this time, we cannot really conclude from the experimental results on the nature of the  $\alpha$  phase: different valence phase or Kondo phase with high  $T_K$ . Other experiments are still needed: eventuality of the occurrence of the inverse  $\alpha \rightarrow \gamma$  transition with negative chemical pressure and onset of magnetism, photoemission experiments, etc. The determination of the critical point will be reported in a forthcoming publication where we will discuss its position in the phase diagram of fig. 1.

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