Solid State Communications, Vol. 36, pp. 77–79
Pergamon Press Ltd. 1980. Printed in Great Britain.

MAGNETIC RE-ENTRANCE IN INTERMEDIATE VALENCE COMPOUNDS

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(*Received* 1 *April* 1980 *by P. Wachter*)

We explore the possibility of magnetic re-entrance in intermediate valence compounds. Using a simplified Anderson–Lattice model we obtain the pressure-temperature magnetic phase diagram. This diagram shows that for some value of the microscopic parameters the temperature induced two transitions (non-magnetic to magnetically ordered to paramagnetic).

We calculate the magnetization and the average occupation number of the localized state. Estimations of the observability of the effect in systems like $CeAl_2$ are made.

IN RARE EARTH intermediate valence compounds the number of electrons occupying the 4*f* shell fluctuates between two successive integers. In most compounds, one of the electronic configurations involved is magnetic while the other is not. This is the case of all intermediate valence compounds containing Ce, Yb, Sm or Eu.

Some of these systems order antiferromagnetically at low temperature, while others show a saturation of the magnetic susceptibility at low temperature without any evidence of long range magnetic order ($CeAl_2$ [1], $CeAl_3$ [1], $CeIn_3$ [2], $CePb_3$ [3]).

In order to understand some of the properties of these systems, several heuristic or quasi-heuristic models have been proposed [4–6]. Recently, a large amount of theoretical work [7] has been devoted to the study of the "Kondon lattice" following the pioneer work of Doniach [8]. In most of these papers, intermediate valence, as the source of the Kondo effect is neglected. Here we will be concerned with the magnetic phase diagram of an "Anderson Lattice" which, at an extreme regime, reduces to the Kondon problem mentioned above.

Mainly, we study the possible existence of magnetic re-entrance in these compounds. Here, the term re-entrance is used in the same sence as in the superconducting case [9]. The fact that the magnetic susceptibility saturates at low temperatures in most of the intermediate valence compounds suggests the idea of a singlet ground state.

The Kondo-like behaviour found in some rare earth compounds like $CeAl_2$, $CeAl_3$, etc. [7], stems from intermediate valence. The relationship between Kondo effect and intermediate valence may be clearly seen in a recently proposed simplified model [10]. In this model, it is shown that mixing between magnetic and non-magnetic configurations can produce a singlet ground state with close lying magnetic states. The energy spectrum of these states is very similar to the one that could be obtained from a similarly simplified version of the Kondo Hamiltonian.

The interplay between mixing effects and ordering of magnetic moments in intermediate valence has been discussed by Gonçalves da Silva [11] using the model proposed by De Chatel [4]. The competing effect of these two mechanisms is displayed in this work.

Thermodynamically, the possibility of magnetic re-entrance in single ground state systems is not as surprising as it could seem at first: in fact, if the ground state of the system is entropyless and non-magnetic, and there are close-lying magnetic levels, temperature can induce a transition to a phase with *non-saturated* long range magnetic order. This is because this phase will carry some entropy which can lower the free energy when T is different from zero. Further increase in temperature will induce a second phase transition at a temperature T_N to a completely disordered phase. The energy gap J between the singlet ground state and the close lying magnetic levels must be of the order of $k_B T_N$ if both transitions are to take place. If this is not the case, either $J \ll k_B T_N$ and as a consequence the thermal energy necessary to pupulate the magnetic levels will also produce the paramagnetic disorder state or $J \gg k_B T_N$ and the magnetically ordered state will be the ground state.

In some intermediate valence systems as for example $CeAl_2$ [1] J may be varied by the application of pressure or by alloying (chemical pressure) because both processes can change the energy difference between the two configurations, J being a function of this energy difference. Thus it seems possible that in some cases one

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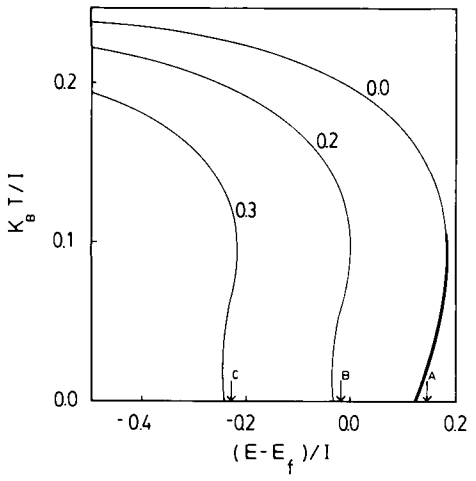

Fig. 1. Temperature–$(E-\epsilon_F)/I$ phase diagram for $V/I = 0.3, 0.2$ and 0. The thin-lines represent second order transitions. The thick-line represents first order transitions. The arrows A, B and C are related to Fig. 2.

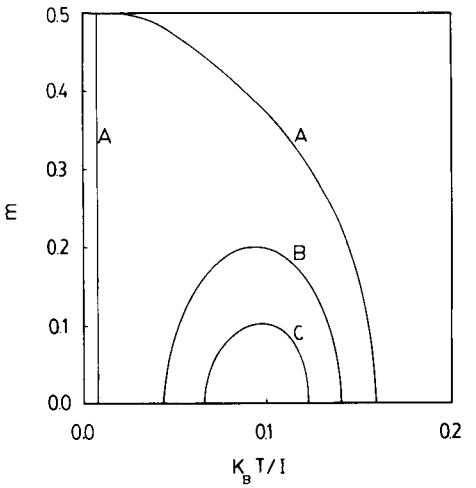

Fig. 2. Magnetization as a function of temperature for $(E-\epsilon_F)/I = -0.23, -0.3, 0.13$ and $V/I = 0.3, 0.2$, 0 respectively. Curve A, B and C corresponds to the parameters indicated by the arrows A, B and C in Fig. 1.

may obtain the energy balance between J and $k_B T_N$ required for the existence of re-entrance. We will now substantiate the idea of re-entrance by resorting to the simplified model or [10]. In order to include the effect of magnetic order, we will add to the Hamiltonian of [10] a term coupling the local moments at different sites. A theory of the magnetic interactions resulting from hybridization has been worked out by G. da Silva and Falicov [12]. The validity of the theory is restricted to the case of integral occupation of the $4f$ shell. Since there is no theory of general validity we will simply introduce interactions between $4f$ shell spins in a phenomenological way. This is done by adding a term of the form $\frac{1}{2}\Sigma_{i\neq j} I \mathbf{S}_i \cdot \mathbf{S}_j$, which will be treated in the molecular field approximation. This procedure allows to separate the Hamiltonian in a sum of single-site Hamiltonians H:

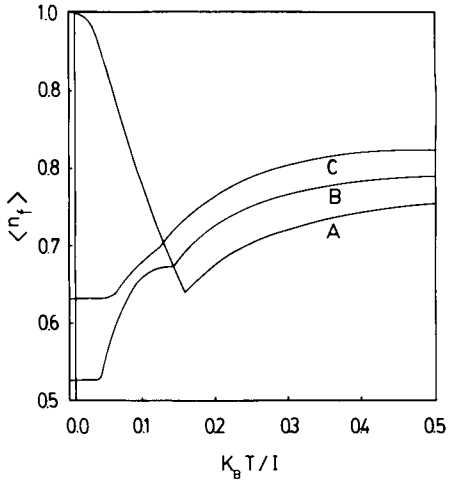

Fig. 3. Average local-state occupation number as a function of temperature. Same values of the parameters as in Fig. 2.

$$H = \sum_\sigma E f_\sigma^+ f_\sigma + U n_{f\uparrow} n_{f\downarrow} + \epsilon_F \sum_\sigma c_\sigma^+ c_\sigma + \sum_\sigma V(f_\sigma^+ c_\sigma + c_\sigma^+ f_\sigma) - I m S_z + \frac{I}{2} m^2 \qquad (1)$$

where the notation is as in [10] and

$$S_z = \tfrac{1}{2}(f_\uparrow^+ f_\uparrow - f_\downarrow^+ f_\downarrow); \quad m = \langle S_z \rangle. \qquad (2)$$

To diagonalize the model Hamiltonian (1) is a simple matter. The magnetization m as a function of the temperature and the microscopic parameters is obtained by minimization of the free energy.

As discussed in [10] the calculations can be reduced to the two-particle subspace. In Fig. 1 we show the phase diagram in the temperature vs $(E-\epsilon_F)/J$ plane for different values of V/J, note that re-entrance is obtained for *all values* of V/J. The behaviour of the magnetization and the average occupation number as functions of temperature are shown in Figs. 2 and 3 respectively for some values of $(E-\epsilon_F)/J$ where re-entrance occurs.

In formulating these ideas, we had in mind the Ce compounds which show magnetic order and some indication of Kondo behaviour or incipient valence instability. One can expect that in these systems the application of pressure or alloying will increase the Kondo temperature thus destroying magnetic order. According to our ideas, re-entrance should appear at pressures near the critical pressure for magnetic order p_N. The better known candidates to display re-entrance

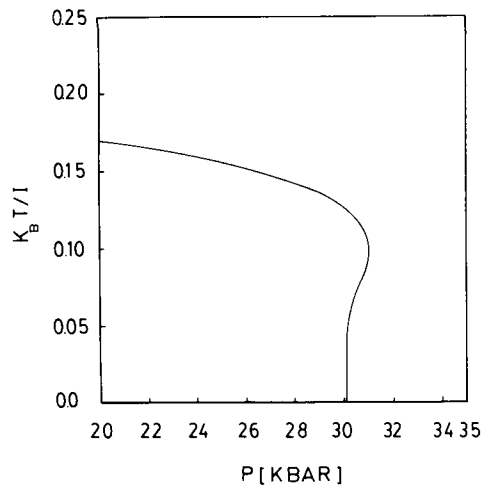

Fig. 4. $p-T$ magnetic phase diagram $E - \epsilon_F = E_0 + \alpha p$, where $E_0/I = 122$ and $\alpha/I = 0.73$ (kbar)$^{-1}$. With this choice of parameters the re-entrance zone is about 1 kbar wide. Arrows are related to Fig. 5.

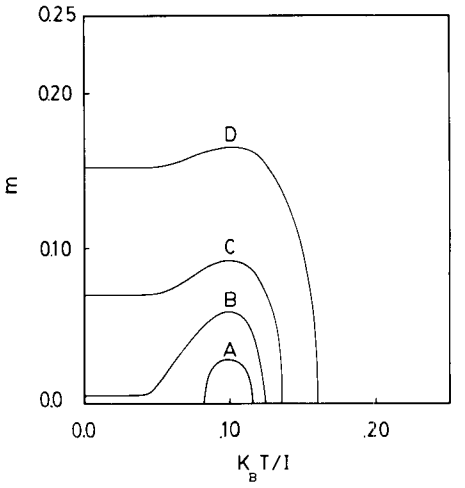

Fig. 5. Magnetization as a function of temperature for the same values of V/I, E_0/I and α/I as in Fig. 4. Curves A, B, C and D correspond to the pressure values indicated by arrows in Fig. 4. Note that the effect of incipient re-entrance appears at pressures well below the critical pressure.

would be $CeAl_2$, Ce_3Al_{11}, $CeIn_3$. Among these $CeAl_2$ is the one on which more experimental information is available. For this compound it has been estimated that p_N is lower than the pressure p_c at which a strong valence instability would appear at zero temperature. Using reasonable values for valence unstable Ce compounds and assuming that $E - \epsilon_F$ is a linear function of pressure, we can draw an approximate phase diagram in the $p-T$ plane as shown in Fig. 4.

In Fig. 5 we show the behaviour of the magnetization as a function of temperature for different values of pressure.

As shown in Fig. 3, the occupation number $\langle n_f \rangle$ of the $4f$ shell has an anomalous behaviour in the magnetic phase. Since this quantity is connected with the volume, the thermal expansion coefficient should reflect these results.

For $E - \epsilon_F$ negative and much larger than V the problem reduces to the Kondo lattice problem. It is easy to show using a similarly simplified Hamiltonian of the form $H = J\mathbf{S}\cdot\mathbf{s} - ImS_z + (I/2)m^2$ that magnetic re-entrance occurs also in this case.

In our model I is considered an independent parameter. In general, I will also be a function of $E - \epsilon_F$ [11]. Since we are here concerned with re-entrance and it appears for all values of V/I, we will not discuss further the pressure dependence of I.

We should also mention here that the single site, molecular field model does not allow to distinguish between different types of ordering (ferro–antiferro or helical).

Crystal field effects are more likely to be important in the low "Kondo temperature" compounds [13]. Crystal field splittings reduce the entropy of the magnetic state, and as a consequence they may inhibit re-entrance in some systems.

In conclusion, we have explored the possibility of magnetic re-entrance in intermediate valence compounds, and found that it can appear in a small region of the $p-T$ phase diagram. Our estimations of the parameters necessary for re-entrance indicate that the phenomenon may be observed experimentally.

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