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SPATIAL CORRELATIONS IN A SIMPLE MODEL OF A MIXED VALENCE SYSTEM

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Résumé.- Dans le cadre d’une généralisation du modèle de valences mixtes de Falicov et Kimball nous recherchons les configurations spatiales des états ioniques de terre rare à un électron, énergétiquement les plus favorables.

Abstract.—Within a simple generalization of Falicov and Kimball’s model for mixed valence systems we discuss the energetically favorable spatial configurations of rare earth ions having an occupied f-state.

In a group of rare-earth (R.E.) metals and compounds known as mixed valence systems the average number of localized 4f-electrons is not an integer and depends on temperature and pressure \( T \). These systems are characterized by two configurations of the R.E. ions, i.e. 4f\(^{n}\) and 4f\(^{n-1}\)5d, having similar energies which may coexist in the crystal. In order to describe such a system we assume two types of electron states: (a) localized atomic-like f-states with energy \( E \) and a large intraband Coulomb repulsion \( U_{ff} \), so that a double occupancy of the f-levels is excluded and (b) extended d-states with negligible \( U_{dd} \). The interband interaction \( U_{fd} \) plays an important role \(/2/\). Although we do not consider the hybridization explicitly, we take into account the effect of the interband exchange and distinguish between \( U_{fd} = \frac{J}{4} \) for parallel and \( U_{fd} = \frac{3J}{4} \) for antiparallel f and d spins. Then the Hamiltonian is given by

\[
H = \sum_{K,\sigma} \varepsilon_{K} \hat{a}_{K}^{\dagger} \hat{a}_{K}^{\phantom{\dagger}} + \sum_{j} n_{j} \left[ E + \sum_{K} \frac{1}{2} \Gamma_{K} \left( \varepsilon_{K} - E \right) \hat{S}_{j}^{z} \hat{S}_{j}^{z} \right] + U_{fd} \sum_{j} \hat{S}_{j}^{z} \hat{S}_{j}^{z} - J \sum_{j} \hat{S}_{j}^{z} \hat{S}_{j}^{z} \varepsilon_{K} \hat{a}_{K}^{\dagger} \hat{a}_{K}^{\phantom{\dagger}} \varepsilon_{K} \hat{a}_{K}^{\dagger} \hat{a}_{K}^{\phantom{\dagger}} (1)
\]

where \( \varepsilon_{K}^{\dagger} \) (\( \varepsilon_{K}^{\phantom{\dagger}} \)) is the creation (annihilation) operator of a 5d-electron with wave vector \( \vec{K} \), spin \( \sigma \) and band energy \( \varepsilon_{K} \), while \( n_{j} = 0 \) (1) is the occupation number of the f-electron with 1/2 spin, \( \hat{S}_{j}^{z} \), at the site \( \hat{a}_{K}^{\dagger} \) and \( \hat{a}_{K}^{\phantom{\dagger}} \) is the total number of lattice sites. The degeneracy of f- and d-bands is neglected.

We are interested in the ground state energy of the system, the average occupation of the f-levels and possible correlations between ions with occupied f-level, for which the Hamiltonian (1) provides a reasonable description. However, the lifetime of the f-levels, not considered here, plays an important role in the magnetic and transport properties of the system.

In the molecular field approximation \(/2/\) at zero temperature the equilibrium condition is given by the shifted f-level equated to the shifted Fermi level of the d-band:

\[
E + n_{c} U_{fd} = E_{F} + n_{f} U_{fd}
\]

where \( n_{c} = N_{c}/N \), \( n_{f} = N_{f}/N \) and \( N_{c}(N_{f}) \) is the total number of f (conduction) electrons. For a system with one electron per site, \( N_{c} + N_{f} = N \), and a square density of states the Fermi energy \( E_{F} \) is given by

\[
E_{F} = \frac{(E + U_{fd})}{1 - 4U_{fd}}
\]

where \( p_{f} \) is the density of states at the Fermi level. If \( p_{f} U_{fd} < 1/4 \), the f-level occupation number varies continuously with \( E \), but for \( p_{f} U_{fd} > 1/4 \), \( n_{f} \) shows a jump.

The system can be considered as an alloy of ions with occupied and empty f-level. Alloy theories like the coherent potential approximation (C.P.A.) \(/3/\) yield a similar picture: a metallic phase \( (n_{f} = 0) \), an insulating phase \( (n_{f} = 1) \) and first order, as well as, smooth transitions among them. Excitonic phases have been found within the split-band regime of C.P.A., i.e. for large values of \( U_{fd} \).

Within these effective scattering theories the energy of the system is only given by the average f-level occupancy, but independent of the configuration of the scatterers. However, for a given number of f-electrons, \( N_{f} \), the energy of the system at low temperatures should depend on the spatial distribution of the f-electrons \(/4/\). There will be one or more spatial configurations which are energetically favorable at \( T = 0 \).
We expand the ground-state energy perturbationally in terms of the scattering strengths $U_{fd}$ and $J$ for given $N$ and $N_f$. The second order correction to the mean field theory is for a parabolic band

$$\left( U_{fd}^2 + \frac{2}{3} J^2 \right) \frac{N}{N} \sum_q X(q)$$

(4)

$$+ 3 \pi \rho \frac{\sigma}{N} \sum_{i \neq j} F(2k_F | \mathbf{R}_i - \mathbf{R}_j |) x \left[ U_{fd}^2 N_1 n_j + J^2 z_1 z_j \right]$$

with $k_F$ being the Fermi momentum, $X(q)$ the susceptibility of the conduction electrons and $F(X) = (X \cos X - \sin X)/X^4$

(5)

As in the RKKY-theory the interaction between scatterers is mediated by the conduction electrons. The oscillating function $F(2k_F R)$ has its absolute maximum at $R = 3/k_F$ and its first and deepest minimum $F$ at $R = 4.5/k_F$. This favors the $f$-occupied sites to arrange themselves such that the distance between them is nearly $R_o$, if the lattice fits this condition. Hence, the $f$-sites are likely to form clusters of parallel spins by adjusting the bonding distances nearly $R_o$, in order to minimize the energy. Higher order than the second in the expansion of the energy, as well as the use of actual energy bands of the crystal instead of the parabolic one, give rise to an anisotropic interaction and to modifications of expression (5) for short distances, i.e. $R_o$. The anisotropy will favor certain bonding angles in the formation of clusters.

While the spin dependent interaction in equation (4) is originated by spin-density oscillations in the electron gas, the particle number interaction in equation (4) is caused by charge density oscillations. The charge-density oscillations are screened by the Coulomb interaction between $d$-electrons, $U_{dd}$, and also the hybridization between $f$- and $d$-electrons tends to suppress the particle number interaction. Spin-density oscillations are not affected by $U_{dd}$ and the hybridization additionally generates a spin-flip interaction between the $f$-occupied sites. Since the particle number interaction is reduced, we have to consider also the possibility of formation of clusters with bonding distance $R_q$ and antiparallel spins between neighboring $f$-occupied sites. The hybridization also allows transitions between configurations having similar energies.

The size of the clusters sensitively depends on $N_c$ and the crystal symmetry. For small $N_c$ we expect the formation of excitons between $f$-holes and $d$-electrons. At concentrations where $N_f$ is of the order of $N_c$ we should also consider the formation of order in a more extended region. We have discussed /4/ the extreme case of formation of a superlattice for $N_f = \frac{1}{3} N$ in a one-dimensional lattice for $J = 0$. The groundstate configuration of the system for $N_f = \frac{1}{3} N$ is clearly that of triple periodicity. The original band is divided into three bands within the reduced zone scheme, separated by energy gaps. The available conduction electrons, i.e. $N_c = \frac{2}{3} N$ can just be accomodated in the first band, if we consider the spin degeneracy. The ordered configuration is stable with respect to changes in $N_f$ if the shifted $f$-level lies within the gap of the shifted $d$-band. This provides the range for $E$ in which the system will be locked at $N_f = \frac{N}{3}$ within the superlattice configuration.

A similar situation appears in a two-dimensional triangular lattice, where the superlattice forms triangles $\sqrt{3}$ times larger in size than the original ones. In this case, however, the Fermi surface does not match exactly the boundaries of the first Brillouin zone of the reduced zone scheme and a larger $U_{fd}$ and $J$ is required to produce the above effect. We do not find such idealized cases in simple three dimensional lattices. However, the formation of a superlattice in a certain plane (charge density and spin density waves) may reduce the energy of the system even if the Fermi surface does not strictly coincide with the Brillouin zone boundary, according to the Hume-Rothery rule for alloys.

References

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