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d-f EXCHANGE INTERACTION INDUCED VALENCE TRANSITION IN MIXED-VALENCE SYSTEMS

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Abstract–Role of exchange interaction is studied using extended Falicov–Kimball model. A discontinuous valence transition is observed at a critical f-level energy. Transition is sharper for smaller exchange interaction. A double-peak structure in specific heat appears for $E \le E_c$ For antiferromagnetic type of exchange interaction, a Curie contribution to the susceptibility is observed.

***Keywords*:** mixed-valence systems; Falicov–Kimball model; *d-f* exchange interaction

1. Introduction

Mixed-valence (MV) phenomenon has been known since 1912 [1], but, still now it is of intense theoretical interest [23] due to its anomalous physical properties [4,5,6]. In MV compounds, the 4*f* shell loses its stability and an electronic phase transition occurs driven by a change of pressure or temperature [7]. For this, the *f*-electrons acquire partial band nature and the valency becomes non-integral. MV systems include a large number of rare-earth compounds (compounds of Sm, Tm, Ce, Eu), transition metal compounds (compounds of Fe, Ti, V). Experiments on samarium compounds (SmS, SmSe and SmTe) clearly demonstrate a semiconductor to metal valence transition induced by pressure [8]. From lattice constant measurement, the intermediate valence of SmS has been found to be 2.8 [9]

On the other hand, various theoretical approaches have been developed to explain the MV phenomena and anomalous properties related [10-12] The Falicov–Kimball model (FKM) [13] and its extensions [2,3,11] are most successful for the study of zero and finite temperature properties of MV systems. Considering electron–phonon interaction (EPI) induced hybridization in FKM, authors showed that EPI favors first-order valence transition, reproduces the nature of the variation of specific heat with temperature and increases the rate of growth of antiferromagnetic correlations [3,14]. FKM extended by correlated hopping interaction induces insulator to metal transition at a critical *f*-level energy [11]. It has also been argued that nonlocal Coulomb interaction within FKM plays an important role in MV phenomena. With the increase of this interaction a sharper valence transition and more ordered state is obtained [12].

Though the role of spin-dependent exchange interaction [15] is important in MV systems, but a few results exist in this aspect. Authors considered a *d-f* exchange induced interaction in the periodic Anderson model to explain the pairing mechanism in heavy-fermion superconducting systems [16] Incorporating *d-f* exchange interaction in FKM, it has been observed that magnetic

ordering as well as Curielike contribution to susceptibility is destroyed for higher values of exchange interaction [17]. But, the effect of this interaction on valence transition and specific heat of the MV systems has not been studied at all. This is the scope of the present work.

In this work, we have used a two-band FKM Hamiltonian extended by *d-f* exchange interaction. Considering a 2D square cluster of four sites, we have investigated the role of exchange interaction in valence transition, specific heat and susceptibility of the MV systems.

2. Formulation

The Hamiltonian we have considered in this problem is

$$\begin{aligned} H = E\sum_{i\sigma} f_{i\sigma}^{\dagger} f_{i\sigma} + U\sum_{i} f_{i\uparrow}^{\dagger} f_{i\uparrow} f_{i\downarrow}^{\dagger} f_{i\downarrow} + G\sum_{i\sigma\sigma'} d_{i\sigma}^{\dagger} d_{i\sigma} f_{i\sigma'}^{\dagger} f_{i\sigma'} \\ +V\sum_{\langle i,j\rangle\sigma}\left(f_{i\sigma}^{\dagger} d_{j\sigma} + d_{j\sigma}^{\dagger} f_{i\sigma}\right) + t_1\sum_{\langle i,j\rangle\sigma} d_{i\sigma}^{\dagger} d_{j\sigma} + J\sum_{i}\left(d_{i\downarrow}^{\dagger} f_{i\uparrow}^{\dagger} - d_{i\uparrow}^{\dagger} f_{i\downarrow}^{\dagger}\right)\left(f_{i\downarrow} d_{i\uparrow} - f_{i\uparrow} d_{i\downarrow}\right), \end{aligned} \tag{1}$$

where $\langle i, j\rangle$ are all pairs of nearest-neighbor (NN) sites on the two-dimensional square lattice; $f_{i\sigma}$ and $d_{i\sigma}$ are the usual fermion operators for *f*- and *d*-electrons respectively (σ, σ' = spin). *E* is the *f*-level energy, *G* is the strength of the *f-d* Coulomb interaction, *V* is the *f-d* hybridization interaction, *U* is the on-site Coulomb interaction, *J* is the spin dependent exchange interaction, and t_1 corresponds to quantum-mechanical hopping of the itinerant *d*-electrons between NN sites.

The representative four-site spin state is taken in the form [3,12]

$$\left| n_{1\uparrow}^{f} n_{1\downarrow}^{f} n_{1\uparrow}^{d} n_{1\downarrow}^{d} n_{2\uparrow}^{f} n_{2\downarrow}^{f} n_{2\uparrow}^{d} n_{2\downarrow}^{d} n_{3\uparrow}^{f} n_{3\downarrow}^{f} n_{3\uparrow}^{d} n_{3\downarrow}^{d} n_{4\uparrow}^{f} n_{4\downarrow}^{f} n_{4\uparrow}^{d} n_{4\downarrow}^{d} \right\rangle. \tag{2}$$

The eigenvectors of *H* are represented as a linear combination of basis vectors Eq. (2), *f*-electron density $\langle n_i^f \rangle = (1/N)\sum_{i\sigma} f_{i\sigma}^{\dagger} f_{i\sigma}$, where *N* is the number of lattice sites; *f-d* intersite correlation function $c_{fd} = \langle f_{i\sigma}^{\dagger} d_{j\sigma} \rangle$. Low temperature specific heat is calculated using the relation

$$C = k_B \beta^2 \frac{\partial^2}{\partial \beta^2} \ln Z, \tag{3}$$

where $Z = \sum_{\alpha} e^{-\beta E_{\alpha}}$, the sum is taken over all eigenstates, E_{α}'s are the corresponding eigenvalues, and $\beta = 1/k_B T$, k_B is the Boltzmann constant (taken as unity throughout our calculations). Spin susceptibility for *f*-electrons is taken as

$$\chi = \beta \left\langle \left(n_{i\uparrow}^{f} - n_{i\downarrow}^{f} \right)^2 \right\rangle. \tag{4}$$

3. Results and Discussions

Figure 1 shows the variation of $\langle n_i^f \rangle$ with *E* for different exchange interaction *J*. It is observed that valence transition occurs at a critical *f*-level energy E_c. The transition is sharper for

smaller values of *J*. The exchange interaction considered here is mainly of hybrid pairing type [15] so in increase of *J* decreases $\langle n_i^f \rangle$ without altering E_c.

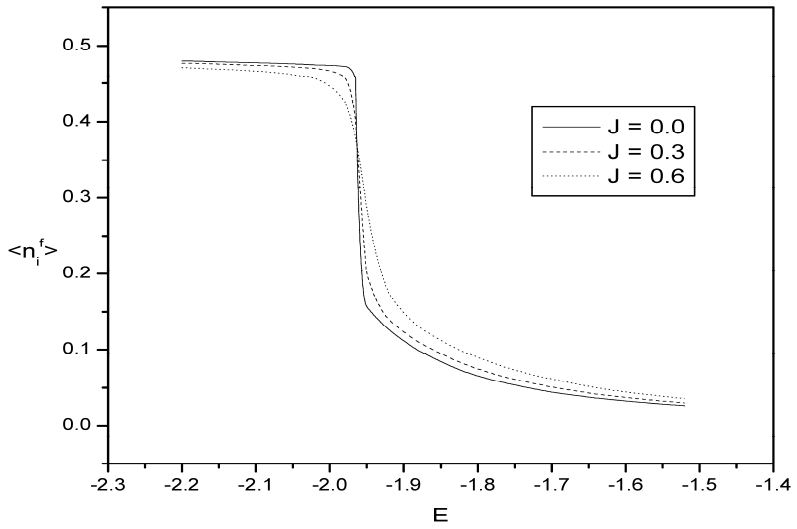

Fig. 1. Variation of $\langle n_i^f \rangle$ with *E* for different values of *J*. Here $V = 0.1$, $U = 5.0$, $G = 2.0$, $t = -1.0$, $T = 0.0$.

In Fig. 2, we have plotted $c_{fd} = \langle f_{i\sigma}^{\dagger} d_{j\sigma} \rangle$ versus *E* for different exchange interaction strengths. In the intermediate valence state, the correlation function is nonzero [18]. With the increase in *E*, the correlation function decreases from a value close to zero, and after a certain *E* value, it increases towards zero. This observation supports that in the insulating or metallic phase c_{fd} should be closer to zero. It is also apparent from the figure that in the insulating or metallic phase, smaller *J* keeps c_{fd} closer to zero indicating sharper valence transition.

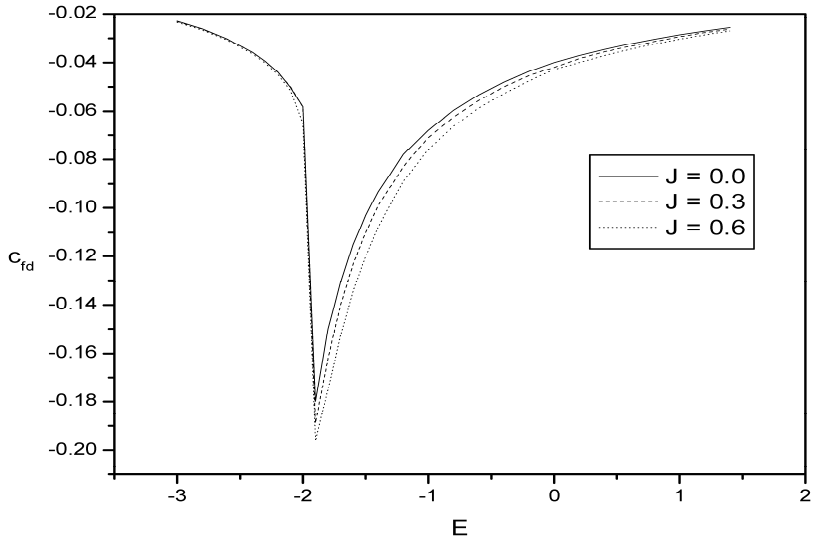

Fig. 2. *f-d* intersite correlation function vs. *E*. Here $V = 0.1$, $U = 5.0$, $G = 2.0$, $t = -1.0$, $T = 0.0$.

The specific heat curves in Figs. 3 and 4 exhibit single-peak as well as double-peak structure [19]. The double-peak structure is observed for $E \le E_c$, where $E_c = -1.8$. The first sharp peak is

due to the presence of a large number of many-body states, which are nearly degenerate with the ground state. The second peak is observed at relatively higher temperatures and is of Schottky-type. For $E > E_c$, a broad single-peak structure is obtained. In this energy region, the many-body states are distributed like a binomial distribution [20] and the degeneracy of the ground state is small. The peak value of the specific heat increases with J (Fig. 4).

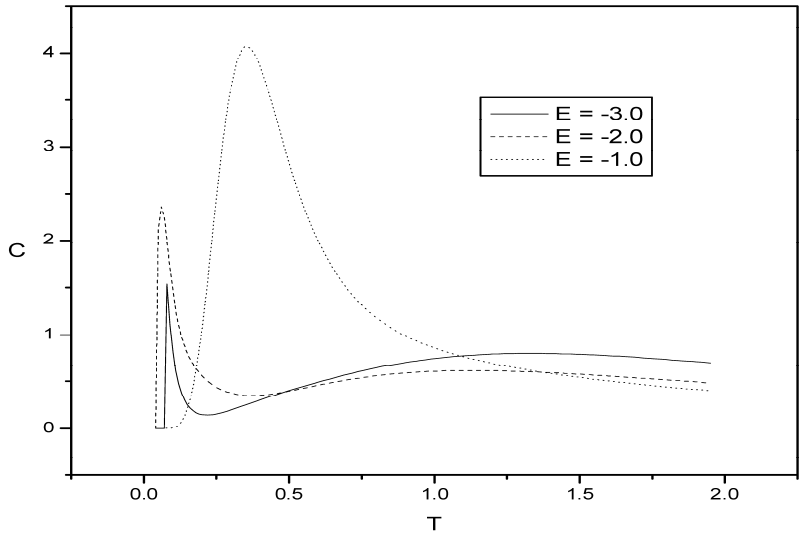

Fig. 3. Variation of specific heat with temperature for different values of E. Here $V = 0.1$, $U = 5.0$, $G = 2.0$, $t = -1.0$, $J = 0.3$.

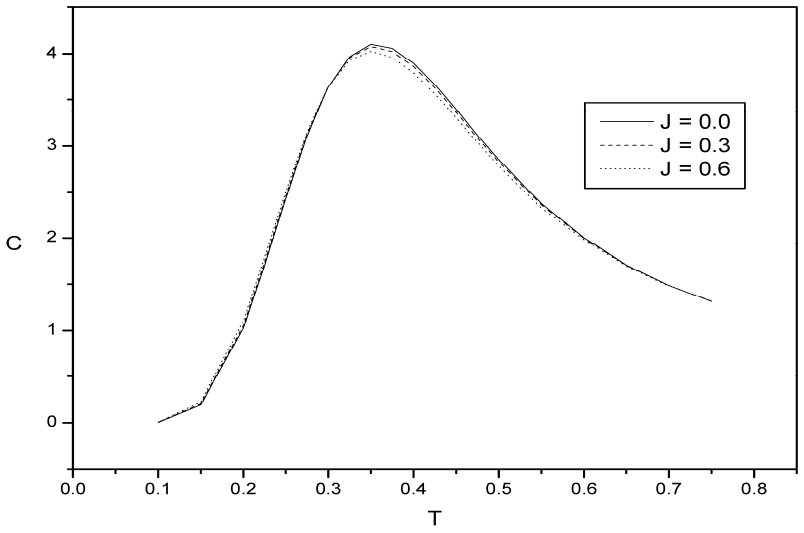

Fig. 4. Specific heat vs. temperature for different values of J. Here $E = -0.1$, $V = 0.1$, $U = 5.0$, $G = 2.0$, $t = -1.0$.

Temperature dependence of the spin susceptibility χ for different values of J are shown in Fig. 5. $J > 0.0$ corresponds to antiferromagnetic type of exchange, appropriate for MV systems [7]. It is observed that susceptibility have peaks at lower temperature region. Similar characteristics has been reported for TmSe which shows a Curie contribution to the susceptibility and is ordered antiferromagnetically at very low temperatures [7].

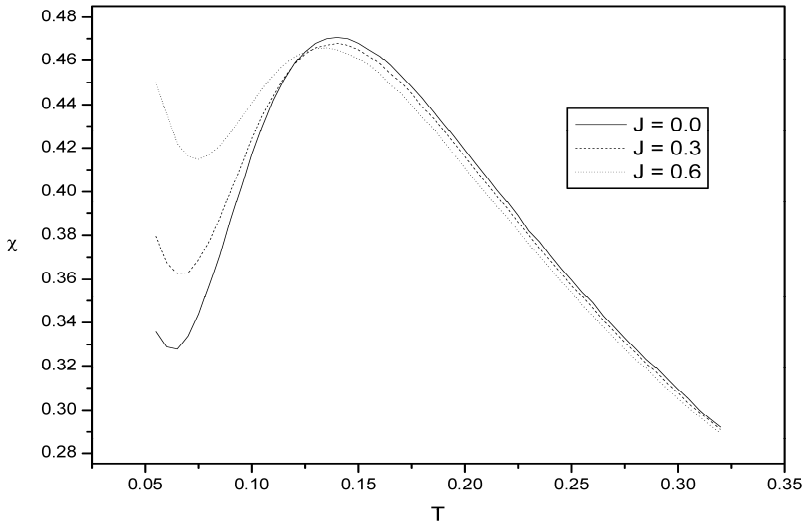

Fig. 5. Temperature dependence of χ for different values of J. Here $E = -1.8$, $V = 0.1$, $U = 5.0$, $G = 2.0$, $t = -1.0$.

4. Conclusion

The effect of *d-f* exchange interaction in MV phenomena has been studied using extended FKM. It appears that valence transition from insulating to metallic phase is sharper for smaller exchange interaction. Specific heat curves show a double-peak structure; a sharp peak at lower temperatures followed by a broad peak of Schottky type at higher temperatures. For antiferromagnetic type of exchange interaction, spin susceptibility forms a peak at lower temperature confirming Curie contribution to susceptibility.

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