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SIGNATURES OF HUBBARD TYPE INTERACTION IN MIXED-VALENT SYSTEMS

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Abstract

The role of Hubbard type interaction between *d*-electrons has been studied using a four-site extended Falicov-Kimball model. A discontinuousvalence transition has been observed. Specific heat curves show a double-peak structure for $E<E_c$. Theeffect of this interaction on entropy has also been examined. A Curie contribution to susceptibility is noticed.

Keywords: Mixed-valent systems; Falicov-Kimball model; Hubbard type interaction.

INTRODUCTION

Different rare-earth compounds show mixed-valence phenomena. They are well studied both theoretically and experimentally [1]. An electronic phase transition driven by an alteration of temperature or pressure is observed in Cerium compounds [2].The *4f*-shell loses its stability while in several ways maintaining its atom-like character in these compounds. The energy difference between states having different *f*-electrons per site (like states $4f^n$ and $4f^{n-1}$plus one conduction bande^-) is very small. This induces resonance transitions between these two states. That's why, *f*-electrons become partial band in nature and the average number of *f*-electrons per site (valence) turns non-integral in value. Thus the non- integral valence makes the properties of mixed-valent compounds anomalous.

The mixed-valent states can be either homogeneous or inhomogeneous. The ionic valence changes both in time and space in homogeneously mixed-valent state (HMVS). This HMVS is observed experimentally in samarium compounds with the valence of *Sm* fluctuating between 2 and 3.

The experiments performed with these compounds so far are the experiments of the specific heat [3], the electrical resistivity [4], the Hall coefficient [5] and the optical reflectivity. All these establish that the MV compounds are paramagnetic semiconductors with an energy gap at low temperatures but they act as 'poor metals' without any energy gap at high (room) temperatures. X-ray diffraction technique performed under high pressure shows that mixed–valent compound *SmS* has a lower gap of energy in metallic phase and thus does not act as a simple metal [6]. Nuclear forward scattering experiments [7] with *Sm*Sindicates first order phase transition induced by pressure from a nonmagnetic to magnetic state.

The homogeneous mixed-valent compounds have unique electronic properties for the coexistence of strongly correlated atomic- like *f*-levels and the wide *sd* bands at or near the chemical potential [8]. This coexist-nature makes difficulty in theoretical calculations. Energy band calculations can't establish whether ground states of *SmS* and SmB_6 are metallic or non-metallic under pressure. But the ground state of LaB_6 [9] is definitely metallic both experimentally and theoretically as the chemical potential lies within the wide *sd* bands.

Many theoretical investigations have been performed so far to clarify the anomalous properties of the MV compounds. The theoretical models used to describe MV states are Periodic Anderson Model (PAM), Falicov-Kimball model (FKM), extended Falicov-Kimball model (EFKM) [10, 11], and PAM extended by *f-d* Coulomb repulsion.

FKMis the most widely used statistical model for describing the ground state properties of the rare-earth and transition metal compounds [12]. Falicov and Kimball introduced this model in 1969. This FKM has two separate types of electronic states for a given material- one is highly correlated localized ion like state and the other is uncorrelated, extended Bloch-like state. Between a conduction electron and a localized *4f* electron at the same lattice site, this model considers a coulomb repulsion. A change in occupation numbers of these electronic states results the metal-insulator transition. The approximations play important role [13] in most of the works.

FKM [14] extended by various interactions [11, 15, 16] has been studied extensively to explain zero and room temperature properties of MV systems. Electron- phonon interaction (EPI) induced hybridization [10, 15], Correlated hopping interaction [16], nonlocal Coulomb interaction, spin dependent exchange interaction [17] play some vital roles in MV phenomena. These interactions induce insulator to metal transition at certain *f*-level energy [16].

In this present work, we have considered the Hubbard type interaction between spin-up and spin down *d*-electrons (U_{dd}). This term has been omitted in most of the previous works related to FKM. According to Lemanski [18], the larger time electrons stay the same site, the interaction between them becomes more important. So, the on-site Coulomb interaction (U) and the *f-d* Coulomb interaction (G) are always larger than this interaction between itinerant *d*- electrons (U_{dd})Farkašovský showed that [19], when the spin-dependent interaction between localized (*f*) and itinerant *(d)*elections (G) is strong enough ($G>4$), the effect of $U_{dd}$is small on the ground state of EFKM. Thus this term can be neglected when the *f-d* interaction (G) is large. But U_{dd}term reveals very strong effects when the strength of the *f-d* Coulomb interaction (G) is small or intermediate. So we consider small *f-d* interaction ($G=1$) and also intermediate on site Coulomb interaction ($U=2$) to study the role of the Hubbard type interaction between *d* electrons (U_{dd}). The value of this interaction $(U_{dd})$is taken of the order of 0.5 and smaller.

We have taken a two-band FKM Hamiltonian extended by Hubbard type interaction between spin up and spin down d- electrons (U_{dd}) in this paper. A 2D square 4 site cluster (Fig. 1) is considered to investigate the importance of this Hubbard type interaction (U_{dd}) in valence transition, entropy, specific heat and susceptibility of the MV systems.

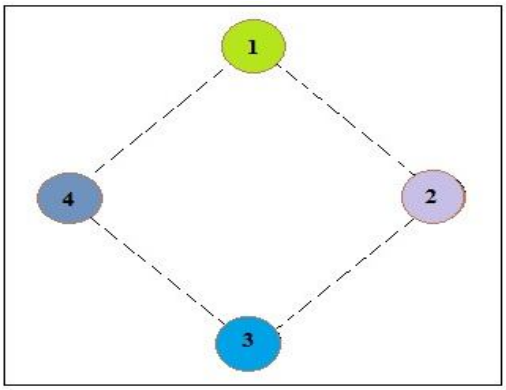

Figure 1: **A four-site lattice**

FORMULATIONS

We have considered the following model Hamiltonian in this problem

$$H = E\sum_{i\sigma} f_{i\sigma}^{\dagger} f_{i\sigma} + U\sum_{i} f_{i\uparrow}^{\dagger} f_{i\uparrow} f_{i\downarrow}^{\dagger} f_{i\downarrow} + G\sum_{i\sigma\sigma'} d_{i\sigma}^{\dagger} d_{i\sigma} f_{i\sigma'}^{\dagger} f_{i\sigma'} + V\sum_{<i,j>\sigma} (f_{i\sigma}^{\dagger} d_{j\sigma} + d_{j\sigma}^{\dagger} f_{i\sigma}) + t\sum_{<i,j>\sigma} d_{i\sigma}^{\dagger} d_{j\sigma} + U_{dd}\sum_{<i,j>} d_{i\uparrow}^{\dagger} d_{i\uparrow} d_{i\downarrow}^{\dagger} d_{i\downarrow} \quad (1)$$

Where <*i*, *j*> represent all pairs of nearest-neighbor *(NN)* sites on the simple two dimensional square lattice,the usual fermion operators for *f* and *d* electrons are denoted by$f_{i\sigma}$and $d_{i\sigma}$ respectively (σ, σ' = spin).*E* is the *f*-level energy, *G* denotes the strength of *f-d* Coulomb interaction, *V* is the *f-d* hybridization interaction *U* represents the on-site Coulomb interaction; and the last term *t* is the kinetic energy which corresponds to quantum mechanical hopping of the itinerant *d*-electrons between *NN* sites.U_{dd} is theHubbard type interaction between spin up and down *d*- elections.

A two dimensional four-site model has been considered to perform exact diagonalization method. This four site representative spin state is taken as in Ref. [16].

Here$\sum_{i\sigma}(< n_{i\sigma}^{f} > + < n_{i\sigma}^{d} >)$ = 2.0, *i*= spin index and σ = spin.

There are altogether 120 basis states and the ground state is a linear combination of these basis states.

We have calculated the *f*-electron density $< n_i^f > = 1/N_S \sum_{i\sigma} f_{i\sigma}^{\dagger} f_{i\sigma}$ and *f-d* inter-site correlation function$C_{fd} =< f_{i\sigma}^{\dagger} d_{j\sigma} >$. N_s= the number of lattice sites.

The entropyper lattice site is

$$S = \frac{1}{N_S}\left(k_B lnZ + \frac{<H>}{T}\right) \quad (2)$$

The low temperature specific heat is given by

$$C = k_B\beta^2 \frac{\partial^2}{\partial\beta^2} lnZ \quad (3)$$

Where= $\sum_\alpha e^{-\beta E_\alpha}$, the sum exists over all theeigenstates, E_α's are the eigenvalues, and $\beta = \frac{1}{k_B T}$, $k_B$being the Boltzmann constant (taken unity to simplify our calculations).

Spin susceptibility for *f*-electrons is represented by
$\chi = \beta < (n_{i\uparrow}^f - n_{i\downarrow}^f)^2 >$(4)

RESULTS AND DISCUSSIONS

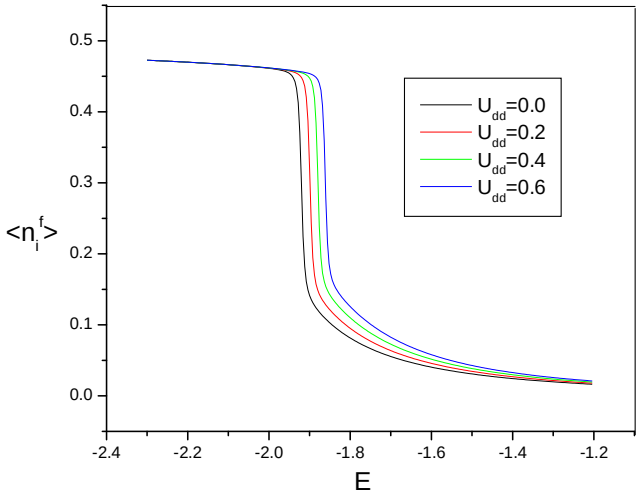

Figure 2: $<n_i^f>$ vs. *E* for different values of U_{dd}.
Here *U*=2.0, *V*=0.1, *G*=1.0, *t*=-1.0

Fig.2 shows the variation of *f*-electron density $<n_i^f>$with *E* for different values of Hubbard type interactionU_{dd}. Sharp insulator to metal transition is observed. The nature of the transition is similar for all values of U_{dd}.The critical f-level energy E_c, at which valence transition occur shifts to higher values for larger U_{dd}. $E_c$has value of the order of -1.9 for valence transitions of all U_{dd} values.

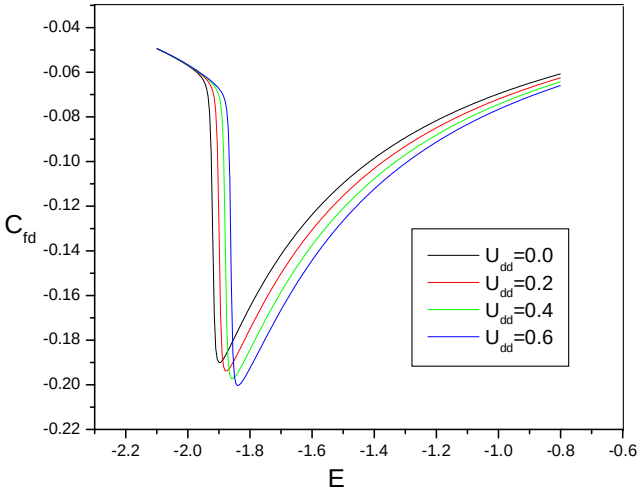

Figure 3: C_{fd} vs. *E* for different values of U_{dd}.
Here *U*=2.0, *V*=0.1, *G*=1.0, *t*=-1.0

In Fig.3, *f-d* correlation function $C_{fd} = < f_{i\sigma}^{\dagger} d_{j\sigma} >$ versus*E*plot is shown for various Hubbard type interactionsU_{dd}. This correlation function is normally non-zero in the intermediate valence state [20]. If *E* is increased, at first the correlation function *(C_{fd})* begins to decrease from a value close to zero, and after a critical *E* value (~ -1.9), C_{fd} gradually increases towards zero. The observation supports the fact that in the metallic or insulating phase C_{fd} should approach closer to zero value. It is also clear from the figure that for the metallic or insulating phase, smaller U_{dd} keeps C_{fd} nearer to zero value indicating a sharper valence transition. The curves also shift towards larger values of E with the increase of U_{dd} confirming delay in transition for higher U_{dd} values.

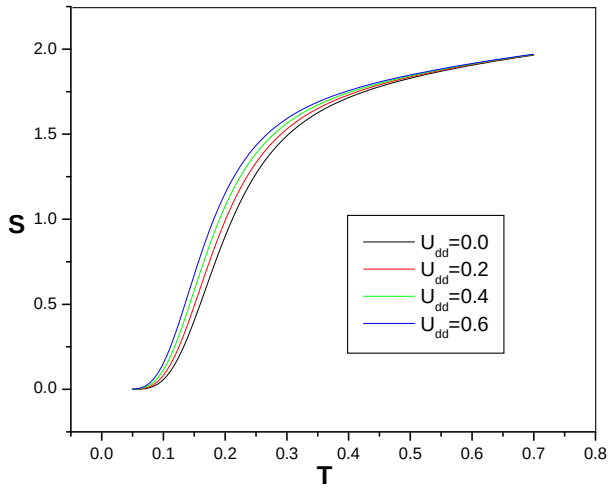

Figure 4: Temperature dependence of entropy *S* for different values of U_{dd}.
Here *E*=-1.5, *U*=2.0, *V*=0.1, *G*=1.0, *t*=-1.0

Fig.4 shows temperature dependence of entropy *S* for different values of U_{dd}. Entropy represents the disorder of the system. From the figure, it is clear that at a certain temperature *T*, entropy decreases with higher values of U_{dd}. So, the system becomes more ordered with Hubbard type interaction U_{dd}. The region where the difference between the curves becomes broad [21] is the transition temperature region [0.1<*T*<0.4]. For *T*>0.45, good convergence is observed.

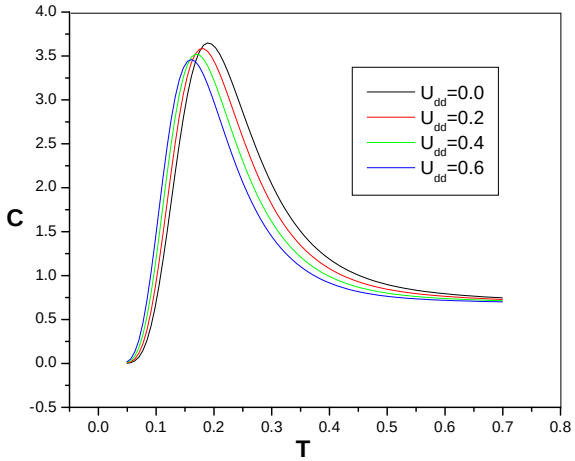

Figure 5: Temperature dependence of specific heat *C* for different values of U_{dd}.
Here *E*=-1.5, *U*=2.0, *V*=0.1, *G*=1.0, *t*=-1.0

The variation of specific heat *(C)* with temperature *T* is shown in Fig. 5 and Fig. 6. In Fig. 5, curves exhibit broad single peak structure [22] for all U_{dd}values. Here *E* (=-1.5)>E_c, whereE_c=-1.9. The peak value of specific heat *C* increases and also shifts to highertemperature region with the increase of Hubbard type interaction between itinerant d electrons *(U_{dd}).*

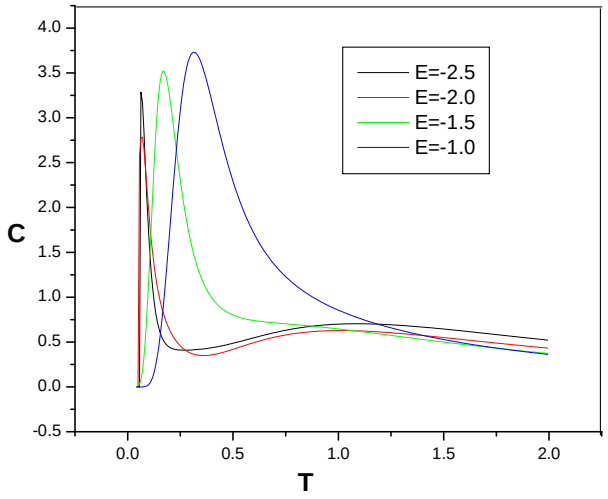

Figure 6: Temperature dependence of specific heat *C* for different values of *E*.
Here U_{dd}=0.4, *U*=2.0, *V*=0.1, *G*=1.0, *t*=-1.0

Fig.6 shows both single and double peak structure of specific heat curves. A two peak structure [23] is obtained for *E*<E_c and broad single peak structure is found when *E*>E_c .The first sharp peak occurs due to a large number of many body states, which are nearly degenerate with the ground state. The second Schottky type peak is observed at higher temperature. This appears due to the binomial distribution [23] of the many body states at this energy region. The non- Fermi liquid behavior of the system is also confirmed by the curves.

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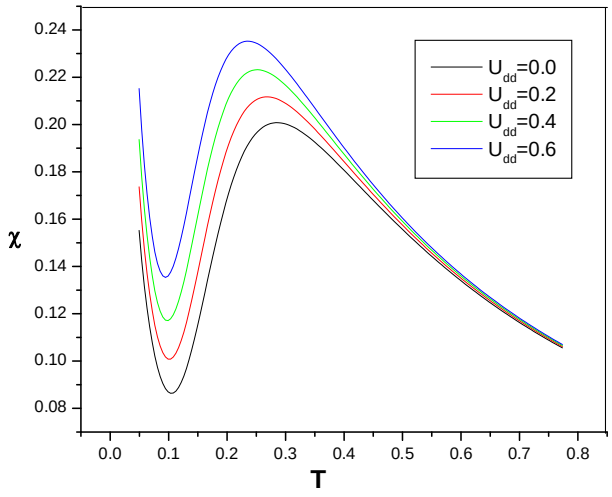

Figure 7: Temperature dependence of spin susceptibility χ for different values of U_{dd}. Here *E*=-1.5, *U*=2.0, *V*=0.1, *G*=1.0, *t*=-1.0

In Fig.7, the variation of spin susceptibility χ against temperature T is shown for different values of U_{dd}. It is observed that the maximum of spin susceptibilityχ is at a definite critical temperature. The peak value of temperature indicates antiferromagnetic ordering in this region. Hubbard type interaction U_{dd} increases the peak value, but shifts it to lower temperature region. Mixed valent *TmSe* is also ordered antiferromagnetically at very low temperatures [8] and shows a Curie contribution to the susceptibility.

CONCLUSIONS

The effect of Hubbard type interaction between spin up and spin down *d*-electrons (U_{dd}) has been studied using EFKM. Theinteraction shifts the *f*-level energy *E* at which valence transition occurs. The *f-d* inter-site correlation function attains non-zero value in the mixed-valent state. With the increase of U_{dd}, more ordered state is found. Specific heat curves exhibit a double peak structure, a sharp peak at very lower temperature followed by a Schottky type peak at higher temperatures. Spin susceptibility shows a peak at lower temperature region verifying the Curie contribution to susceptibility.

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