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On Some Ground State and Finite Temperature Properties of Mixed-Valence Compounds Induced by Next to Next-Nearest-Neighbor (NNNN) Hopping

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ABSTRACT In the present study, effects of next to next-nearest-neighbor (NNNN) hopping of *d*-electrons in the crystal of mixed valence compounds has been discussed. For convenient theoretical calculation and computer simulation within exact diagonalization method, a small cluster of eight lattice sites is considered here to investigate the valence transition through the study of the inter-site and on-site *f-d* correlation functions. Unusual magnetic behavior of mixed valence compounds has also been examined. Antiferromagnetic (AF) order has been developed in the compounds of rare earth elements with the addition of NNNN hopping interaction within the extended Falicov-Kimball model. The extrapolation of the curves of the reciprocal susceptibility (χ^{-1}) intercept at a negative temperature which confirms AF order in the system.

KEYWORDS Mixed valence compound, Extended Falicov-Kimball model, Exact diagonalization method, Valence transition, Antiferromagnetic nature.

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INTRODUCTION

Significantly increasing tendency to use the rare-earth elements in modern technologies and life-styles catches the attention of new researchers [1]. The rare-earth elements, especially Lanthanum (La), Samarium (Sm), Thulium (Tm) etc. exhibit the fluctuating configuration of electrons [2]. The general outermost shell configuration of the rare-earth compounds is$(4f)^n(sd)^m$. By using external pressure or temperature, the *f*-level energy E is increased, as a consequence the stability of the $4f$ shell is lost. Due to the coexistence of two valence states $(4f)^n(sd)^m$ and $(4f)^{n-1}(sd)^{m-1}$, the rare-earth compounds are called mixed-valence compounds. A partially band like nature is developed in rare-earth compounds (i.e., *SmS*, SmB_6, *SmSe, SmTe* etc.). As a consequence, the number of *f*-electrons at each site in the crystal becomes non-integral [2]. This unusual valency is the main reason behind unusual characteristics of the mixed-valence compounds. Various experiments like edge spectrum of L_{III} X-ray absorption of Samarium hexaboride [3,4] prove the anomalous behaviour of MV compounds. The temperature dependent resistivity [5], Schottky typed specific heat [6], linear type specific heat coefficient [7] etc. also support the existence of unusualness of thermodynamical, electrical and magnetic properties of mixed valence compounds. Density-matrix-renormalization-group (DMRG) study has been applied within extended Falicov-Kimball model to study the stability of the excitonic phase [8]. Exact-diagonalization method on small-cluster, DMRG method and an approximate numerical method are used to study the effect of the *f*-electron hoppingwith the support of extended Falicov-Kimball model [9]. A combined approach using exact diagonalization and quantum Monte Carlo methodshas been applied to study magnetization effects of rare-earth tetraborides [10]. An exact diagonalization method along with an approximate method being well-controlled have been used to examine the effects of magnetic field and induced pressure in valence transition with the support of spin one and half Falicov-Kimball model [11]. Many interactions like correlated hopping [12-13], non-local coulomb interaction [14-15], nearest-neighbor (NN) hopping of d-electrons [16] and f-electrons [17], next-nearest-neighbor (NNN) hopping of d-electrons [18], NNN coulomb interaction [19] etc. have already been studied. We observe the fact that the Falicov-Kimball model is a very convenient, appropriate as well as realistic model to investigate the effects of various types of interactions within two band square lattice cluster. So, we decide to use the extension of the conventional Falicov-Kimball model [20] to examine the effect of next-to-next-nearest-neighbor (NNNN) hopping of d-electrons which is unexplored still now.

In the present work, the influence of the NNNN coulomb interaction on some ground state and finite temperature properties of the MV systems has been addressed. The calculations have been made within an 8-site cluster using ED technique. Though finite size effect can't be ignored, but the qualitative nature of the characteristics is almost the same with larger size clusters [21]. Finite-size effect is largely reduced in the thermodynamic limit. Analyzing the results and discussion part, a conclusion has been made at the end.

HAMILTONIAN AND FORMULATION

A cluster of a two-dimensional square lattice with two bands and eight sites is considered here. Taking the total Hamiltonian to be

$$\mathrm{H}=H_0+\mathrm{H}'$$

Where,

$$H_0=\mathrm{E}\sum_{i\sigma} f_{i\sigma}^{+} f_{i\sigma}+\mathrm{U}\sum_i f_{i\uparrow}^{+} f_{i\uparrow} f_{i\downarrow}^{+} f_{i\downarrow}+\mathrm{G}\sum_{i\sigma\sigma'} f_{i\sigma}^{+} f_{i\sigma} d_{i\sigma'}^{+} d_{i\sigma'}+ \mathrm{V}\sum_{<i,j>\sigma}(f_{i\sigma}^{+} d_{j\sigma}+d_{j\sigma}^{+} f_{i\sigma})-t_1\sum_{<i,j>\sigma} d_{i\sigma}^{+} d_{j\sigma}-t_2\sum_{<pq>\sigma} d_{p\sigma}^{+} d_{q\sigma}$$

And

$$\mathrm{H}'=-t_3\sum_{<m,n>\sigma} d_{m\sigma}^{+} d_{n\sigma}$$

The chosen eight-site basis state is in the form

$$|n_{1\uparrow}^{f} n_{1\downarrow}^{f} n_{1\uparrow}^{d} n_{1\downarrow}^{d} n_{2\uparrow}^{f} n_{2\downarrow}^{f} n_{2\uparrow}^{d} n_{2\downarrow}^{d} n_{3\uparrow}^{f} n_{3\downarrow}^{f} n_{3\uparrow}^{d} n_{3\downarrow}^{d} \ldots\ldots\ldots n_{8\uparrow}^{f} n_{8\downarrow}^{f} n_{8\uparrow}^{d} n_{8\downarrow}^{d} >$$

Where, <*i*, j >, <p,q> and < m, n > are NN, NNN and NNNN pairs of sites respectively. $f_{i\sigma}^{+}$ ($f_{i\sigma}$) is the creation (annihilation) operator for the localized f-electrons with spin σ at lattice site *i*. Similarly, $d_{i\sigma}^{+}(d_{i\sigma})$ is the creation (annihilation) operator for the itinerant d-electrons, (σ,σ'=spin). U, G, V are the interaction strengths for on-site Coulomb repulsion, inter-site Coulomb repulsion, and hybridization between f- and d-states respectively. t_1, t_2 and t_3 represent the itinerant d-electrons' quantum-mechanical hopping between NN, NNN and NNNN sites respectively.

The eigen states of H are suitable linear combinations of the basis states.

The on-site *f*-*d* correlation functionc_d^f= <$n_{i\sigma}^f n_{i\sigma'}^d$> = <$f_{i\sigma}^+ f_{i\sigma} d_{i\sigma'}^+ d_{i\sigma'}$>

The inter-site *f*-*d* correlation functionc_{fd}=<$f_{i\sigma}^+ d_{j\sigma}$>

For *f*-electrons, spin susceptibility is defined as$\chi=\beta< \left(n_{i\uparrow}^f - n_{i\downarrow}^f\right) >^2$, where $\beta = \frac{1}{k_B T}$; k_B is Boltzmann constant. The reciprocal susceptibility is denoted by $1/\chi$.

RESULTS AND DISCUSSIONS

In the present calculation, the total number of electrons is restricted to 2. The strengths of the interactions are measured with respect to NN hopping interaction. Here,V=0.5, G=1, U=5, t_1=1, t_2=-0.4. All are measured in eV.

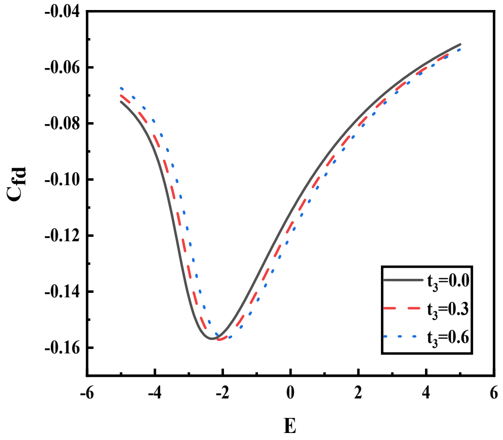

Figure 1: Variation of c_{fd}vs. E for distinct values of NNNN hopping interaction*s* t_3.

The variation of inter-site *f*-*d* correlation function C_{fd} is plotted against *f*-level energy *E* in Fig. 1 and the next-to-next-nearest-neighbour hopping interaction (t_3) is used here as variable. Generally, the non-zero value of the *f*-*d* correlation function confirms the occurrence of insulator to metallic valence transition of the system [22]. Initially, from a value near equals to zero, c_{fd} starts to decline as *E* is increased. After a crucial value of *E*(E_c), c_{fd}increases towards zero. The observation is consistent with the concept that c_{fd}should be closer to zero in the metallic or insulating phase [22]. The splitting of these graphs also supports the fact that the NNNN hopping interaction effects on the valence transition from insulator to metal in mixed valence compounds. E_c differs depending on the value of t_3 and it shifts to the higher value of E with the higher value of t_3.Another observation of figure 1, for smaller values of t_3 the system is less insulating within the region E<E_c and more metallic for the region E>E_c.

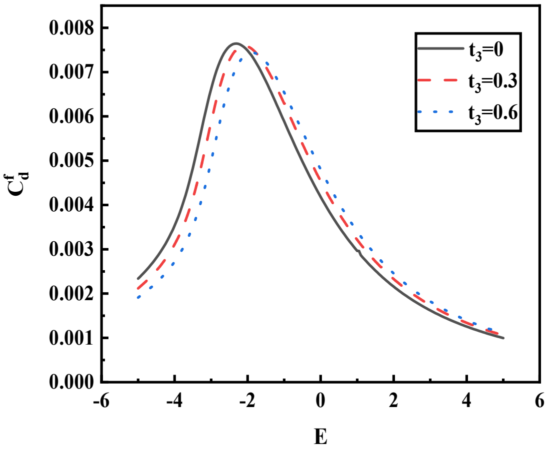

Figure 2: On site *f-d* corelation function c_d^f vs. *E* for distinct values of t_3.

Initially the onsite *f-d* correlation function rises with the increasing value of E. Attaining a high peak value, the value of the f-d correlation function decreases with increasing value of E. The height of the peak of each graph is almost same but it shifts to the higher value of E with the higher value of t_3. The nature of the figure 2 also supports the valence transition from insulating to metallic state of the system. From the observation of figure 2, it also reveals the fact that for smaller values of t_3, the system is more insulating for $E<E_c$ whereas less metallic for $E>E_c$. Figure 3 shows the variation of spin susceptibility χ with temperature (*T*) for different values of t_3. The peak of spin susceptibility versus temperature graph proves the antiferromagnetic property of the material [23, 24]. It is observed that the peak of all graphs is very sharp. Neel temperature (T_N) at which the spin susceptibility is maximum, is almost equal for each graph [23] but the peak height increases with the increasing value of t_3. These observations are coincided with the magnetic behaviour of mixed valence compounds [2]. Above the Neel temperature, the nature of the graphs exhibits the paramagnetic behaviour following Curie-Wiess law [23]. Furthermore, it is also observed that there is a miraculous coincidence of all graphs towards zero-spin susceptibility in the region $T< T_N$.

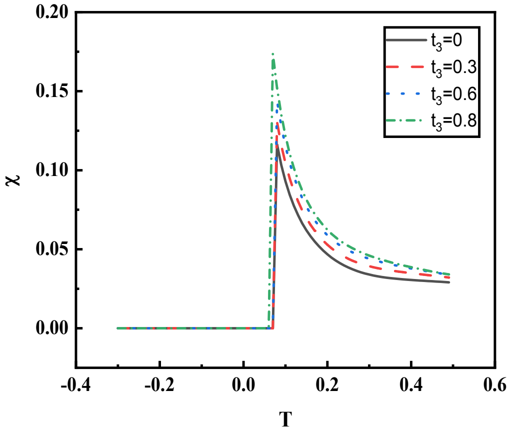

Figure 3: Graph of temperature dependent spin susceptibility for different values of t_3.

From the Curie-Wiess plot ($1/\chi \sim T$) for different values of t_3, it is noted that the reciprocal susceptibility curves intercept at a negative temperature which also confirms the antiferromagnetic nature of the system. All graphs intersect to each other at near equals to zero temperature. Above the intersection point of temperature, for the lower value of t_3, the value of $1/\chi$ shows is increasing property and below it, $1/\chi$ shows decreasing nature.

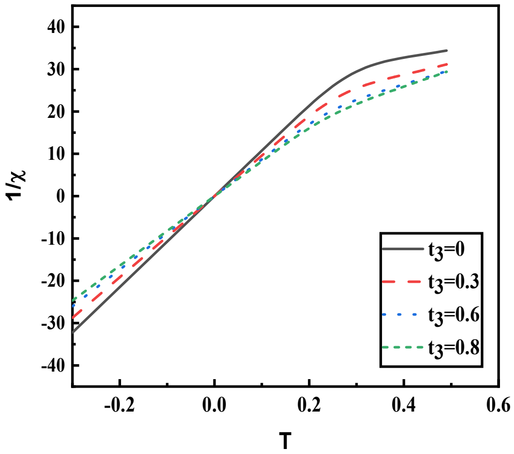

Figure 4: Graph of temperature dependence of reciprocal spin susceptibility ($1/\chi$) for different values of t_3.

CONCLUSIONS

Studying the ground state and temperature dependent magnetic properties of the mixed valence compounds, we can conclude that the NNNN hopping interaction is very significant in the compounds of fluctuating valency such as samarium hexaborides, samarium sulphide etc. Both the inter-site and onsite *f-d* correlation functions exhibit the valence transition from insulator to metal phase. With the increasing value of *f*-level energy *E*, the inter-site *f-d* correlation function becomes negative in value. Whereas with the increasing value of E, the value of on-site *f-d* correlation function is always positive. Owing to their unusual magnetic properties, rare earth elements have many applications. Rare earth magnets are used in hard drives, CD-ROM drives and DVD disc drives etc. In our present study, we also analyse the graphs of spin susceptibility versus temperature and Curie-Wiess plot. Observations of these two types of graphs also confirm the antiferromagnetic nature of the system by the inclusion of NNNN hopping interaction term t_3 to the extended Falicov-Kimball model.

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