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THEORETICAL STUDY FOR PRESSURE EFFECTS IN ORBITAL ORDERING FERROMAGNETS

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Abstract The magnetic properties of orbital ordering systems under high pressures are investigated theoretically on the basis of one-dimensional multi-band Hubbard model with exact diagonalization procedure. Pressure effects are taken into account through the change of the inter-atomic transfer and the orbital energies. It is pointed out that magnetic phase transitions can be possible with the antiferrodistortive structures being kept. It is also shown that saturation of Heisenberg-type intersite exchange coupling J_S occurs for large inter-atomic transfer energy t in high-spin state.

INTRODUCTION

The layered perovskite-type compounds K_2CuF_4 and (p-cyanoanilinium)$_2CuCl_4$ are known as 'orbital ordering ferromagnets'.[1~3] These systems are quasi two-dimensional ferromagnets, and the superexchange interaction between Cu ions in the CuX_4 (X=F,Cl) planes plays a key role in their magnetic properties. In the ground state of these materials the $d_{z^2-x^2}$ and $d_{z^2-y^2}$ orbitals of Cu ions are aligned alternatingly in the CuX_4 plane as shown in Fig. 1,[4] which is called the antiferrodistortive (AFD) orbital ordering. This AFD orbital ordering state is realized by AFD ordering of X^- distortion from the center between Cu^{2+} ions in the CuF_4 planes. Recently quite interesting physical properties have been observed in these compounds under high pressures .[5~8]

The crystal structure of K_2CuF_4 is basically of K_2NiF_4 type and its Curie temperature is T_c=6.25 K.[2] Khomskii and Kugel proposed the 'orbital ordering' model for the origin of ferromagnetism of K_2CuF_4.[4] Ito and Akimitsu confirmed experimentally the AFD orbital ordering by measurements of polarized neutron scattering.[9] Quite recently Ishizuka *et al.* carried out magnetization measurements for K_2CuF_4 under high pressures up to 13 GPa over the temperature range from 1.5 to 18 K.[5] Their results show that the value of T_c is almost constant for pressures $P < 4$ GPa. They have reported also that the magnetic susceptibility at low temperatures is suppressed rapidly above $P_c = 8 \sim 9$ GPa, which indicates the disappearance of the ferromagnetic state. They speculated that at P_c a transition from ferromagnetic to

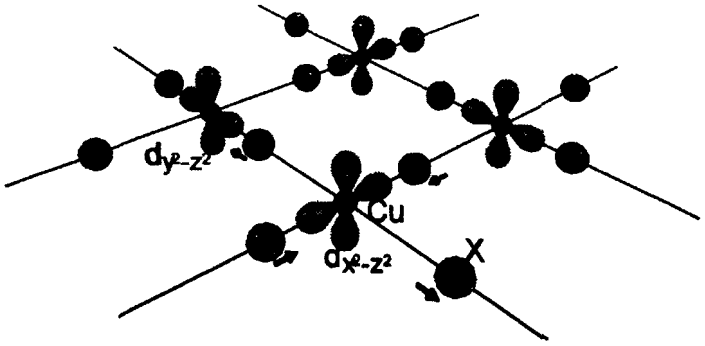

FIGURE 1 The schematic view of the AFD orbital ordering and the AFD ordering of X^- ions in the CuX_2 (X=F or Cl) plane.

antiferromagnetic state is induced by the structural transition from AFD to ferrodistortive (FD) ordering of F^- ions. From Raman scattering measurements Manaka *et al.*[6] have observed that a structural phase transition occurs at a pressure higher than P_c and this result may suggest that structural transition can not be the origin of disappearance of the ferromagnetic state.

(p-cyanoanilinium)$_2CuCl_4$ has the crystal structure similar to K_2CuF_4 and are also an orbital ordering ferromagnet whose T_c is about 10K.[3] Ferromagnetic ordering in $CuCl_4$ planes has been observed also in other similar materials written as $(RNH_3)_2CuCl_4$ where R represents n-alkyl chain or aromatic group.[10~12] By Raman scattering measurements for $(C_2H_5NH_3)_2CuCl_4$ under high pressures Morimoto and Tokura[7] observed above P_c=4 GPa the disappearance of the Raman modes which have become Raman active by the AFD ordering of Cl ions in the $CuCl_4$ planes. These experimental results indicate extinction of the AFD ordering above P_c. Sekine *et al.*[8] measured the magnetic susceptibility of (p-cyanoanilinium)$_2CuCl_4$ under pressures up to 1 GPa, and reported an enhancement of intra-plane ferromagnetic interaction with increasing pressure. They pointed out that it is caused by decrease of the longer Cu-Cl bond length D_L.

Stability of the ferromagnetic state in AFD orbital ordering systems can be basically understood by perturbational treatment of charge transfer between atoms in the multi-band Hubbard model.[13,14] The scheme of the relevant second-order perturbation is shown in Fig. 2, and the ferromagnetic exchange coupling J_S^{Pert} is given by $J_S^{Pert} = 2t^2[\frac{1}{U+V-J} - \frac{1}{U+V+J}]$, where t is the inter-atomic transfer energy,

V the energy difference between two orbitals on the same ions, U the intra-atomic Coulomb energy, and J the intra-atomic exchange energy. It is noted here that the antiferromagnetic state is stabilized if the orbital ordering is FD type,

Applying pressure to AFD orbital ordering systems is expected to give two important effects. One is the enhancement of inter-atomic transfer t, and the other is the decrease of the orbital energy difference V, which is caused by suppression of AFD ordering of lattice distortion. Within the perturbational calculation these two effects does not make the ferromagnetic state unstable, judging from the expression of J_S^{Pert}. The ferromagnetic state is the most stable even in the case of complete extinction of AFD ordering of lattice distortion (V=0 case) as long as the AFD orbital ordering exists. Therefore, within the framework of perturbational treatment the ferromagnetic state becomes unstable only when the AFD orbital ordering is destroyed by structural transition. Then, one question arises: does instability of the ferromagnetic state occur only through structural transition even if the perturbational picture breaks down? To answer to this question we have investigated the magnetic properties of AFD orbital ordering systems under high pressures by using a method which goes beyond the perturbational calculation.

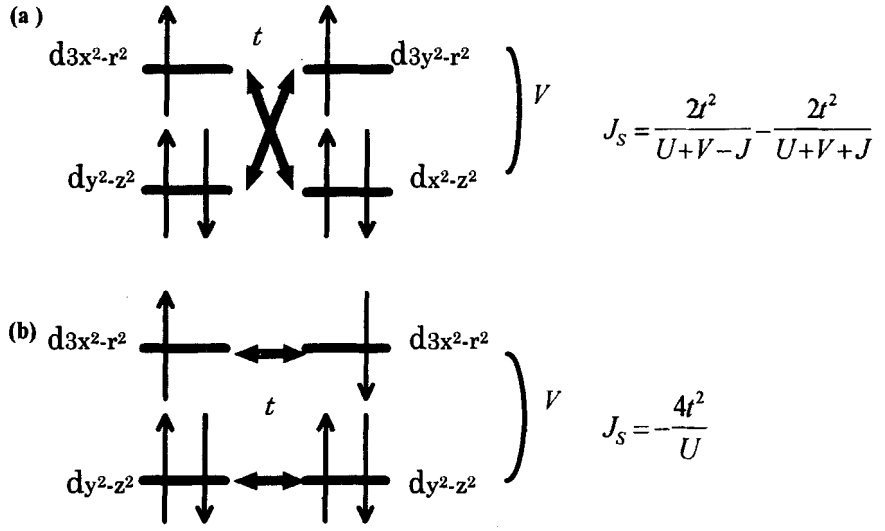

FIGURE 2 The second order perturbation energy for (a) ferromagnetic electron configuration in AFD orbital ordering and (b) antiferromagnetic electron configurations in FD orbital ordering when $U \gg t$. Here U, V, J and t represent orbital energy difference, Coulomb energy, inter-orbital exchange energy and inter-atomic transfer energy.

CALCULATIONS AND RESULTS

To pursue the possibility of the magnetic phase transition without accompanying extinction of AFD ordering we adopt the exact diagonalization procedure for the following multi-band Hubbard Hamiltonian

$$\begin{aligned} H &= \sum_{i\mu\sigma} V_\mu n_{i\mu\sigma} + \sum_{i\mu\nu\sigma\delta} t_{\mu\nu}(c^\dagger_{i\mu\sigma}c_{i+\delta\nu\sigma} + h.c.) \\ &+ \sum_{i\mu} U n_{i\mu\uparrow}n_{i\mu\downarrow} \\ &+ \sum_{i\mu\neq\nu\sigma\sigma'} (U - J\delta_{\sigma\sigma'}) n_{i\mu\sigma}n_{i\nu\sigma'} \\ &+ \sum_{i\mu\nu\sigma} J c^\dagger_{i\mu\sigma}c^\dagger_{i\nu\bar{\sigma}}c_{i\mu\bar{\sigma}}c_{i\nu\sigma}, \end{aligned} \tag{1}$$

where $c^\dagger_{i\mu\sigma}(c_{i\mu\sigma})$ represents creation (annihilation) operator of μ-orbital with σ-spin at the ith ion and $n_{i\mu\sigma}$ is the number operator. The first, the second, the third and the fourth lines represent respectively the orbital and the inter-molecular transfer energies, the intra-orbital Coulomb interaction, the inter-orbital Coulomb energy and the S_zS_z part of exchange interaction, and the S_+S_- part of exchange interaction. The intra-orbital and the inter-orbital Coulomb energies are assumed to be the same.

Keeping in mind K_2CuF_4 and (cyanoanilinium)$_2CuCl_4$ we consider only two $d\gamma$ states of Cu ions. As orbital functions of the $d\gamma$ states we adopt two sets ($d_{z^2-x^2}$, $d_{3y^2-r^2}$) or ($d_{z^2-y^2}$, $d_{3x^2-r^2}$) , and consider the situation in which the $d_{z^2-x^2}$ and $d_{z^2-y^2}$ orbitals are aligned alternatingly. The role of halogen ions is considered only as charge transfer paths between Cu ions. The hole number is fixed as one per site, *i.e.* the system is quarter-filling. For simplicity actual calculations have been carried out for the one-dimensional atom arrangements. Strictly speaking, the transfer energy between adjacent $d_{z^2-y^2}$ and $d_{3y^2-r^2}$ and that between adjacent $d_{z^2-x^2}$ and $d_{3x^2-r^2}$ are different, but for simplicity they are assumed to be the same and represented by t. Further we assume that the transfer energy between adjacent $d_{z^2-x^2}$ and $d_{z^2-y^2}$ is vanishing.

We have adopted the exact diagonalization procedure of finite size chains with use of periodic boundary condition. Lanczos method and Householder method are respectively used for calculating ground state properties and those at finite temperature. In this paper we are concerning with the insulating case and consider only the case of large U. Throughout this paper the value of U is fixed as U/J=20. As an example of our calculational results we show in Fig. 3 the phase diagram of the ground state in the plane of $\tau \equiv t/J$ vs $v \equiv V/J$, which is obtained for the chain size N=6.

It is clearly seen that the ferromagnetic state is the ground state for a wide range in the $\tau - v$ plane. If we increase the value of τ for a fixed value of v, the ferromagnetic state ($S_{\rm tot}$=3) is taken over by the spin singlet state ($S_{\rm tot} = 0$) at a critical value $\tau_{\rm c}$, and the value of $\tau_{\rm c}$ decreases with decreasing v. It means that for sufficiently large τ the ferromagnetic state can become unstable against the spin singlet state without structural transition. This is an important consequence that cannot be obtained by the perturbational calculation. Here we note that $S_{\rm tot} = 1$ state in upper region of Fig. 3 has appeared by the size effect.

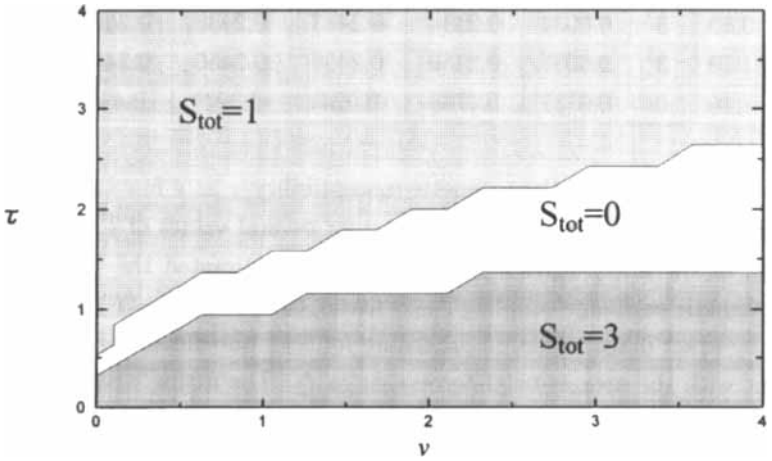

FIGURE 3 The phase diagram of the ground state obtained in the plane of $\tau \equiv t/J$ vs $v \equiv V/J$ for six Cu ions. The Coulomb energy is set to be U/J=20.0.

In order to clarify the nature of phase transition from the ferromagnetic to the spin-singlet state, we have calculated the fluctuation of electron number $\langle(\delta n)^2\rangle$ and the spin-spin correlation function $\langle \boldsymbol{S} \cdot \boldsymbol{S}_\delta \rangle$ which are defined by

$$\langle(\delta n)^2\rangle = \frac{1}{2N}\langle \sum_i (\sum_{\mu\sigma} n_{i\mu\sigma} - \sum_{\mu\sigma}\langle n_{i\mu\sigma}\rangle)^2\rangle \tag{2}$$

$$\langle \boldsymbol{S} \cdot \boldsymbol{S}_\delta \rangle = \frac{1}{N}\sum_i \langle \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+\delta}\rangle. \tag{3}$$

In Table I we show the values of $\langle \boldsymbol{S} \cdot \boldsymbol{S}_\delta \rangle$ and $\langle(\delta n)^2\rangle$ obtained for N=8, U/J=20.0, V/J=2.0. It is clearly seen that when going from the ferromagnetic to the spin-singlet state $\langle \boldsymbol{S} \cdot \boldsymbol{S}_\delta \rangle$ changes dramatically, but $\langle(\delta n)^2\rangle$ keeps quite a small value. It is concluded that both the states are the Mott insulating state, and the phase transition is regarded as 'spin phase transition' without charge redistribution. Furthermore, the δ-dependence of $\langle \boldsymbol{S} \cdot \boldsymbol{S}_\delta \rangle$ in the spin singlet state strongly suggests

that this state is a helical state. We speculate enhancement of antiferromagnetic interaction between second nearest neighbors stabilizes a helical state. In fact, this suggestion is supported by calculation in forth-order perturbation. We expect this transition will occur also in two or three dimensional systems.

TABLE I Examples of $\langle(\delta n)^2\rangle$ and $\langle \boldsymbol{S}\cdot\boldsymbol{S}_\delta\rangle$ in ferromagnetic and spin singlet states. (N=8, U/J=20.0, V/J=2.0)

t/J	S_{tot}	$\langle(\delta n)^2\rangle$	$\langle \boldsymbol{S}\cdot\boldsymbol{S}_1\rangle$	$\langle \boldsymbol{S}\cdot\boldsymbol{S}_2\rangle$	$\langle \boldsymbol{S}\cdot\boldsymbol{S}_3\rangle$	$\langle \boldsymbol{S}\cdot\boldsymbol{S}_4\rangle$
0.80	3	0.0034	0.2484	0.2483	0.2483	0.2483
1.20	3	0.0087	0.2459	0.2456	0.2456	0.2456
1.40	0	0.0131	0.1768	-0.0241	-0.2947	-0.4455

We have calculated also the magnetic susceptibility χ as a function of temperature. In Fig. 4(a) we show $\chi(T)$ calculated for several values of t with U/J=20 and V/J=2 in the ferromagnetic region. We have estimated the value of effective ferromagnetic exchange coupling J_S by fitting the obtained $\chi(T)$ to the results calculated by exact diagonalization procedure for S=$\frac{1}{2}$ one-dimensional Heisenberg ferromagnet with the nearest-neighbor exchange J_S. The fitting have been carried out at low temperatures because it is difficult to make the fitting at higher temperatures when t is large. Since the magnitude of the intra-atomic Coulomb energy U is roughly estimated to be 1$\sim$10 eV, the temperature region in consideration is below 50 K. Figure 4(b) shows the value of J_S estimated as a function of τ=t/J for U/J=20 and V/J=2. We show in Fig. 4(b) also the value of J_S calculated by the second-order perturbation, *i.e.* $J_S^{\rm Pert} = 2t^2[\frac{1}{U+V-J} - \frac{1}{U+V+J}]$. Both the results agree well each other if τ is sufficiently small. However, J_S deviates from $J_S^{\rm Pert}$ with increasing τ and it shows a trend of saturation just before τ reaches τ_c. It may be caused by softening of spin wave excitation as the presage of magnetic phase transition to helical structure.

DISCUSSION

From the results shown in Figs. 3 and 4(b) we can draw interesting consequences about the pressure effects on orbital ordering ferromagnets. First we consider the ferromagnetic system which lies near the boundary between the ferromagnetic and the spin-singlet state in the $\tau - v$ plane in Fig. 3. Judging from the saturation behavior of J_S in the vicinity of the boundary as shown in Fig. 4(b) the value of T_c may be little dependent on pressure. Further we can expect that applying pressure may bring the system to the spin-singlet state across the boundary, *i.e.* transition from

the ferromagnetic to the spin-singlet state might be caused by pressure without accompanying structural transition. Next we consider the ferromagnetic system which lies far from the boundary in the $\tau - v$ plane. In this case the exchange coupling J_S is expected to increase with increasing pressure, and hence we expect increase of T_c by pressure. As to the magnetic transition, on the other hand, it may be difficult to bring the system to the region of spin-singlet state by pressure only. Then, in this case the structural change from AFD to FD ordering of lattice distortion would be necessary to cause the disappearance of the ferromagnetic state. Judging from the experimental results summarized in Introduction, we may conclude that K_2CuF_4 corresponds to the former case and (p-cyanoanilinium)$_2CuCl_4$ to the latter case.

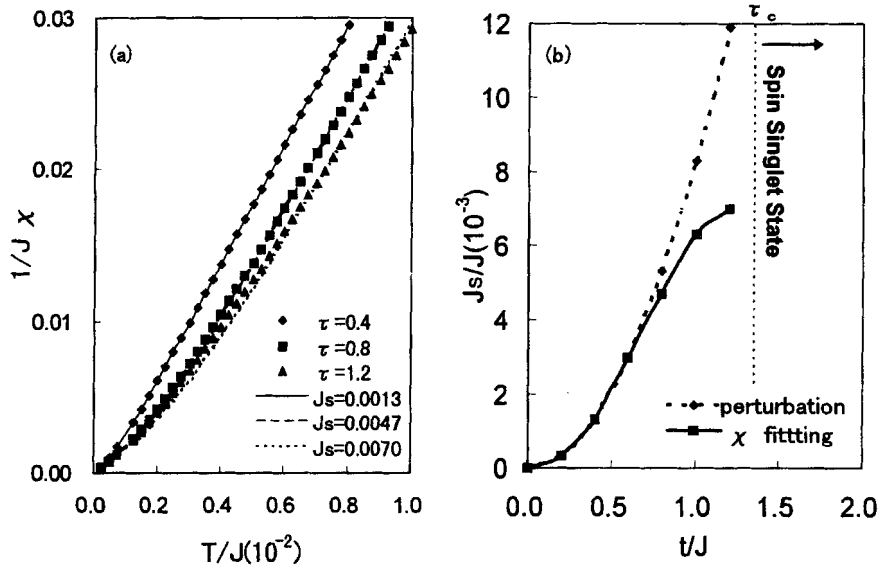

FIGURE 4 (a) The magnetic susceptibility at low temperatures. The marks represent the results obtained by exact diagonalization method for multi-band Hubbard model and the lines the results for Heisenberg model. (b) The effective exchange energy J_S as a function of $\tau \equiv t/J$. The full curve represents the results estimated by fitting the susceptibility of multi-band Hubbard model to that of Heisenberg model, and the dotted curve the results obtained from calculations in second-order perturbation.

In this paper we have regarded the role of halogen ions simply as charge transfer paths between Cu ions. This assumption may be reasonable for Mott insulating systems. For insulator of charge-transfer type, however, we may take into account

explicitly the orbitals of halogen ions. We have neglected also inter-plane exchange coupling completely because we have concerned with the magnetic properties in the CuX_4 planes. To determine the transition temperature as the three dimensional system the inter-plane exchange coupling plays an important role, but their magnitude is quite small and it is beyond the scope of this paper to discuss the pressure effects on the inter-plane exchange coupling.

We are studying the magnetic properties of AFD orbital ordering systems also for the case of small U. Our preliminary results indicate a possibility of metallic orbital ordering ferromagnetism. The details will be reported elsewhere.

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