Metallic state driven by frustrated electronic correlation in Cu-O double chain of $PrBa_2Cu_4O_8$

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A proposal is made that the metallic state observed in the Cu-O double chain unit of $PrBa_2Cu_4O_8$ is a peculiar state driven by geometrical frustration. We treat one-dimensional 1/4-filled extended Hubbard models with competing intersite Coulomb interactions appropriate for this compound, and estimate the charge gap using Lanczos exact diagonalization method. It is argued that the charge ordered insulating states, stabilized in the absence of frustration, can be ''melted'' when the degree of frustration is large so that a metallic state is realized. In the limit of large on-site Coulomb interaction U, the systems can be mapped onto one-dimensional $S=1/2XXZ$ models, where our metallic state corresponds to a spin-liquid state due to the competing z component of the exchange couplings.

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Charge ordering (CO) phenomena have been attracting interest in the field of transition metal oxides[1] as well as organic conductors.[2] Among them, low dimensional 1/4-filled compounds often show CO transition due to intersite Coulomb interactions.[3] Recently, both the Cu-O single chain unit in $PrBa_2Cu_3O_7$ (Pr1237) and the Cu-O double chain unit in $PrBa_2Cu_4O_8$ (Pr1248), whose structures are schematically shown in Fig. 1, have been found to show 1/4-filled one-dimensional (1D) dispersion in photoemission measurements by Mizokawa *et al.*[4,5] These compounds are characteristic since the Cu-O chain units can be investigated without being disturbed by the double CuO_2 layers, such as in the isostructural YBCO systems showing high-T_c superconductivity. The CuO_2 planes show antiferromagnetic Néel ordering, at 285 K in Pr1237 and at 200 K in Pr1248, indicating that the holes are not successfully doped into the CuO_2 planes as in the YBCO. As for such difference in the CuO_2 planes between these Pr-containing and YBCO systems the scenario that in Pr1237 the Pr-O hybridized states trap holes has been most successful.[6]

The electronic states of the Cu-O chain in Pr1237 and the Cu-O double chain in Pr1248, on which we focus in this article, are quite different. That is, the former is insulating[7] while the latter shows a metallic ground state.[8] Naively it is difficult to understand such a difference, because the doubling of an insulating single chain is not expected to make the system metallic. Actually, in both cases the low energy physics should be described by one-band 1/4-filled models,[9] as shown by photoemission experiments mentioned above.

The origin of the insulating behavior in the Cu-O single chain in Pr1237 (Ref. 7) is suggested by NQR signals to be the existence of CO observed below 100 K.[10] This can be naturally understood in terms of the 1/4-filled 1D extended Hubbard model with on-site Coulomb interaction U and nearest-neighbor Coulomb interaction V. In this case, the ground state is the ''Wigner crystal''-type CO state for sufficiently large values of U and V compared to the transfer integral t.[11–13]

On the other hand, in Pr1248, the metallic conduction is actually carried by the Cu-O chain unit, which is confirmed by a recent measurement of the anisotropy in the resistivity,[8] consistent with the fact that the CuO_2 plane is undoped. Since the values of the transfer integrals and the Coulomb energies should be similar to the Cu-O single chain in Pr1237, one expects the similar CO insulating state also in Pr1248. As a matter of fact, Fujiyama *et al.*[14] have observed a large enhancement in the NQR relaxation rates T_1^{-1} and T_2^{-1}, suggesting that large charge fluctuation is present in this compound. In order to resolve this unexpected metallic behavior, we propose in this article that the geometrical frustration[15] in the Cu-O double chain, as shown in Fig. 1(b), can cause melting of the CO state.

To investigate such a possibility, we consider two models for the Cu ions. Both are contained as limiting cases of the generalized extended Hubbard model where the Hamiltonian is represented as

$$H=t_1\sum_{i,\sigma}(c^{\dagger}_{i\sigma}c_{i+1\sigma}+\text{H.c.})+t_2\sum_{i,\sigma}(c^{\dagger}_{i\sigma}c_{i+2\sigma}+\text{H.c.})$$
$$+U\sum_i n_{i\uparrow}n_{i\downarrow}+V_1\sum_i n_i n_{i+1}+V_2\sum_i n_i n_{i+2}, \quad (1)$$

where σ is a spin index which takes $\uparrow$ and $\downarrow$, $n_{i\sigma}$ and $c^{\dagger}_{i\sigma}$ ($c_{i\sigma}$) denote the number operator and the creation (annihilation) operator for the electron of spin σ at the ith site, respectively, and $n_i=n_{i\uparrow}+n_{i\downarrow}$.

The first model is the 1D 1/4-filled model with not only the on-site Coulomb interaction U and the nearest-neighbor intersite Coulomb interactions V_1, but also the next-nearest-neighbor one V_2, which is the case of $t_2=0$ in Eq. (1). The interactions of this model are shown schematically in Fig. 2(a), which is called model **1** in the following.

This model has been investigated in another context within mean field approximation[16] and by weak coupling renormalization group arguments.[17] Both showed that for the cases of $V_1 \gg V_2$ and $V_1 \ll V_2$, the ''Wigner crystal'' (1010)-type CO state and another type of CO state, respectively, is stabilized. In the latter CO state the charge density on each site along the chain can be schematically represented as (1100), having the period of four sites which corresponds to

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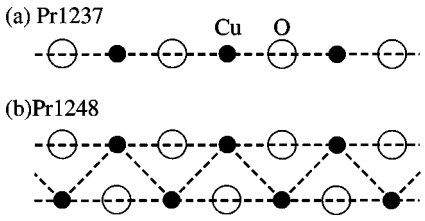

FIG. 1. Structures of (a) the Cu-O single chain in $PrBa_2Cu_3O_7$ and (b) the Cu-O double chain in $PrBa_2Cu_4O_8$. The black and white circles represent Cu and O ions, respectively, and the dotted lines are the Cu network.

$2k_F$. This state is discussed to be relevant to the mixed $2k_F$ spin-density-wave and $2k_F$ charge-density-wave state found in quasi-1D organic conductor $TMTSF_2X$.[18]

The other 1/4-filled model studied here is the two extended Hubbard chains with nearest-neighbor Coulomb interaction V_2, coupled by zigzag intersite Coulomb interaction V_1, i.e., $t_1=0$ in Eq. (1). This model is schematically shown in Fig. 2(b), where one can see that it is equivalent to a ''single chain'' model with next-nearest-neighbor transfer integrals t_2, which is called model **2**. The only difference between the two models is the kinetic energy term. The latter model is rather appropriate for Pr1248, because in the actual compound, as seen in Fig. 1(b), the Cu-O-Cu bond angle for the nearest Cu sites is close to 90° which makes the transfer integral between them negligibly small, while the bond angle for the next-nearest Cu sites is close to 180°, which will provide a larger transfer integral.[19] This is actually the situation of the two-chain model described in Fig. 2(b). On the other hand, the ratio of the values between V_1 and V_2 in the actual compound will be around $V_1/V_2=\sqrt{2}$ if we assume the bare point charge approximation with the $1/r$ dependence for the long range Coulomb interaction.

For these models we estimate the charge gap following the treatment of Mila and Zotos,[11] who investigated proper-

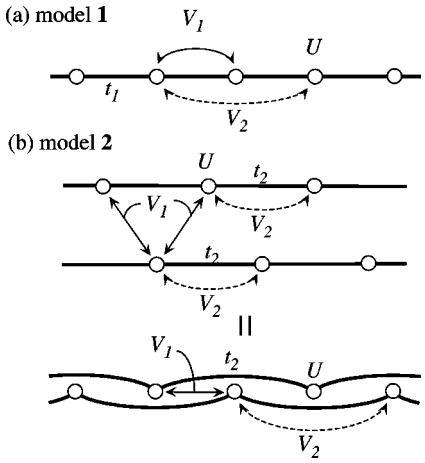

FIG. 2. Models for the Cu sites, (a) model **1** and (b) model **2** where the frustrated intersite Coulomb interactions V_1 and V_2 are shown by solid and dotted arrows, respectively. The Cu sites are represented as circles where the onsite Coulomb interaction U is indicated, whereas the bonds with transfer integrals t_1 or t_2 are connected with thick lines.

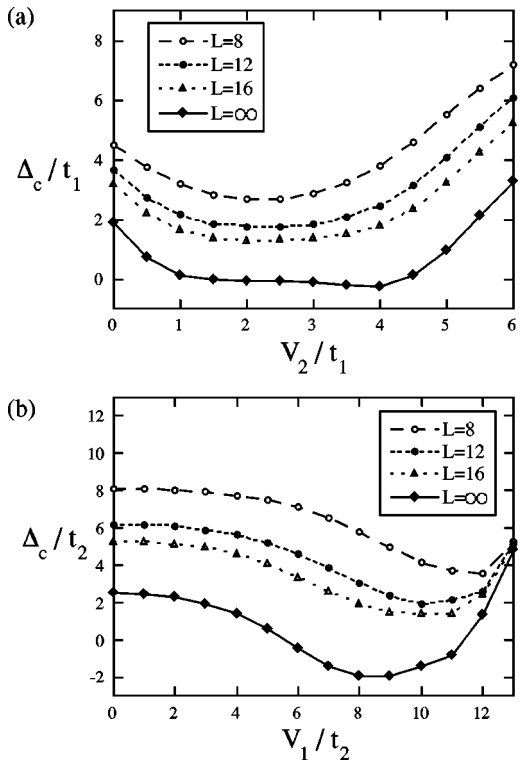

FIG. 3. Charge gap Δ_c for (a) model **1** and (b) model **2**. In (a) the parameters are fixed at $U/t_1=10$ and $V_1/t_1=5$ and the value of V_2/t_1 is varied, while in (b) $U/t_2=20, V_2/t_2=5$ are fixed and the value of V_1/t_2 is varied. Δ_c for clusters with finite sizes of $L=8,12,16$ and the extrapolated value for infinite size system $L=\infty$ are shown, while the extrapolation is based on the $L=8$ and $L=16$ systems (see text).

ties of the simple 1D extended Hubbard model. The gap function for finite systems, $\Delta_c(L;N)=E_0(L;N+1)+E_0(L;N-1)-2E_0(L;N)$, where $E_0(L;N)$ is the ground state energy of N particles on L sites ($N=L/2$ for our case of 1/4-filling), is computed by Lanczos exact diagonalization. Then the charge gap is obtained by extrapolating the values in two system sizes of $L=8$ and $L=16$ by linear fitting. We do not use the $L=12$ data though it is shown in Fig. 3, because we could not obtain meaningful results by extrapolating the quadratic form of $1/L$ by the three $L=8,12,16$ systems, as discussed in Ref. 11. Thus very good accuracy is not expected, though qualitative arguments can be pursued.

The results for model **1** for the case of fixed $U/t_1=10$ and $V_1/t_1=5$ by varying V_2/t_1 is shown in Fig. 3(a), where a possible metallic state is found. For the case of small $V_2/t_1<1$, the charge gap is finite, which should be due to the existence of (1010)-type CO, as in the known case of $V_2=0$ where the system is identical to the simple 1D extended Hubbard model.[11,13] On the other hand, for $V_2/t_1>4.5$, the system also posseses a charge gap, which is due to the another (1100)-type CO state[16,17] as mentioned above. Surprisingly, in contrast to the previous studies, the system seems to show a metallic state with $\Delta_c=0$ in the intermediate region of $1.5<V_2/t_1<4$, i.e., $0.3<V_2/V_1<0.8$, where the degree of frustration is large. The renormalization group calculations by Yoshioka *et al.*[17] rather suggest a bond-

ordered-wave state in the region between (1010) and (1100)-types of CO. However, since their arguments are based on weak coupling scheme, they may not be relevant to strong coupling systems with large Coulomb interactions, such as Pr1248.

The results of calculations on model **2**, as shown in Fig. 3(b), also show a possibility of a metallic state in the region of large degree of frustration. Here, the parameters are set at $U/t_2=20, V_2/t_2=5$ and the value of V_1/t_2 is varied. It can be seen that for $V_1/t_2<5$ and $V_1/t_2>12$ the system shows a finite charge gap, where the CO states of (1010) and (1100) types should be responsible, respectively, as in the case of model **1**. In the intermediate values of V_1/t_2, the extrapolated value provides negative values, which we believe to be due to the small system sizes we have used. Compared to the model **1**, the model **2** can be interpreted rather as a two chain model and the computations are effectively for 4×2 and 8×2 sites. Nevertheless, the charge gap Δ_c decreases as V_1/t_2 is increased from 0 and a metallic state with $\Delta_c=0$ is expected in the region of $7<V_1/t_2<11$, i.e., $0.45<V_2/V_1<0.7$.

In both models **1** and **2**, although the system sizes used here are rather small, we believe that the interesting possibility of the realization of metallic states can be pointed out. However, computations on larger system sizes are needed to be conclusive whether a small gap persists or not.

Next, we consider the limit of large U. In such a limit, 1/4-filled extended Hubbard systems are known to be described by 1/2-filled interacting spinless fermion models. Actually a model of spinless fermions with competing intersite Coulomb interactions has been investigated by Zhuravlev *et al.*[20] who found a metallic state for the case of large degrees of frustration, consistent with the results in the extended Hubbard models discussed above. Furthermore the spinless fermion models are mapped via Jordan-Wigner transformation onto 1D $S=1/2$ XXZ models with competing interactions for our case of $t_1=0$ or $t_2=0$. The mapped Hamiltonian is represented as

$$H=\sum_i \{J_1^{xy}(S_i^xS_{i+1}^x+S_i^yS_{i+1}^y)+J_1^zS_i^zS_{i+1}^z + J_2^{xy}(S_i^xS_{i+2}^x+S_i^xS_{i+2}^x)+J_2^zS_i^zS_{i+2}^z\}, \quad (2)$$

where the antiferromagnetic coupling constants corresponding to the model **1** are $J_1^{xy}=2t_1, J_2^{xy}=0, J_1^z=V_1, J_2^z=V_2$ and those for model **2** are $J_1^{xy}=0, J_2^{xy}=2t_2, J_1^z=V_1, J_2^z=V_2$. Note that the spin model described in Eq. (2) is known to have a dimerized spin-gapped ground state for some region of parameters.[21] However the absence of competition in the xy component in our case, i.e., $J_2^{xy}=0$ or $J_1^{xy}=0$ in models **1** and **2**, respectively, is believed to exclude such possibility. Then the two CO states of (1010) and (1100) types and the metallic state in the electron systems discussed above correspond to the Ising Néel state of $(\uparrow\downarrow\uparrow\downarrow)$ and $(\uparrow\uparrow\downarrow\downarrow)$-types and the XY spin-liquid state with no gap, respectively. The frustration in the z-components can give rise to such a spin-liquid ground state, as we confirm by calculations on the model corresponding to model **1** (Ref. 22) in the following.

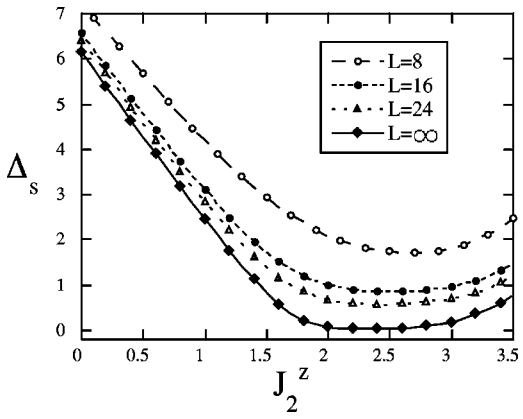

FIG. 4. Ising gap Δ_s for model **1** where the parameters are fixed at $J_1^{xy}=1, J_2^{xy}=0$, and $J_1^z=5$ and the value of J_2^z is varied. The values for $L=8,16,24$ are shown and the extrapolation to infinite size system $L=\infty$ is done by quadratic form of $1/L$.

We calculate the Ising gap $\Delta_s(L)=E_0(S_z=1;L)-E_0(S_z=0;L)$, where $E_0(S_z=M;N)$ is the ground state energy within the restriction of total spin M on L sites by using Lanczos exact diagonalization. The results in clusters of $L=8,16$ and 24, are plotted as a function of J_2^z for fixed values of $J_1^{xy}=1, J_2^{xy}=0$ and $J_1^z=5$ in Fig. 4. The extrapolation to infinite system size is done by the quadratic form of $1/L$, so the results are expected to be more accurate than the ones for the extended Hubbard systems above using linear extrapolations for only two clusters. From Fig. 4 we can see that the ungapped ground state is in fact realized for $2<J_2^z<2.7$, i.e., $0.4<J_2^z/J_1^z<0.55$, which can be specified to be the spin liquid state in our case of antiferromagnetic couplings. This result again supports the existence of the frustration induced metallic state in the large U limit.

Finally let us discuss the relevance of the metallic state proposed here to the actual Cu-O double chain in Pr1248. The value of the transfer integrals in the Cu-O double chain is estimated to be $t_1\simeq0$, as discussed above, and $t_2\simeq0.85$ eV, as has been estimated for the Cu-O chain in $R\mathrm{Ba_2Cu_3O_{6+x}}$ (R=Y or rare earth).[23] This estimation also gives $J\simeq0.2$ eV in the t-J model, corresponding to $U\simeq15$ eV by the relation $J\simeq4t_2^2/U$. These values provide a rough estimate of $U/t_2\simeq17$, thus we can naturally expect V_1/t_2 and V_2/t_2 to be at least few times larger than 1, where our results above for the extended Hubbard systems does not change qualitatively.

As is pointed out by Takenaka *et al.*[24] from optical measurements and by Mizokawa *et al.*,[5] a slight deviation of the filling from 1/4 can be the origin of the metallic conduction in the Cu-O double chain unit. Nevertheless, Pr1248 is the only compound possessing a Cu-O subsystem responsible for a metallic ground state, avoiding instabilities such as CO transition or Anderson localization, despite numerous efforts of synthesizing such metal. So one should rather conclude that the frustration in the intersite Coulomb interaction is playing an important role to stabilize this metallic state, e.g., the combinatory effect of the frustration making the charge gap small, as shown in our calculations, and the deviation from 1/4-filling.

The NQR data by Fujiyama *et al.* are apparently inconsistent from the metallic behavior in the resistivity, since they suggest some glasslike slowing down of the charge motion below around 50 K.[14] We speculate what NQR is detecting is the local ''freezing'' of the charges induced by disorder such as defects or impurities. Such kind of local freezing is naturally expected since our highly correlated metallic state is near the CO phase, while it will not disturb the conduction path existing as a whole. This picture is similar to the argument of Kohno *et al.*[25] on the disorder induced spin-glass-like state coexisting with the superconducting order parameter, in the vicinity of the first-order boundary between magnetic state and superconducting state. However, in our case the CO and metallic states seem to provide a phase boundary of second-order, so their discussion cannot be adopted here as it is.

In conclusion, the possibility of a new metallic state close to the instability toward charge ordering in the Cu-O double chain unit of $PrBa_2Cu_4O_8$ is investigated. It is argued that the geometrical frustration in the intersite Coulomb interaction makes the charge ordered states unstable, and melting of this charge ordering leads to a metallic state. Extension of such idea to other frustrated systems is interesting, while there is actually a study on the two-dimensional square lattice with competing nearest-neighbor and next-nearest-neighbor interactions in a quite different context.[26]

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