RAPID COMMUNICATIONS

PHYSICAL REVIEW B **82**, 241104(R) (2010)

Quantum electric dipoles in spin-liquid dimer Mott insulator κ-ET$_2$Cu$_2$(CN)$_3$

Chisa Hotta
Department of Physics, Faculty of Science, Kyoto Sangyo University, Kyoto 603-8555, Japan

(Received 29 November 2009; revised manuscript received 28 October 2010; published 22 December 2010)

We present an effective dipolar-spin model based on the strong coupling analysis, which may explain the possible origin of "spin-liquid insulator." The issue is related to a dimer Mott insulator reminiscent of an organic triangular lattice system, κ-ET$_2$Cu$_2$(CN)$_3$, whose gapless spin-liquid state has been discussed in the context of geometrical frustration of exchange coupling, J, between spins on dimer orbitals. It turns out that another degrees of freedom within the insulator, *quantum electric dipoles* on dimers, interact with each other and modify J significantly through the dipolar-spin coupling, resulting in a possible "dipolar-spin liquid."

DOI: 10.1103/PhysRevB.82.241104 PACS number(s): 72.80.Le, 75.40.−s, 72.80.Ng, 75.50.Mm

A well known terminology "spin liquid" continues to attract attention ever since the Anderson's resonating valence-bond picture was presented.[1] This state of matter is recently discussed in organic solid, κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ (BEDT-TTF abbreviated as ET), in the context of absence of magnetic orders and of the possibility of gapless excitations.[2–5] The solid has a triangular lattice structure at half-filling in unit of dimerized molecules and is driven toward a Mott insulating state by the strong on-dimer Coulomb interaction.[6] The origin of its spin-liquid state is then ascribed to the frustration effect from the nearly regular triangular geometry of the spin-exchange coupling, $J'_{\rm eff}/J_{\rm eff}\sim 1$, which is estimated from the corresponding effective transfer integrals between dimer orbitals, $t'_{\rm eff}/t_{\rm eff}\sim 1.05$.[7] Theoretical works are developed successively within the half-filled single band Hubbard model (SBH) on the triangular lattice;[8–12] an exotic nonmagnetic (gapless) insulator is found in the anisotropy range of $t'_{\rm eff}/t_{\rm eff}\sim 0.7-1$.[8] Some interpretations are given by many-body spin exchanges beyond the Heisenberg model and the spinon Fermi surface[13,14] or by vision excitation.[15]

Recently, however, κ-ET$_2$Cu$_2$(CN)$_3$ is reported to have anomaly at $T\sim 6$ K in lattice expansion coefficient[16] as well as in dielectric constant which shows a relaxor ferroelectric-like behavior above this temperature.[17] They suggest that the electronic degrees of freedom is still active in the insulating state. Coincidentally, model parameters are replaced from the above-mentioned ones[7] by the *ab initio* calculation to $t'_{\rm eff}/t_{\rm eff}\sim 0.8$,[18,19] $V/U_{\rm dimer}\sim 0.4$ with $U_{\rm dimer}/t\sim 15$,[18] where V and $U_{\rm dimer}$ are the interdimer and on-dimer Coulomb interactions, respectively. Therefore the geometrical frustration effect is not strong. Instead, the intersite Coulomb interaction, V, is large which shall play certain role in the low-energy physics of this intriguing state. Since the system is quarter filled in unit of molecule, there is an instability toward charge order by V, which may compete with the Mott insulator.[20] In this Rapid Communication, we explicitly include V which had not been considered in the previous studies of κ-ET$_2$Cu$_2$(CN)$_3$ and demonstrate another scenario for the suppression of magnetic orders. We describe charge degrees of freedom in the insulating state as "quantum electric-dipoles" which fluctuate within the dimer. Dipoles couple to spins through the interdimer fluctuation of charges. The suppression of dipolar fluctuation by V leads to the significant degrease of J'/J and of magnetic correlations.

We go back to the basic model of organic solids in unit of molecule,[20] a quarter-filled two-band extended Hubbard model, whose Hamiltonian is given as

$$\mathcal{H}=\sum_{\langle i,j\rangle}\left[\sum_{\sigma=\uparrow\downarrow} t_{ij}(c^\dagger_{i\sigma}c_{j\sigma}+\text{H.c.})+V_{ij}n_in_j\right]+\sum_i Un_{i\uparrow}n_{i\downarrow}. \tag{1}$$

Here, $c^\dagger_{j\sigma}/c_{j\sigma}$ are creation/annihilation operators of electrons with spin $\sigma(=\uparrow,\downarrow)$ and $n_{j\sigma}=c^\dagger_{j\sigma}c_{j\sigma}$ and $n_j=n_{i\uparrow}+n_{i\downarrow}$ are number operators. The model includes on-site (U) and nearest-neighbor (V_{ij}) interactions. We consider strong dimerization effect, namely, each pair of sites connected by strong interactions, $(t_{ij},V_{ij})=(t_d,V_d)$, called "dimers" has one electron (i.e., half-filled in unit of dimer) on an average.

The half-filled SBH in Refs. 8–12 is a limiting case of quarter-filled Eq. (1), $t_d\gg t_{ij}$ and $V_{ij}=0$; In Eq. (1) each dimer has sixteen bases which is reduced to four bases in SBH by the "dimer approximation." This four bases could account for charge fluctuation between dimers and describe both metal and dimer Mott insulator. Whereas, details of the two dimerized sites are neglected, e.g., a doubly occupied basis of SBH, $(\uparrow\downarrow)$, represents only one bonding state among six doubly occupied states of Eq. (1), $(\uparrow\downarrow,0),(0,\uparrow\downarrow),(\uparrow,\downarrow),(\downarrow,\uparrow),(\uparrow,\uparrow),(\downarrow,\downarrow)$, where $\sigma/0$ denote the presence/absence of spin-σ electrons on (site-1,site-2). The *intradimer charge disproportionation/fluctuation is not considered*, which is no longer legitimated when V_{ij} is large ($\gtrsim t_d$).[18]

Instead, we take the strong coupling limit (insulator) of Eq. (1) as $t_{ij}/U, t_{ij}/V_d, V_{ij}/U, V_{ij}/V_d\to 0$. This approximation projects out bases having double occupancy on dimers with energy of order U or V_d, and describes *both dimer Mott and charge ordered insulators*. The remaining bases keep exactly one fermion per dimer as, (site-1,site-2) $=(\uparrow,0),(0,\uparrow),(\downarrow,0)$, and $(0,\downarrow)$. We introduce electric-dipolar and spin operators, $\hat{P}$ and $\hat{S}$. Then, the above four states are described in the $2\otimes 2$ spinor representation as, $(P^z,S^z)=(\frac12,\frac12),(-\frac12,\frac12),(\frac12,-\frac12)$, and $(-\frac12,-\frac12)$. The quantization z axis of dipoles is fixed to the dimer-bond direction in real space. In the following, we derive the effective Hamiltonian by treating t_{ij} and $V_{ij}(\neq V_d)$ perturbatively, by which *the charge fluctuation between dimers* is taken into account.

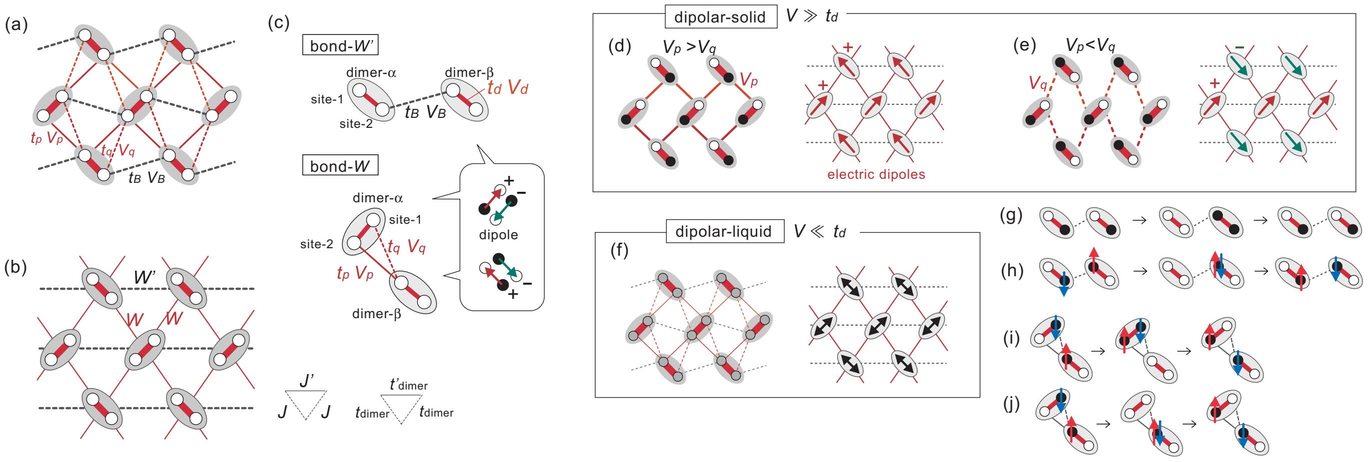

FIG. 1. (Color online) (a) κ-type lattice structure adopted to Eq. (1) in unit of molecule (circle) and bold line represents dimer bonds, (t_d,V_d). (b) Anisotropic triangular lattice in unit of dimer, transformed from panel (a). (c) Two different types of connections between dimers in panel (a). Polarized (d) and (e), and unpolarized (f) configurations of quantum dipoles. Charges avoid neighboring alignment along the bond with strong V_{ij} as shown explicitly in the fermionic representation (left panels). Panels (g)–(j) are the representative second-order perturbation processes, which generate effective interactions in Eq. (3), where filled circles and arrows represent the electrons and spins, respectively.

For the realization of Eq. (1) in the bulk system, we choose a model lattice of κ-type organic solids[21] shown in Fig. 1(a); the interdimer interactions are $(t_{ij},V_{ij}) = (t_p,V_p),(t_q,V_q),(t_B,V_B)$ along three different bonds. If we take dimer as a unit, this lattice is mapped to an anisotropic triangular lattice in Fig. 1(b), whose horizontal (W') and diagonal (W) interdimer bonds originate from (t_B,V_B) and $(t_p,V_p),(t_q,V_q)$ in Fig. 1(a), respectively. The effective Hamiltonian, $\mathcal{H}_{\rm eff}=\mathcal{H}^{(1)}+\mathcal{H}^{(2)}+\mathcal{H}^{(3)}+\mathcal{H}^{(4)}$, is generated in unit of dimer in Fig. 1(b). The first-order Hamiltonian is

$$\mathcal{H}^{(1)} = \sum_{l\in \text{bond } W,W'} W_0^l P_\alpha^z P_\beta^z + \sum_\gamma t_d (P_\gamma^+ + P_\gamma^-), \qquad (2)$$

where $W_0'=V_B$ and $W_0=V_q-V_p$. Equation (2) is nothing but a transverse Ising model of dipoles, where a competition of correlation and local quantum fluctuation of dipoles is imbedded, namely, the Ising interaction term $W_0^l(\sim V_{ij})$ versus the transverse field t_d. Representative dipolar states are shown in Figs. 1(d)–1(f); when $t_d \ll V_{ij}$, there are two different spatial orders depending on the geometry of V_{ij}. At $t_d \gg V_{ij}$, dipoles fluctuate and stay spatially uniform. The former "dipolar-solid" corresponds to charge order and the latter "dipolar-liquid" to dimer Mott insulator. At this order, the spin degrees of freedom are fully degenerate.

Degeneracy of spins is lifted at the second order level. The second-order terms for two bonds ($W^l=W'$ and W) which connect dimer α and β yields[22]

$$\begin{aligned}\mathcal{H}_l^{(2)} = &-W_{\rm pp}^l P_\alpha^z P_\beta^z + \hat{W}_{\rm p}^l (P_\alpha^+ + P_\alpha^-) + \hat{W}_{\rm ss}^l \mathbf{S}_\alpha \cdot \mathbf{S}_\beta \\ &- W_{\rm pss}^l (P_\alpha^z P_\beta^z)(\mathbf{S}_\alpha \cdot \mathbf{S}_\beta) + \hat{W}_{\rm pss}^l (P_\alpha^+ + P_\alpha^-)(\mathbf{S}_\alpha \cdot \mathbf{S}_\beta).\end{aligned} \qquad (3)$$

Let us first focus on bond W'. The first $(P_\alpha^z P_\beta^z)$ term originates from the process in Fig. 1(g). Noteworthy is the emergence of a dipolar-spin coupling term, $(P_\alpha^z P_\beta^z)(\mathbf{S}_\alpha \cdot \mathbf{S}_\beta)$, which together with $\hat{W}'_{\rm ss}$-term originate from the process in Fig. 1(h); exchange of spins occurs only when fermions occupy nearest neighbor sites, i.e., when dipoles are antiferroelectric $(P_\alpha^z, P_\beta^z) = (-\frac{1}{2},\frac{1}{2})$. This four-body term reminds of the Kugel-Khomskii Hamiltonian discussed in manganites[23,24] in the context of orbital-spin coupling.

The diagonal bond W consists of two interactions (p,q), each generating terms in the same manner as bond W'. In addition, there are processes shown in Figs. 1(i) and 1(j); Dimers exchange their fermions through two connections p and q by ending up flipping P_α^z, namely, fermion in dimer α changes its site location. This generates the two terms with $(P_\alpha^+ + P_\alpha^-)$ in Eq. (3) only for bond W, i.e., $W_{\rm p}'=W_{\rm pss}'=0$.

Spins follow dipoles through these second-order dipolar-spin coupling terms in Eq. (3). Effective interactions between spins on neighboring dimers (α,β) are evaluated from the expectation values of coefficient of $\mathbf{S}_\alpha \cdot \mathbf{S}_\beta$ of Eq. (3) as

$$J' = \langle \hat{W}'_{\rm ss} \rangle - W'_{\rm pss} \langle P_\alpha^z P_\beta^z \rangle,$$

$$J = \langle \hat{W}_{\rm ss} \rangle - W_{\rm pss} \langle P_\alpha^z P_\beta^z \rangle + \langle \hat{W}_{\rm pss} (P_\alpha^+ + P_\alpha^-) \rangle. \qquad (4)$$

In order to examine the actual competition between t_d and V_{ij}, we perform the exact diagonalization on $\mathcal{H}_{\rm eff}$ in finite dimer clusters.[25] We adopt $(t_p,t_q)=(0.7,-0.25)$ in unit of $t_B=1$, which describes κ-ET$_2$Cu$_2$(NCS)$_3$,[7] and take $(U,V_d)=(15,10)$. These values are interpreted to coefficients W^l and $\hat{W}^l$ of $\mathcal{H}_{\rm eff}$. For the choice of V_{ij}, we take $V_q>0$ and $V_p=V_B=0$, concentrating on the type of dipolar solid given in Fig. 1(e), which is sufficient to clarify the essential physics of the competition of V_{ij} and t_d.

We first elucidate the phase diagram on the plane of t_d and V_q as shown in Fig. 2(a). As anticipated, the dipolar-solid [Fig. 1(e)] and liquid [Fig. 1(f)] appears at large V_q and t_d, respectively. The solid-liquid phase boundary is determined as a minimum of charge gap of the $U=\infty$ limit of Eq. (1).

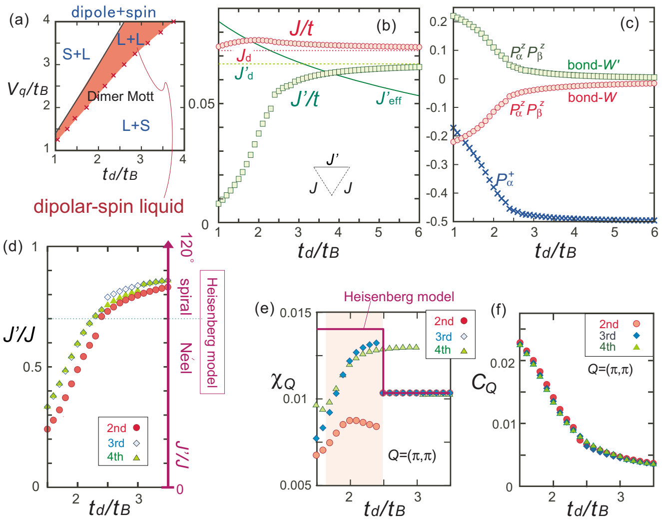

FIG. 2. (Color online) Results of diagonalization with $(t_B,t_p,t_q)=(1,0.7,-0.25)$ and $(U,V_d,V_p,V_B)=(15,10,0,0)$. (a) t_d-V_q diagram with solid and liquid phases, e.g., S+L denotes the phase with Solid dipoles ($U=\infty$) and Liquid spins (at second order). Along its $V_q=3$ line, (b) J and J', and (c) $\langle P^z_\alpha P^z_\beta\rangle$ and $\langle P^+_\alpha\rangle$ are shown. Broken lines, J_d and J'_d, are the $t_d\to\infty$ limit of J and J' from Eq. (4) with $\langle P^z_\alpha P^z_\beta\rangle=0$ and $\langle P^\pm_\alpha\rangle=-0.5$. Solid line, $J'_{\rm eff}$, gives the conventional dimer approximation. Panels (d)–(f) show the comparison up to second-, third-, and fourth-order perturbations; (d) J'/J, structural factors of (e) spins χ_Q, and (f) charges C_Q with $Q=(\pi,\pi)$. Solid line in panel (e) is χ_Q of the Heisenberg model of corresponding J'/J in (d) on the same cluster.

Next, we vary t_d along the fixed line of $V_q=3$ in the phase diagram at the second order level, $\mathcal{H}_{\rm eff}=\mathcal{H}^{(1)}+\mathcal{H}^{(2)}$. Figure 2(b) shows that J' is suppressed in the dipolar solid at small t_d, and increases significantly by t_d. This can be explained by the remarkable t_d dependence of $\langle P^z_\alpha P^z_\beta\rangle$ shown in Fig. 2(c); In Eq. (4), the second term of J' with the constant coefficient, $W'_{\rm ppss}=\frac{4t_B^2}{U-V}>0$, has large negative contribution to J' by $\langle P^z_\alpha P^z_\beta\rangle\simeq 0.25$ at $t_d\sim 1$, which goes to zero as $\langle P^z_\alpha P^z_\beta\rangle\to 0$ at $t_d\to\infty$. Similar discussion holds for J; the second/third terms of Eq. (4) are increasing/decreasing functions of t_d, since $W_{\rm ppss}=\frac{4t_q^2}{U-V_q}-\frac{4t_p^2}{U-V_p}<0$, $\langle P^z_\alpha P^z_\beta\rangle\simeq-0.25\to 0$, and $\hat{W}_{\rm pss}=(\frac{t_pt_q}{U-V_q}+\frac{t_pt_q}{U-V_p}+\frac{t_pt_q}{V_d-V_q}+\frac{t_pt_q}{V_d-V_p})(P^z_\beta+\frac{1}{2})>0$, $\langle P^\pm_\alpha\rangle\simeq-0.2\to-0.5$. The two cancel out, keeping J almost unchanged by t_d.

One important point is the unexpected decrease of J' due to V_{ij}. In general, V_{ij} works to screen U and to enhance J.[26] This effect actually appears in the increase in denominator of $W_{\rm ppss}\propto(U-V_{ij})^{-1}$ by V_{ij}. However, in our case V_{ij} works directly on dipoles at the first-order level and varies $\langle P^z_\alpha P^z_\beta\rangle$ more significantly than their coefficients, suppressing J'. By contrast, $J'_{\rm eff}=4t'^2_{\rm eff}/U_{\rm dimer}$ obtained by the conventional dimer approximation based on SBH shows a "screening effect" as shown in Fig. 2(b), where $t'_{\rm eff}=\frac{t_B}{2}$, and $U_{\rm dimer}=2t_d+\frac{U+V_d}{2}-\frac{U-V_d}{2}[1+(\frac{4t_d}{U-V_d})^2]^{1/2}$.

Another interesting aspect is the strong correlation between J and J'. In the dipolar-solid state, the dipolar vectors are bound to particular spatial directions, which contribute to both J and J' through $\langle P^z_\alpha P^z_\beta\rangle\sim\pm 0.25$. The antiparallel dipoles along bond W' always suppresses J', whereas along bond W, the antiparallel dipoles in Fig. 1(d) suppress J but parallel ones in Fig. 1(e) do not. *In both cases*, however, we confirmed that J'/J is suppressed at small t_d [see Fig. 2(d)].

In this way, at small t_d, J'/J becomes small, namely, *the geometry of spin interactions approaches a square lattice*. For reference, we consider the bulk ground state of the Heisenberg model;[15,27–30] at $J'/J\lesssim 0.7$ the antiferromagnetic order sets in, which is reflected in the spin structural factor, χ_Q, as a single peak at $\boldsymbol{Q}=(\pi,\pi)$. Figure 2(e) shows the peak amplitude of χ_Q of our model versus the Heisenberg model calculated on the same finite cluster. The phase transition of the spin sector takes place at $J'/J\sim 0.7$, i.e., at $(t_d/t_B)_c\simeq 2.4$, which gives the phase boundary in Fig. 2(a). At $t_d/t_B>(t_d/t_B)_c$ well inside the dipolar-liquid phase, the present model has the same χ_Q as the Heisenberg one. By contrast, χ_Q is significantly suppressed from that of the Heisenberg one at $t_d/t_B\lesssim(t_d/t_B)_c$. This indicates that *in approaching the dipolar-solid phase, the dimer spin degrees of freedom is no longer mapped onto the Heisenberg model even at the second-order level*. In such case, the multiple spin exchanges which emerge as higher order perturbation terms may become important. Therefore, we calculate all the perturbation processes up to fourth order $\mathcal{H}_{\rm eff}=\mathcal{H}^{(1)}+\mathcal{H}^{(2)}+\mathcal{H}^{(3)}+\mathcal{H}^{(4)}$ (up to eight-body interactions and including the four-dimer ring exchanges[31] which maximally amount to $J_4/t\sim 0.0027$). The numerical results up to third and fourth orders are compared with the second order ones in Figs. 2(d)–2(f); J'/J as well as the structural factor of dipoles [C_Q in Fig. 2(f)] are almost unchanged. The spin structural factor χ_Q is rather sensitive to the orders of perturbation, however, in the vicinity of the dipolar-solid/liquid phase boundary, $t_d=1.7$–2.4, there remains a strong suppression of magnetic correlation χ_Q at all orders [for all $\boldsymbol{Q}\neq(\pi,\pi)$]. The corresponding region is described as "dipolar-spin liquid" phase in Fig. 2(a). It apparently not originates from spin degrees of freedom alone. We consider that the liquid dipoles develop their short-range correlation, which rumple the distribution of charges, resulting in a spatially nonuniform value of J's within the certain imaginary time scale, leading to the possible spin liquid state. Thus, in the dimer system, the four-body dipolar-spin interactions in Eq. (3) play comparably important role as a well-known higher order ring exchange terms[31] in liquidizing the spin sector.

To summarize, we derived an effective dipolar-spin model relevant in the insulating phases of the quarter-filled extended Hubbard model with lattice dimerization. The intradimer charge degrees of freedom is described as quantum electric dipoles fluctuating by t_d (the interdimer transfer integral). At large t_d the conventional dimer Mott insulator, namely, a dipolar liquid, is stable. The interdimer Coulomb interaction, V, competes with t_d and at large V/t_d a dipolar-solid (charge order) emerge. The spins couple to the dipoles through the interdimer charge fluctuation, and in approaching the dipolar solid from a liquid phase, strong modification of spin-spin interactions, J and J', as well as significant suppression of the antiferromagnetic correlation is observed, indicating the existence of a dipolar-spin liquid.

We anticipate that the so-called spin-liquid Mott insulator κ-ET$_2$Cu$_2$(NCS)$_3$ lies in our dipolar-spin liquid phase at low temperature, where both spins and charges remain short range ordered. The final comment is given on the comparison of parameters with experiments and other theories. κ-ET$_2$Cu$_2$(NCS)$_3$ undergoes a metal-insulator transition at $\sim$0.4 GPa.[2] The *ab initio* calculation shows that t_{ij} varies by 1.3 times from ambient pressure to 0.75GPa,[19] which brings $U_{\text{dimer}}/t_{\text{eff}}$ from 15 to 11.[18,32] These values are about twice as large as the conventional empirical estimate of $U_{\text{dimer}}/t_{\text{eff}} \sim 7-8$.[2] In such case, our perturbative treatment up to fourth order can be qualitatively adopted, at least at ambient pressure. Starting from the same t_{ij} (Ref. 7) the conventional dimer approximation on a SBH reaches the effective Heisenberg coupling, $J'_{\text{eff}}/J_{\text{eff}} \sim 1$, whereas our dipolar-spin-liquid always has $J'/J \sim 0.6-0.7$. Interestingly, our J'/J coincides with a result of the *ab initio* calculations as, $\sqrt{J'/J} \sim t'_{\text{eff}}/t_{\text{eff}} \sim 0.8$.[18,19] Thus, we interpret the *ab initio* results as a renormalized effective value of J's after including V. Regarding the interpretation of 6 K anomaly, we expect the following scenario; at high temperature (T), the thermal fluctuation of dipoles is dominant (dipolar liquid is stable). At $T \sim 0$, the dipoles remain short range ordered as well due to the quantum fluctuation (t_d), and so as the spins which follow dipoles. In lowering T, the dipolar(electronic) correlation once grows but the system still remains a dipolar liquid toward $T=0$. $T=6$ K is possibly a maximally correlated point, i.e., maximum of V against dipolar fluctuation (t_d, T), where J'/J is suppressed at most. In fact, a relaxor ferroelectriclike behavior of dielectric constant indicates a pseudotransition at $T_c = 6$ K.[17] The lattice anisotropy also takes a local maximum here, which implies that J'/J also pass through an extreme value. To confirm this scenario, further development in both theories and experiments are required. Thus, so far, one cannot exclude the possibility that the "gapless spin liquid" may not be the result of the geometrical frustration but of a strong correlation between spins and charges (dipoles).

Note added in proof: We recently became aware of a complementary study (Ref. 33) concentrating on the dielectric properties.

We thank T. Sasaki, I. Terasaki, and M. Imada for discussions. This work is supported by Grant-in-Aid for Scientific Research under Grants No. 21110522, No. 19740218, and No. 22014014 from the Ministry of Education, Science, Sports and Culture of Japan.

---

[1] P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).

[2] Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, Phys. Rev. Lett. **91**, 107001 (2003).

[3] S. Yamashita, Y. Nakazawa, M. Oguni, Y. Oshima, H. Nojiri, Y. Shimizu, K. Miyagawa, and K. Kanoda, Nat. Phys. **4**, 459 (2008).

[4] M. Yamashita, N. Nakata, Y. Kasahara, T. Sasaki, N. Yoneyama, N. Kobayashi, S. Fujimoto, T. Shibauchi, and Y. Matsuda, Nat. Phys. **5**, 44 (2009).

[5] A. P. Ramirez, Nat. Phys. **4**, 442 (2008).

[6] K. Kanoda, Physica C **282-287**, 299 (1997).

[7] T. Komatsu, N. Matsukawa, T. Inoue, and G. Saito, J. Phys. Soc. Jpn. **65**, 1340 (1996).

[8] H. Morita, S. Watanabe, and M. Imada, J. Phys. Soc. Jpn. **71**, 2109 (2002).

[9] T. Koretsune, Y. Motome, and A. Furusaki, J. Phys. Soc. Jpn. **76**, 074719 (2007).

[10] T. Yoshioka, A. Koga, and N. Kawakami, Phys. Rev. Lett. **103**, 036401 (2009).

[11] B. Kyung and A.-M. S. Tremblay, Phys. Rev. Lett. **97**, 046402 (2006).

[12] R. T. Clay, H. Li, and S. Mazumdar, Phys. Rev. Lett. **101**, 166403 (2008).

[13] O. I. Motrunich, Phys. Rev. B **72**, 045105 (2005).

[14] S.-S. Lee, P. A. Lee, and T. Senthil, Phys. Rev. Lett. **98**, 067006 (2007).

[15] Y. Qi, C. Xu, and S. Sachdev, Phys. Rev. Lett. **102**, 176401 (2009).

[16] R. S. Manna, M. de Souza, A. Bruhl, J. A. Schlueter, and M. Lang, Phys. Rev. Lett. **104**, 016403 (2010).

[17] M. Abdel-Jawad, I. Terasaki, T. Sasaki, N. Yoneyama, N. Kobayashi, Y. Uesu, and C. Hotta, Phys. Rev. B **82**, 125119 (2010).

[18] K. Nakamura, Y. Yoshimoto, T. Kosugi, R. Arita, and M. Imada, J. Phys. Soc. Jpn. **78**, 083710 (2009).

[19] H. C. Kandpal, I. Opahle, Y.-Z. Zhang, H. O. Jeschke, and R. Valentí, Phys. Rev. Lett. **103**, 067004 (2009).

[20] H. Seo, C. Hotta, and H. Fukuyama, Chem. Rev. **104**, 5005 (2004).

[21] H. Kino and H. Fukuyama, J. Phys. Soc. Jpn. **65**, 2158 (1996).

[22] Coefficients W and $\hat{W}$ are of order t_{ij}^2/M $(M=U, V_d, U-V_{ij})$ and $\hat{W}$ include P_j^z term. The denominator includes V_{ij} from surrounding dimers while the modification is small at $U, V_d \gg V_{ij}$ and we neglect them for simplicity.

[23] K. I. Kugel and D. I. Khomskii, Sov. Phys. JETP **37**, 725 (1973); Sov. Phys. Usp. **25**, 231 (1982).

[24] L. F. Feiner, A. M. Oleś, and J. Zaanen, Phys. Rev. Lett. **78**, 2799 (1997).

[25] Size dependence of J and J' is less than 2% among $2\times4, 3\times4, 4\times3$ clusters in Fig. 1(b). We adopt 3×4 for Fig. 2.

[26] J. van den Brink, M. B. J. Meinders, J. Lorenzana, R. Eder, and G. A. Sawatzky, Phys. Rev. Lett. **75**, 4658 (1995).

[27] Zheng Weihong, R. H. McKenzie, and R. P. Singh, Phys. Rev. B **59**, 14367 (1999).

[28] A. E. Trumper, Phys. Rev. B **60**, 2987 (1999).

[29] B. Bernu, C. Lhuillier, and L. Pierre, Phys. Rev. Lett. **69**, 2590 (1992).

[30] L. Capriotti, A. E. Trumper, and S. Sorella, Phys. Rev. Lett. **82**, 3899 (1999).

[31] G. Misguich, B. Bernu, C. Lhuillier, and C. Waldtmann, Phys. Rev. Lett. **81**, 1098 (1998).

[32] Organic crystals have soft lattices and modify their t_{ij} by a factor of 1.3–1.5 or more by the pressure of 0.5–1GPa. For experiments, see M. Watanabe, Y. Nogami, K. Oshima, H. Mori, and S. Tanaka, J. Phys. Soc. Jpn. **68**, 2654 (1999).

[33] M. Naka, and S. Ishihara, J. Phys. Soc. Jpn. **79**, 063707 (2010).