Purely electronic THz polarization in dimer Mott insulators

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We theoretically discover purely electronic polarization modes in THz frequency region in dimer Mott insulators $\kappa$-(BEDT-TTF)$_2$X. The unusual low-frequency modes arise from the coupling between the oscillation of intradimer electric dipole moments and that of alternating interdimer bond orders. These collective motions play an important role in the dynamical dielectric properties of the dimer Mott insulators. Near the phase boundary of the dimer Mott transition, the ferroelectric ground state is realized by introducing electron-lattice coupling.

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Low-dimensional strongly correlated electron systems with a quarter-filled band have recently attracted much attention. BEDT-TTF salts are typical two-dimensional systems with anisotropic triangular lattices, and the strong correlation and frustration act cooperatively to generate exotic phases. Among the BEDT-TTF salts, $\kappa$-(BEDT-TTF)$_2$X (X: a counter anion) exhibit the Mott insulator phase \cite{1,2},\textsuperscript{2} exoect superconducting phase \cite{3}, spin liquid phase \cite{4,5}, and so on. The BEDT-TTF molecular lattice is distorted to form dimers in $\kappa$-(BEDT-TTF)$_2$X. Hybridized two sites can be effectively treated as a single site, and the valence bond is regarded as a half-filled one. As a result, $\kappa$-(BEDT-TTF)$_2$X exhibits the Mott insulator phase if the effective on-site Coulomb energy is large enough. The state is called the dimer Mott insulator.

Recently quite interesting charge excitation phenomena have been observed in the dimer Mott insulators: photoinduced phase transition to a metallic state \cite{10}, and anomaly in dielectric properties \cite{11}. In particular, the latter suggests that low-energy charge excitation exists in the dimer Mott insulators in contrast to the case of the Mott insulators.

In this letter, we show for the first time that the dimer Mott insulator has THz electric polarization, which purely arises from the electron dynamics. The ferroelectricity which arises from the electron dynamics has been observed in some materials, and these ferroelectrics have unconventional origins such as charge order generation \cite{12,13}. We propose another new origin of ferroelectricity in this paper.

We adopt the 1/4-filled extended Hubbard Hamiltonian for holes on the two-dimensional anisotropic triangular lattice, which includes the degrees of freedom in a dimer. It is given by

$$H = \sum_{<n,m>} (\beta_{n,m} \hat{p}_{n,m} + V_{n,m} n_n n_m) + U \sum_n n_n \gamma n_{\gamma \downarrow}$$ \hspace{1cm} (1)

where $<n,m>$ denotes the neighbor site pairs, $c_{n,\sigma}$ ($c_{n,\sigma}^\dagger$) is the annihilation (creation) operator for a hole of spin $\sigma$ at the site $n$, $\beta_{n,m}$ ($V_{n,m}$) is the transfer integral (the Coulomb interaction energy) between the sites $n$ and $m$, $\hat{p}_{n,m} = \sum_{\sigma} (c_{n,\sigma}^\dagger c_{n,\sigma} + c_{n,\sigma} c_{n,\sigma}^\dagger)$, $U$ is the on-site Coulomb interaction energy, $n_{n,\sigma} = c_{n,\sigma}^\dagger c_{n,\sigma}$, and $n_n = \sum_{\sigma} n_{n,\sigma}$. The 4 × 4 cluster of the system size $N = 16$ with the periodic boundary condition is used.

We calculate the quantum state excited by light pulse expressed by the vector potential $A(t) = eA \exp(-(t/D)^2) \cos(\omega_0 t)$ of a Gaussian profile. We consider the one-photon excited states in this paper. To the first order in $A$, the solution $|\psi(t)\rangle$ of the Schrödinger equation subject to the pulse is given by $|\psi(t)\rangle = |\psi_0\rangle + |\psi^{(1)}(t)\rangle$. The ground state $|\psi_0\rangle$ and the first order solution $|\psi^{(1)}(t)\rangle$ are numerically calculated.

We consider the first-order changes of the hole density $\rho^{(1)}(t) = (\langle \psi_0 | n_n | \psi^{(1)}(t) \rangle + \text{c.c.})/A$ and the bond order $p^{(1)}_{n,m}(t) = (\langle \psi_0 | \hat{p}_{n,m} | \psi^{(1)}(t) \rangle + \text{c.c.})/A$ induced by the pulse excitation. Since the absolute value of the bond order shows the strength of the bond, we define the difference in the absolute value of the bond orders between $|\psi(t)\rangle$ and $|\psi_0\rangle$ as $\rho^{(1)}_{n,m}(t) = |\hat{p}_{n,m} + p_{n,m}(t)\rangle - |\hat{p}_{n,m}\rangle$, where $\hat{p}_{n,m}$ is the bond order for the ground state. The bond is stronger in $|\psi(t)\rangle$ than in $|\psi_0\rangle$ for $|\rho^{(1)}_{n,m}| > 0$.

As shown in Fig. 1, there are four nonequivalent bonds, and they are labeled by b1, b2, p, and q according to...
Mori et al. [17]. The b1 bond is much stronger than the other ones, and the two BEDT-TTF molecules connected by the b1 bond form a dimer. There are two dimers in the unit cell, and they are labeled by I and II as shown in this figure. The transfer integral \( \beta_{b1} \) and \( V_{b1} \) denote \( \beta_{n,m} \) and \( V_{n,m} \) for the b1 bond, respectively, and the others are denoted in the same way. The transfer integrals for b1, p, and q bonds are fixed to the following values for \( \kappa \)-(BEDT-TTF)\(_2\)Cu[N(CN)\(_2\)]Br deduced from the extended Hückel calculation [17]: \( \beta_{b1} = 0.265 \) eV, \( \beta_p = 0.109 \) eV, and \( \beta_q = -0.038 \) eV. As for the Coulomb parameters, we use the following values: \( U = 0.7 \) eV [18, 19], \( V_{b1} = 0.45 \) eV, \( V_{b2} = V_p = V_q = 0.25 \) eV. With these fixed parameters, we show the \( \beta_{b2} \) dependence of various physical quantities in this paper because the spin frustration can be controlled by changing \( \beta_{b2} \).

We first show the physical properties of the ground state. The spin correlation function discontinuously changes at \( \beta_{b2} = 0.073 \) eV. For \( \beta_{b2} \leq 0.073 \) eV, the spin correlation is always negative between the dimers I and II, showing that the ground state is an antiferromagnetic (AFM) state. For \( \beta_{b2} \geq 0.074 \) eV, the spin correlations are much smaller than those for the AFM ground state, showing that the ground state is a paramagnetic (PM) state. Decreasing \( \beta_{b1} \), the ground state discontinuously changes from the AFM state to the PM state. The PM ground state changes continuously as \( \beta_{b1} \) is decreased even to the value of \( \beta_{b2} \) or \( \beta_p \). This shows that the PM state is stable without dimerization, and therefore it is not a dimer Mott insulator of a spin liquid state. We also calculate the probability \( W_s \) that a dimer is singly occupied. The probability \( W_s \) also discontinuously changes at the phase boundary, and \( W_s \geq 0.85 \) holds all through the AFM ground state region. This indicates that the AFM state is a dimer Mott insulator. On the contrary, \( W_s \) decreases continuously to about 0.5 as \( \beta_{b1} \) is decreased. This result strongly suggests that the PM state is metallic. In the realistic parameter region, the ground state is either the AFM dimer Mott insulator or the PM metal, and the phase transition between them occurs by changing various parameters. This result is consistent with previous ones [18, 19]. The physical properties of these AFM and PM states are basically unchanged in the realistic parameter range, and the essentially same results are obtained.

In Fig. 2 we show the \( \beta_{b2} \) dependence of light absorption spectrum \( \alpha(\omega) \) in the energy region of THz light. The dominant peaks in \( \alpha(\omega) \) are in the region \( \omega \gtrsim 0.2 \) eV. In addition to these large peaks, there are much smaller peaks in the THz region both in the cases of light excitation from the AFM and PM ground states. It should be emphasized that such low energy peaks are not observed in the simple Mott and charge ordered insulators.

We next show the time dependence of physical quantities induced by a THz light pulse. In all the following cases, the center frequency \( \omega_p \) of the pulse is chosen to be resonant to the largest peak in the energy region shown in Fig. 2. The used duration \( D = 100 \) eV\(^{-1}\) is large enough that the contributions from the large peaks in the higher energy region are negligible.

We first show the results in the case of the excitation from the AFM ground state. In Fig. 3 we show the time dependence of charge and bond order induced by the THz light when the light is polarized to the c-direction at \( \beta_{b2} = 0.068 \) eV. The b1, b2, p and q bonds are shown by the red, the green, the dark blue, and the light blue lines, respectively, in Fig. 3 (a). Moreover, there are

![FIG. 2: (Color online) Light absorption spectrum \( \alpha(\omega) \) when the light is polarized (a) to the a-direction and (b) to the c-direction for various values of \( \beta_{b2} \). The interval of \( \beta_{b2} \) is 0.006 eV.](image)

![FIG. 3: (Color online) The charge and bond order induced by the THz light polarized along the c-direction for \( \beta_{b2} =0.068 \) eV. (a) Nonequivalent bonds and sites are distinguished by colors and kinds (solid or dashed) of lines. (b) \( \rho_n^{(1)}(t) \) and (c) \( |p|_{n,m}^{(1)}(t) \) are shown by the lines of the colors and kinds that specify the site \( n \) and the bond \( n, m \), respectively, in (a).](image)
two nonequivalent p (q) bonds with different bond orders in the photoexcited state $|\psi(t)\rangle$. These two nonequivalent bond orders are distinguished by the solid and the dashed lines. Two sites forming a dimer also become nonequivalent, and they are distinguished by the solid red and the dashed green ellipsoids. We show $\rho_{n}^{(1)}(t)$ and $|p|_{n,m}^{(1)}(t)$ in Figs. 3 (b) and (c), respectively, for the sites and the bonds shown in Fig. 3 (a). As seen from these figures, $\rho_{n}^{(1)}(t)$ and $|p|_{n,m}^{(1)}(t)$ oscillate coherently. The quantities shown by the solid lines and the dashed lines oscillate out of phase.

Before analyzing the present results, we introduce bond order alternation between dimers in much simpler 1D quarter-filled electron-lattice coupled systems. The dimer Mott insulator with alternating bond lengths and bond orders between the dimers is schematically shown in Fig. 4. The site connected by the stronger bond becomes charge-rich because electrons are more stabilized on the stronger bond. The state becomes the ground state with the deformed lattice in a parameter range $20$–$22$.

The collective motion induced by the THz light pulse can be regarded as the bond order alternation between the dimers. As seen from Fig. 3 (c), the amplitudes of the induced bond order oscillation for the p and q bonds are much larger than those for the other bonds, and therefore we focus on the p and q bonds. As seen from Fig. 3 (a), the interdimer bond orders alternate along the a-direction, and the amplitude of the alternation oscillates with time. Since charges are attracted by stronger bonds, when the bonds shown by the solid (dashed) lines become stronger, the sites shown by the solid red (dashed green) ellipsoids become charge-rich as seen from Fig. 3 (b). In this way, the bond order and the charge density oscillations are strongly coupled in the collective mode, and the energy of the charge oscillation is significantly reduced by the coupling. The excitation induces the polarization along the c-direction due to the electric dipole moment on each dimer.

It should be emphasized that the lattice deformation is not considered here. In the previous works, interdimer bond order alternation occurs as a result of electron-lattice coupling. On the other hand, in the present case, the induced collective motion of the bond order alternation coupled with polarization has purely electronic origin. We have found this purely electronic low-energy excitation also in the one-dimensional dimer Mott insulators without electron-lattice coupling.

When the light is polarized to the a-axis, the collective motion of the interdimer bond order alternation is induced by the THz light pulse. The collective motion is just like the case of the excitation from the PM ground state schematically shown in Fig. 4 (a). The bond orders for the p and q bonds alternate along the c-direction. The bond orders and the electric dipole moments oscillate coherently in the mode, and the electric polarization along the a-direction is induced by the excitation.

We next show the results in the case of the excitation from the PM ground state. When the light is polarized to the c-axis, the collective motion shown in Fig. 4 (a) is induced just like the case of the AFM ground state. In Fig. 5, we show the result when the light is polarized to the a-axis at $\beta_{a2} = 0.098$ eV. As seen from this figure, the amplitude of the induced oscillation for the b2 bonds is the largest between the bonds in this case, and it is much larger than the largest ones in the other cases. However, the induced dipole moment is much smaller in this case compared with the other cases. This can be understood as follows. As seen from Fig. 5 (a), a dimer is connected by two solid b2 bonds or two dashed b2 bonds. The dominant motion of the b2 bonds does not accompany the bond order alternation between the dimers, and the coupling with the charge motion is very weak.

As a result of electronic degrees of freedom in a dimer, weak charge disproportion is coupled with the interdimer bond order alternation. Therefore, there exist no such low-energy charge excitations in the Mott insulators. Furthermore, these collective modes occur irrespective of the AF spin order and the Mott insulating phase. Spin frustration also does not play an important role for these modes. The formation of the dimer and strong correlation effects are essential for these modes.

The ferroelectric phase is not obtained within the present model. However, the ground state becomes ferroelectric by introducing electron-lattice coupling. For
Motional spectrum narrowing of an intermolecular phonon mode is observed in $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ around $T \approx 30 \text{K}$ [28], and this can be attributed to the collective modes presented in this paper. These modes are strongly coupled with the phonon mode of interdimer bond length alternation. This is consistent with the fact that the narrowing occurs only in one specific phonon mode. Narrowing does not occur for $T < 5 \text{K}$. This is because the ground state becomes ferroelectric and these modes disappear in the temperature region. Furthermore, the correlation time of the fluctuation mode roughly agrees with the energies of these collective modes apart from the phase boundary.

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