Infrared Investigation of the Charge Ordering Pattern in the Organic Spin Ladder Candidate (DTTTF)$_2$Cu(mnt)$_2$

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Abstract

We measured the variable temperature infrared response of the spin ladder candidate (DTTTF)$_2$Cu(mnt)$_2$ in order to distinguish between two competing ladder models, rectangular versus zigzag, proposed for this family of materials. The distortion along the stack direction below 235 K is consistent with a doubling along $b$ through the metal-insulator transition. While this would agree with either of the ladder models, the concomitant transverse distortion rules out the rectangular ladder model and supports the zigzag scenario. Intramolecular distortions within the DTTTF building block molecule also give rise to on-site charge asymmetry.

Quantum spin ladders have attracted considerable interest as intermediaries between one-dimensional chains and two-dimensional square lattices [1,2,3,4]. Additional interest has arisen from theoretical studies which find that hole-doped spin ladders can support superconductivity [2,5]. Whereas most systems are structural ladders, organic ladder-like compounds such as dithiophentrathiafulvalene copper malonitrile dithiolate, (DTTTF)$_2$Cu(mnt)$_2$ are formed by the coupling of molecular building blocks (Fig. 1(a)). This system is particularly attractive because it belongs to a family of quasi-isostuctural compounds, with tunable properties depending on the counterion ($M = Pt, Cu, Au, Ni$) [3,4]. That the cation stacks of (DTTTF)$_2$Cu(mnt)$_2$ have a $\frac{1}{4}$-filled band with delocalized charge and spin at high temperatures, and are therefore described by an electronic extended Hubbard Hamiltonian, as opposed to the localized Heisenberg spin Hamiltonian, brings additional complexity to the field.

Two different theoretical models, the rectangular [4,6,7,8] and the zigzag ladder [9], have been proposed for this family of coupled stack materials (Figs. 1(d) and (e)). Although determination of the wavevector dependence of the magnon bands [10] is the strongest test of spin ladder character and can in principle distinguish between the models, inelastic neutron scattering experiments on (DTTTF)$_2$Cu(mnt)$_2$ are limited by sample quantity and isotopic decoration requirements [11]. The cations have homogeneous charge within the rectangular model and are charge ordered within the zigzag model [9]. An alternate approach to distinguishing between the models involves detailed comparison of vibrational property measurements with theoretical predictions.

(DTTTF)$_2$Cu(mnt)$_2$ is a donor-acceptor salt that displays the characteristic herringbone chain structure of many organic molecular solids (Fig. 1(a)). The $\frac{1}{4}$-filled band donor stack is weakly metallic at room temperature with $\sigma_{dc} \sim 12 \, \Omega^{-1} \, \text{cm}^{-1}$ [12]. (DTTTF)$_2$Cu(mnt)$_2$ has a sharp second-order metal-insulator transition at 235 K, which doubles the unit cell along the stacking direction, $b$ [12,4]. Within the rectangular ladder model, each dimer unit cell of (DTTTF)$_2Cu^{+}$ radical cations along the stacking $b$-axis is thought to act as a single site with spin $S = \frac{1}{2}$ below this transition temperature [13,4]. The rungs of the proposed ladder lie along $c$ and are formed by close S=S contacts between DTTTF molecules in adjacent stacks. From susceptibility measurements, magnetic exchange strengths are estimated to be $J_\parallel \sim 121$ K and $J_\perp \sim 218$ K [4]. The ratio of $J_\perp/J_\parallel$ is 1.8, indicative of intermediate coupling. The spin gap is 130 K [4]. Interestingly, application of pressure recovers the metallic state [12]. The structural, magnetic, and electrical properties of doped DTTTF-based materials were also studied, [7] but
superconductivity was not observed.

In order to investigate the charge ordering and bond distortion patterns (if any) of (DTTTF)$_2$Cu(mnt)$_2$ below the metal-insulator transition, we measured the temperature-dependent infrared vibrational properties of this material. We compare the results with those of (DTTTF)$_2$Au(mnt)$_2$ and with theoretical predictions of intermolecular charge ordering in the rectangular and zigzag ladders. We find that the zigzag ladder model provides a more appropriate description of the large transverse structural distortion that accompanies the 235 K metal-insulator transition. A mode analysis provides the microscopic basis for this distortion. We briefly discuss the consequences of intramolecular distortions for charge ordering within the DTTTF building block molecule in both the charge transfer salt and neutral molecular solid.

Single crystals of (DTTTF)$_2$Cu(mnt)$_2$ were grown as described previously. Typical dimensions were $2 \times 0.3 \times 0.1$ mm. Our work was done on the largest (bc) crystal face. As shown in Fig. 1(b), the crystal surfaces were somewhat striated. Variable temperature infrared reflectance measurements were carried out on these small crystals using a Bruker 55 Fourier transform infrared spectrometer and attached microscope accessory. Both wire grid and polaroid film polarizers were used, as appropriate. Measurements were taken at several different temperatures using a cryostat and temperature controller setup, concentrating on the temperature range near the phase transitions. The cooling rate was slow ($\sim$ a few K/min) to avoid breakage. Careful aperturing minimized the impact of surface quality and small crystal size (Fig. 1b)). A Kramers-Kronig analysis was tried in an attempt to relate the measured reflectance to the optical constants of the material. In many cases, the procedure worked well, but in a few cases, less reasonable results were obtained. We therefore elect to present and discuss the absolute reflectance spectra of (DTTTF)$_2$Cu(mnt)$_2$, which captures the important physics of this system over the full temperature range of investigation without the variability of a Kramers-Kronig analysis.

The 300 K optical properties of (DTTTF)$_2$Cu(mnt)$_2$ are highly anisotropic and similar to those of the Au analog, with a combination of electron-molecular vibrational and infrared active modes of $B_u$ symmetry plus a strong charge transfer band in the chain direction. Along $b$, the largest modes appear at $\sim$770 and 1300 cm$^{-1}$ in the reflectance spectrum. We attribute these features to terminal C-S and C-C stretching vibrations of the DTTTF cation based on our dynamics calculations. These modes are...
transverse distortions. The strong structural modification involving both leg and diagonally include a large spin gap, charge ordering, and a complex tative charge and bond ordering [9]. Predictions of the model ground state shown in Fig. 1(e) is a consequence of coopera-
due to electron-molecular vibrational coupling [14]. In the totally symmetric and activated along the chain direction (Fig. 2(a) and (b), the spectral response above and below 235 K is consistent with a doubling along $b$ through the metal-insulator transition [12,4]. There is also a striking transverse distortion as evidenced by changes in the c-polarized reflectance spectra. Analysis of the vibrational modes that probe the interchain interactions shows that symmetry breaking involves the C-S bending and stretching modes of the DTTTF cation, combined C-C + C-S stretching and C-H wagging, and S-C=C-H wagging perpendicular to the chain (Fig. 2(c) and (d)). This result has important implications for the intermolecular charge ordering pattern as discussed below.

The variable temperature spectral response of $(\text{DTTTF})_2\text{Cu(mnt)}_2$ is different than that of the Au analog. Two separate transitions are observed (220 and 70 K) in the latter. The broad 220 K metal-insulator transition is driven by massive symmetry breaking along the rung direction, whereas the 70 K magnetic transition is associated with mode modifications in the rail direction [8]. In contrast, the rung- and rail-directed lattice distortions are coupled in $(\text{DTTTF})_2\text{Cu(mnt)}_2$. Both occur near 235 K, consistent with the observation of a sharper transition. This may be a consequence of stronger interchain interactions (see below).

We now discuss the implications of the combined b-axis doubling and large transverse distortion at the metal-insulator transition for the intermolecular charge ordering pattern in $(\text{DTTTF})_2\text{Cu(mnt)}_2$. Within the rectangular ladder model of Fig. 1(d), bond alternation along the rails is a necessity but charge ordering is not anticipated [9]. The symmetry between the chains implies that this model cannot account for the strong transverse distortion in $(\text{DTTTF})_2\text{Cu(mnt)}_2$: specifically, the symmetry breaking involving C-S, C-C, and complex wagging motion perpendicular to chain direction (Fig. 2(c) and (d)). The proposed Heisenberg spin ladder model with $(\text{DTTTF})_2^{2+}$ dimers acting as the $S = \frac{1}{2}$ sites (Fig. 1(c)) is therefore not applicable to this class of materials.

The zigzag ladder model provides a more promising framework for understanding intermolecular charge ordering in $(\text{DTTTF})_2\text{Cu(mnt)}_2$. The bond-charge density wave ground state shown in Fig. 1(e) is a consequence of cooperative charge and bond ordering [9]. Predictions of the model include a large spin gap, charge ordering, and a complex structural modification involving both leg and diagonally transverse distortions. The strong c-polarized distortions observed in the spectra (Fig. 2) are consistent with these predictions. Indeed, the zigzag ladder model can potentially also explain the occurrence of two distinct transitions in $(\text{DTTTF})_2\text{Au(mnt)}_2$ but single transition behavior in $(\text{DTTTF})_2\text{Cu(mnt)}_2$. Recall that the co-operative distortion of Fig. 1(e) requires a minimum interchain hopping $t_{\text{int}} > 0.59t$, where $t$ is the intrachain one-electron hopping integral [9]. We believe that $t_{\text{int}}$ in $(\text{DTTTF})_2\text{Au(mnt)}_2$ may be smaller than this threshold value at high temperatures, and the nearly independent stacks undergo the usual high temperature $4k_F$ charge ordering transition observed also in the quasi-one-dimensional TMTTF-based $\frac{1}{2}$-filled band systems [15]. The charge disproportionation is then exactly as in Fig. 1(e), but all bonds are uniform. This would give rise to the observed asymmetry between the stacks [8]. As the temperature is lowered to below 70 K, either because of lattice contraction or molecular rotation $\sigma_4$, $t_{\text{int}}$ is larger than the threshold value, the system behaves as the zigzag ladder in the spin singlet subspace, and the co-operative bond distortions of Fig. 1(e) occur. Within this scenario $t_{\text{int}}$ in the Cu-analog is already larger than 0.59t, which leads to the single observed transition involving both charge and spin. Complete theoretical proof of this scenario requires the demonstration of a single transition in the $\frac{1}{2}$-filled band zigzag ladder with large $t_{\text{int}}$ and work is currently in progress.

In order to evaluate the molecular charges in the low temperature phase, we followed the approach outlined by Yamamoto et. al. [17] and selected an unperturbed, infrared-active vibrational mode that, from our dynamics calculations [8], is sensitive to charge. Several authors have observed that vibrational frequencies depend linearly on average molecular charge in the absence of strong coupling [14]. The advantage of using an unperturbed (rather than strongly coupled) mode for the analysis is that complementary Raman data is not required [17]. Our analysis focused on an infrared-allowed out-of-phase C-C stretch of DTTTF (Fig. 3). This mode is similar in character to $\nu_{2\pi}$ in the BEDT-TTF building block molecule [17]. Accounting for the typical 3% overestimate of calculated frequencies and the flat vs. boat-shaped nature of the neutral vs. cationic building block molecules (see Fig. 4 and discussion, below), we compared the calculated results and the associated linear fit ($\rho = -0.022\omega + 29.82$) with the experimental optical conductivity. From features at $\sim 1319.5$ and $1334.5$ cm$^{-1}$ in $\sigma_1(\omega)$, we estimate the difference in the site charges in the charge-ordered low temperature phase to be $\sim 0.35 - 0.4$. These numbers should be compared with those obtained by Raman spectroscopy. The absence of strong low tem-
temperature splitting of the C-H stretching mode on the cation (Fig. 2(f)) indicates that charge rich and charge poor regions are located at the heart of the DTTTF building block molecule.

Although not part of the aforementioned zigzag model for intermolecular charge ordering, on-site charge asymmetry within the DTTTF molecule is expected from the chemical and structural point of view. Examination of the structure (Fig. 4(a)) shows that the DTTTF cations are locally distorted, with irregular bond lengths (and angles) \( |\Delta \rho| = |\rho_{\text{ave}} - \rho_{\text{loc}}| < 0.1 \) with respect to the average 4 K charge distribution. Mode splitting of a similar size (~10 cm\(^{-1}\)) has been observed in (TTM-TTP)\(_2\) and attributed to an asymmetric deformation of the organic building block molecule and consequent non-uniformity of the intramolecular charge distribution \([18]\). Pressure may suppress the intermolecular charge ordering and on-site charge inhomogeneities in (DTTTF)\(_2\)Cu(mnt)\(_2\), leading to the metallic state \([12]\).

We measured the variable temperature infrared response of the spin ladder candidate (DTTTF)\(_2\)Cu(mnt)\(_2\) in order to assess the intermolecular charge ordering pattern within the context of two recent recent theoretical predictions. The low temperature distortion along the chain direction through the 235 K metal-insulator transition is consistent with expectations based on structural studies for a doubling along \( b \). At the same time, there is a large transverse distortion. The presence of this transverse lattice distortion rules out rectangular ladder models and suggests that the zigzag ladder model with its cooperative charge and bond ordering may be more appropriate for (DTTTF)\(_2\)Cu(mnt)\(_2\). Comparison of these results with our previous work on the Au analog material shows that the metal-insulator transitions are quite different. Coupled chain- and rung-directed distortions are observed in (DTTTF)\(_2\)Cu(mnt)\(_2\), whereas they are separate in the Au compound. We suspect that this is a consequence of stronger interchain interaction in the Cu-based system. A mode analysis provides microscopic information on the vibrational processes driving the metal-insulator transition in (DTTTF)\(_2\)Cu(mnt)\(_2\).

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