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# Signatures of electron-electron correlations in the optical spectra of $\alpha$ -(BEDT-TTF)<sub>2</sub>MHg(SCN)<sub>4</sub> ( $M$ =NH<sub>4</sub> and Rb)

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We interpret the optical spectra of  $\alpha$ -(BEDT-TTF)<sub>2</sub>MHg(SCN)<sub>4</sub> ( $M$ =NH<sub>4</sub> and Rb) in terms of a 1/4 filled metallic system close to charge ordering and show that in the conductivity spectra of these compounds a fraction of the spectral weight is shifted from the Drude-peak to higher frequencies due to strong electronic correlations. Analyzing the temperature dependence of the electronic parameters, we distinguish between different aspects of the influence of electronic correlations on optical properties. We conclude, that the correlation effects are slightly weaker in the NH<sub>4</sub> compound compared to the Rb one.

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## I. INTRODUCTION

The physical properties of layered molecular conductors are known to be influenced by electron-electron interactions. The comparative strength of the electronic correlations can be tuned by small modifications of the chemical composition of the crystals, that might result in different ground states for isostructural compounds. In addition, the behavior of the correlated systems depends essentially on the conduction-band filling<sup>1,2</sup>; while for half-filled systems the on-site correlations  $U$  are of importance, the quarter-filled systems stay metallic at any values of  $U$ , if the inter-site correlations  $V = 0$ .

The importance of electronic correlations in 1/4-filled two-dimensional organic conductors was investigated for the  $\theta$ -(BEDT-TTF)<sub>2</sub>MM'(SCN)<sub>4</sub> family<sup>3,4</sup>, where a charge-order metal-insulator transition is observed at the temperature decrease. On the other hand, extensive theoretical studies were performed for the electronic correlations in 1/4-filled layered molecular metals close to the charge-order transition<sup>5,6,7,8</sup>. Here we present an optical study of 1/4 filled metals  $\alpha$ -(BEDT-TTF)<sub>2</sub>MHg(SCN)<sub>4</sub> ( $M$ =NH<sub>4</sub>,Rb), aimed on obtaining the effective mass and scattering rate of charge carriers, in order to compare them with theory and to distinguish between the electronic correlations and other factors defining their behavior. While in this family of compounds is known that superconductivity ( $T_c = 1$  K) competes with a density-wave ( $T_c = 8-10$  K) ground state, we argue that the properties at temperatures between 300 and 6 K are determined by the distinct ratios of inter-site Coloumb repulsion  $V$  to the bandwidth.

## II. RESULTS

The polarized reflectivity of single crystals of  $\alpha$ -(BEDT-TTF)<sub>2</sub>MHg(SCN)<sub>4</sub> ( $M$ =NH<sub>4</sub>, Rb) was mea-

sured in the conducting plane along the main optical axes (parallel and perpendicular to the stacks of BEDT-TTF molecules) in the frequency range between 50 and 6000 cm<sup>-1</sup>. The sample was cooled down to 6 K with a rate of 1 K/min; spectra were taken at 300, 200, 150, 100, 50 and 6 K. In order to measure the absolute values of reflectivity, the sample was covered *in situ* with 100 nm and used as a reference; this technique is described in Ref. [9].

In agreement with the calculated higher values of transfer integrals between the stacks of BEDT-TTF molecules<sup>10</sup>, the reflectivity is always higher in the direction of the  $E \perp$  stacks. The reflectivity increases on cooling for both salts, as expected for metals. In the conductivity spectra, the wide finite-frequency electronic features are observed in addition to a comparatively narrow zero-frequency peak. Furthermore, the narrow features in the 400-1600 cm<sup>-1</sup> range near the frequencies of the BEDT-TTF intramolecular vibrations are known to be the  $a_g$  vibrations of BEDT-TTF activated by the electron-molecular vibrational coupling<sup>11</sup>; they are out of the scope of this paper.

## III. DISCUSSION

To follow the electronic spectral features we performed a Drude-Lorentz fit of the experimental data. In both polarizations the spectra of these compounds are described well by a Drude peak, a maximum at about 1000 cm<sup>-1</sup> and an overdamped maximum at about 2400 cm<sup>-1</sup>. The high-frequency maximum can be distinguished in the whole temperature range; the frequency does not change with temperature. The low-frequency maximum is separated from the Dude-peak by a pseudogap only below  $T = 200$  K when the Drude-peak becomes narrow enough, though the fit suggests that the maximum exists already at room temperature. On cooling down to 6 K this feature shifts from 1000 to 800 cm<sup>-1</sup>.

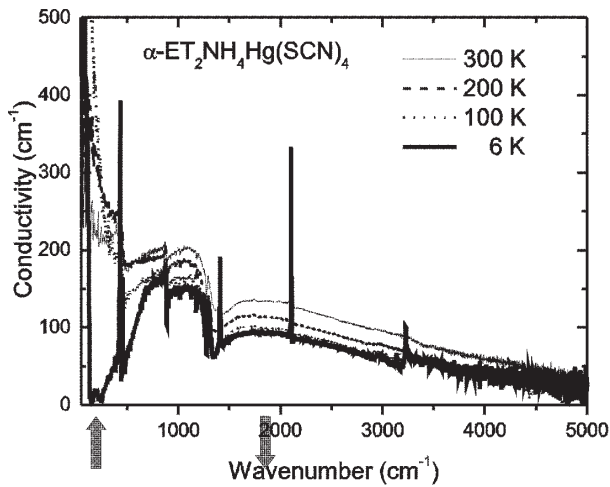


FIG. 1: Optical conductivity of  $\alpha$ -(BEDT-TTF) $_2$ NH $_4$ Hg(SCN) $_4$  in  $E||$ stacks polarization. The arrows indicate the increase of Drude spectral weight and the decrease of high-frequency features on cooling.

The observed bands cannot be interpreted as interband transitions, according to the band structure calculations<sup>10</sup>, since they do not occur at known transition energies. We attribute the observed electronic features to the spectral weight shifted from the Drude-peak to higher frequencies due to the influence of electronic correlations; a similar interpretation was proposed for the spectra of  $\theta$ -phase compounds<sup>7,12</sup>, where a very intense feature and a pseudogap at 300  $\text{cm}^{-1}$  was previously observed in the low temperature spectra of  $\alpha$ -(BEDT-TTF) $_2$ KHg(SCN) $_4$  and interpreted as an indication of the fluctuating charge ordering<sup>8</sup>.

In a one-band approximation, these three electronic features together give us the total spectral weight<sup>13</sup>  $\omega_p^2 = 8 \int_0^{\omega_c} \sigma_1(\omega) d\omega$  received by the integration up to frequency  $\omega_c$ . The minimum in the conductivity spectrum indicates the exhaustion of the band, i.e. the band width  $W$ . Consequently, the contraction of the crystal on cooling, which changes the size of the transfer integrals, results in a change of the total spectral weight, as estimated by the one-dimensional tight-binding approximation:

$$\omega_p^2 = \frac{16td^2e^2}{\hbar^2V_m} \sin\left\{\frac{\pi}{2}\rho\right\} \quad (1)$$

The calculated temperature dependence of the transfer integrals<sup>14</sup> shows a striking in-plane anisotropy: about a 7% increase of the inter-stack transfer integrals is expected on cooling the crystals from 300 down to 4 K, while two of the three in-stack transfer integrals stay

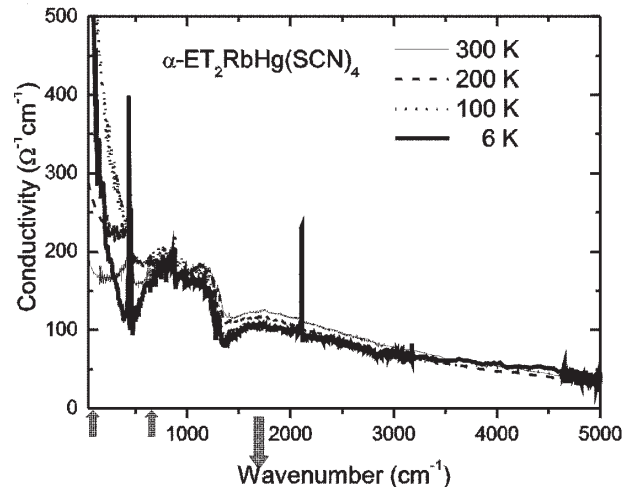


FIG. 2: Optical conductivity of  $\alpha$ -(BEDT-TTF) $_2$ RbHg(SCN) $_4$  in  $E||$ stacks polarization. The arrows indicate a weak increase of Drude spectral weight and the 1000  $\text{cm}^{-1}$  feature, and the decrease of the mid-infrared feature on cooling.

constant. In agreement with it, the spectral weight estimated from our optical experiments does not change on cooling for the polarization  $E||$ stacks, but a considerable increase is observed in the  $E\perp$ stacks direction: for the Rb-compound it is about 10%, in agreement with the  $t$  change, while the increase of the spectral weight for the NH $_4$  compound amounts up to 30%, well above the expectations. In addition, the increase of the transfer integrals leads to a decrease of the  $V/t$  ratio that defines the distribution of the spectral weight between the Drude-like peak and high frequencies<sup>7</sup>. Indeed, a pronounced shift of the spectral weight from the mid-infrared to the zero-frequency peak is observed in the spectra of polarization  $E\perp$ stacks.

Neither the total spectral weight, nor the hopping parameters change in the  $E||$ stacks direction. Therefore, the observed shift of the spectral weight from the high-frequency features to the Drude peak on cooling (indicated by arrows in Fig. 1, 2) is consistent with predictions of the charge fluctuation scenario<sup>7</sup>. A discussion of the main ingredients of this theory is revised in the following section.

#### IV. COMPARISON TO CHARGE FLUCTUATION SCENARIO

The simplest model to describe the relevant electronic properties of the  $\alpha$ -type salts is a one band extended

Hubbard model at one-quarter filling on the square lattice. This model contains a kinetic energy scale given by the hopping,  $t$ , the on-site Coulomb repulsion,  $U$  and the intersite Coulomb repulsion,  $V$ . This last Coulomb repulsion accounts for the Coulomb repulsion between two electrons on the two nearest-neighbors molecules. From quantum chemistry it is known that  $U$  is larger than the bandwidth,  $W = 8t$  whereas  $V$  is comparable to the hopping and therefore cannot be neglected. In fact the model contains a transition from a metal to a charge ordered state induced by  $V$ , when  $V = 2t$  (Ref.<sup>6</sup>) at zero temperature. Close to the charge ordering transition it is found from exact diagonalization calculations that: (i) the Drude weight is rapidly suppressed; (ii) the optical spectral weight is redistributed so that a net shift from low frequencies into a mid-infrared band occurs; (iii) a characteristic low frequency feature appears in the optical spectra as a consequence of the presence of the strong charge fluctuations occurring in the metallic phase close to the transition.

At non-zero temperatures, exact diagonalization cannot be used reliably due to the system size, and so one needs to rely on other theoretical methods. Slave-boson, CPA (Coherent Potential Approximations) and large- $N$  calculations on the extended Hubbard model predict that sufficiently close to  $V_c$  and within the metallic phase, increasing the temperature drives the system into the charge ordered phase. This reflects the unusual 're-entrant' character of the metal-charge ordered transition, which leads to an interesting temperature dependence of the electronic properties of the metal when being close to a checkerboard charge ordering transition at  $T=0$  such as an increase in the electron effective mass with increasing temperature<sup>7</sup>. This behavior is different from the one found in a conventional metal in which increasing the temperature would tend to suppress the renormalization of the electrons due to their interaction with other electrons, phonons, etc, effectively decreasing their effective mass enhancement as  $T \rightarrow T_F$ , where  $T_F$  is the Fermi temperature of the metal. Apart from the increasing effective mass with increasing temperature characteristic of the charge ordering transition, the scattering rate,  $1/\tau(T) \propto T^2$  behavior for  $T < T^*$  becomes linear:  $1/\tau(T) \propto T$  for  $T > T^*$  due to the onset of the charge fluctuations just like in the case of the interaction of electrons with other boson-like excitation such as phonons<sup>15</sup>. The temperature  $T^*$  defines the distance of the metal from the critical point at which the charge ordering transition occurs. Hence,  $T^* \rightarrow 0$  as  $V \rightarrow V_c$ . In a few words,  $T^*$  is the characteristic energy scale describing the onset of the charge fluctuations. This energy scale is then very small:  $T^* \ll T_F$  whenever the system is sufficiently close to the charge ordering transition.

Summarizing, the charge ordering scenario predicts for a metal close to the charge ordered phase ( $V \lesssim V_c$ ): (i) a suppression of the coherent part of quasiparticles compared to the electrons of the non-interacting ( $V = 0$ ) system, (ii) the destruction of the quasiparticles becom-

ing more incoherent as the temperature is gradually increased above  $T > T^*$  from  $T = 0$ , (iii) a linear dependence of the scattering rate:  $1/\tau(T)$  for  $T > T^*$ . The slope of  $1/\tau(T)$  increases as the system is driven closer to the transition.

Indeed, this explains the experimentally observed decrease of the Drude weight with increasing temperature in the spectra of E||stacks direction in these compounds. The effective mass of the charge carriers  $m_D$  was calculated from the Drude plasma frequency  $\omega_p$ :  $\omega_p = \left(\frac{4\pi N e^2}{m_D}\right)^{1/2}$ . The observed decrease of the plasma frequency with temperature can either be caused by an enhancement of the effective mass or a decrease of the number of carriers. Since the later one seems unlikely, we assume the carrier concentration to be constant with temperature and interpret the observed change of  $\omega_p$  as an increase in the effective mass. For the Rb compound  $m^*$  increases from  $4.2m_e$  to  $5.1m_e$  and from 4.1 to 4.9 for the  $\text{NH}_4$  compound with increasing the temperature from 6 to 300 K is observed, in agreement with prediction (ii) of the charge fluctuating scenario. Also, the temperature behavior of the Drude scattering rate (Fig. 3), though characterized by only six points, is distinctly linear with temperature down to about 50 K, while below this temperature it changes to a much slower dependence in agreement with prediction (iii).

The absolute yields of the scattering rate of the Drude-component are higher in the Rb compound, resulting in the presence of some spectral weight in the pseudogap at about  $300 \text{ cm}^{-1}$ . In addition, it shows a much larger slope in the scattering rate, therefore we conclude from point (iii) that the Rb compound closer is to the charge ordering transition than the  $\text{NH}_4$  salt. Other explanations for the different scattering rates would be difficult since the compounds are isostructural and have very similar properties. For instance, a different number of defects in the two salts would give a constant shift in the values of scattering rate between the two compounds but would have difficulties in explaining the different observed slopes. Phonons could also give changes in the temperature dependence however at much larger temperatures than the charge fluctuation scale,  $T^*$  as the Debye frequency is expected to be of the order  $T_F$ . The magnitude of the characteristic temperature scale for the charge fluctuations,  $T^*$  is theoretically of about  $T^* \approx 0.2t$ . Taking estimates for  $t = 0.06 \text{ eV}$ , the estimates for  $T^*$  are of the right order of magnitude compared to the experiments.

## V. CONCLUSIONS

The optical investigations of  $\alpha$ -BEDT-TTF<sub>2</sub>MHg(SCN)<sub>4</sub> (M= $\text{NH}_4$  Rb) compounds reveal the anisotropic behavior of the crystals upon lowering the temperature. Perpendicular to the stacks, the total spectral weight increases on cooling with the increase of

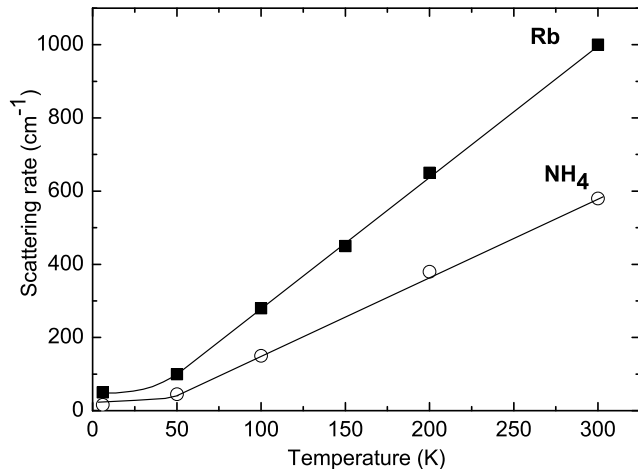


FIG. 3: Temperature dependence of Drude scattering rate in E||stack direction for the NH<sub>4</sub> and Rb salt.  $T^*$  is calculated assuming  $t=0.060$  eV.

the overlap integrals  $t$ , while the respective decrease of the  $V/t$  ratio leads to the shift of the spectral weight from the finite-frequency features to the Drude-peak. No increase of the total spectral weight is observed parallel to the stacks, as these transfer integrals do not change on cooling. We attribute the weak shift of the spectral weight and an increase of the effective mass with temperature to the 're-entrant' character of the charge ordering transition driven by the Coulomb repulsion  $V$  by which the critical  $V_c$  is decreased with increasing temperature. The larger slope of the scattering rate of the charge carriers and the larger effective masses of the Rb compound compared to NH<sub>4</sub>, suggests that the Rb salt is closer to the charge ordering transition than the NH<sub>4</sub> salt. This conclusion is based on a comparison with the predictions of the properties of metals under the effect of charge fluctuations.

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