Pressure-Induced Changes in the Optical Response of the Quasi-1D Organic Salt $(TMTTF)_2AsF_6$

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The polarization-dependent infrared reflectivity of $(TMTTF)_2AsF_6$ is studied as a function of pressure (<6 GPa) at room temperature. At high enough pressure the mid-infrared response along the stacking axis a resembles that of the conducting TMTSF analogs in qualitative accordance with the generalized temperature-pressure phase diagram of the Bechgaard-Fabre salts.

1. INTRODUCTION

The quasi-one-dimensional (quasi-1D) organic Bechgaard-Fabre salts $(TMTTF)_2X$ and $(TMTSF)_2X$, with monovalent anions X have a very rich pressure-temperature phase diagram with a great variety of different phases and ordering phenomena[1]. The crystals consist of weakly coupled molecular stacks, along which the charge transport occurs. Hereby, the type of the molecule (TMTSF or TMTTF) and of the anions X determine the coupling between the molecular stacks and thus the dimensionality of the system (chemical pressure effect). In particular, the $(TMTTF)_2X$ salts consist of basically uncoupled chains, which are half-filled due to dimerization along the chains. They thus constitute systems of electrons confined to the chains and forming a Mott-Hubbard insulating state.

For such a quasi-1D interacting electron system the possibility of a dimensional crossover and deconfinement transition was intensively studied theoretically[2]. A first attempt to observe the predicted deconfinement transition was made by comparing the optical spectra of different Bechgaard-Fabre salts[3]. Here, we present the results of an infrared spectroscopy study on $(TMTTF)_2AsF_6$ as a function of external pressure, which makes it possible to extract information on the carrier dynamics when the interstack coupling is continuously tuned.

2. EXPERIMENTAL

Polarized reflectivity spectra were recorded at room temperature utilizing a Bruker IFS 66v/S FT-IR spectrometer in the mid-infrared (MIR) frequency range. A diamond anvil cell equipped with type IIA diamonds suitable for infrared measurements was used for the generation of pressures up to 6 GPa. Finely ground CsI powder was chosen as quasi-hydrostatic pressure medium. To focus the beam on the small sample in the pressure cell, an infrared microscope (Bruker IRscope II) coupled to the spectrometer was used. The intensity spectrum reflected from the lower diamond-air interface of the diamond anvil was used as a reference. The measured reflectivity spectra refer to the absolute reflectivity at the sample-diamond interface, denoted as R_{s-d}. The final reflectivity spectra are somewhat affected by multiphonon absorptions of diamond which cannot be perfectly compensated in the range 1700 - 2700 cm^{-1}. Therefore, these data were not used in the analysis.

3. RESULTS

The reflectivity spectra for both polarizations in the (a,b)-plane are presented in Fig. 1 for four different pressure values. As expected, the overall reflectivity for $\mathbf{E}\|b'$ is lower compared to the stacking direction $\mathbf{E}\|a$. When external pressure is applied the spectra change gradually. Along the stacks ($\mathbf{E}\|a$) the strong MIR band around 4600 cm^{-1} dominates the reflectivity spectrum. Several sharp vibrational modes are observed below 2000 cm^{-1} which are electron-molecular vibration (emv) coupled A_g modes of the TMTTF molecule[4]. The vibrational modes harden linearly with pressure by 2-6 cm^{-1}/GPa. The low-frequency part (< 2000 cm^{-1}) of the reflectivity continuously increases with increasing pressure, while the intensity of the MIR band remains almost constant in the whole studied pressure range.

In the b'-direction the reflectivity level is almost frequency independent for low pressure values except for the broad MIR band at approximately 5300 cm^{-1}. The pronounced peak around 700 cm^{-1} (see inset in Fig. 1) is related to the F_{1u} symmetry vibrations of the octahedral AsF_6 anion[5]. The application of higher pressure (> 2 GPa) causes a pronounced increase of the reflectivity at low frequencies ($\nu < 2000$ cm^{-1}). The position of the MIR band remains almost unchanged while the intensity decreases.

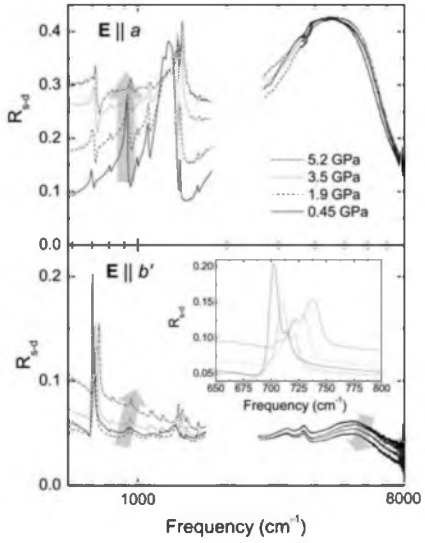

Fig. 1. Reflectivity spectra of $(TMTTF)_2AsF_6$ as a function of pressure for $\mathbf{E}\|a$ and $\mathbf{E}\|b'$ at room temperature. Inset: Pressure dependence of the AsF_6 vibrational mode.

4. ANALYSIS AND DISCUSSION

According to the generalized pressure-temperature phase diagram the optical properties of the TMTTF compounds should resemble those of the TMTSF analogs at high enough pressure. The sample-air reflectivity (R) spectra of $(TMTTF)_2AsF_6$ were extracted from the R_{s-d} data as described in Ref. 6 for direct comparison to the TMTSF compounds. In Fig. 2 the reflectivity ($\mathbf{E}\|a$) of $(TMTTF)_2AsF_6$ at the lowest and highest pressure are compared to the ambient-pressure $(TMTSF)_2PF_6$ spectrum. With increasing pressure the $(TMTTF)_2AsF_6$ spectrum changes its character from insulating to conducting, becoming very similar to the $(TMTSF)_2PF_6$ spectrum. Simultaneously, the strength of the vibrational modes decreases indicating a weakening of the emv coupling strength, known from the TMTSF salts.

The rising reflectivity in the low-frequency part of the spectra for $\mathbf{E}\|b'$ evidences the gradual onset of a Drude-like conductivity perpendicular to the molecular stacks. This indicates an increase of the charge-transfer integral in the b' direction, which was suggested as a reason for the crossover from a Mott-Hubbard insulating to a conducting state[3]. The fit of the Drude response allows to extract the pressure dependence of the effective mass and the transfer integral t_b. A complete analysis will be published elsewhere[6].

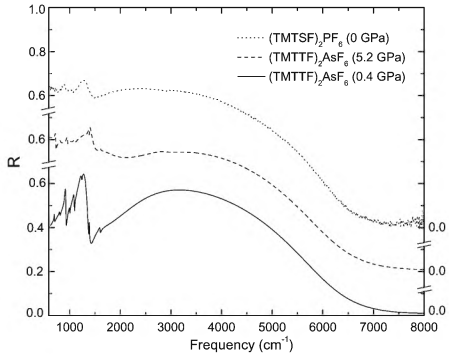

Fig. 2. Comparison of the simulated sample-air reflectivity of $(TMTTF)_2AsF_6$ at low and high pressure with the ambient-pressure reflectivity of $(TMTSF)_2PF_6$.

5. CONCLUSIONS

The obtained pressure-dependent infrared data on $(TMTTF)_2AsF_6$ suggest the predicted crossover from a Mott insulator to a metallic state as the pressure increases ($p > 3.5$ GPa). The typical features inherent to the TMTSF salts gradually emerge in the optical spectra of $(TMTTF)_2AsF_6$ for $\mathbf{E}\|a$. Perpendicular to the stacks the gradual onset of an overdamped Drude-like conductivity is observed.

ACKNOWLEDGEMENTS

We thank G. Untereiner for crystal growth and M. Dumm for discussion. Financial support by the DFG (Emmy Noether program) is acknowledged.

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