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Temperature dependence of the Peierls gap in $(\text{TaSe}_4)_2\text{I}$

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Abstract. - We have determined the longitudinal optical conductivity of $(\text{TaSe}_4)_2\text{I}$ in the energy range from 50 meV to 2 eV at different temperatures between 15 K and 420 K. We find a clear evidence that the free carriers are condensed into a charge density wave ground state not only below the transition temperature of 263 K but also at higher temperature up to the limits of the chemical stability of this compound.

1. Introduction

As the one-dimensional metallic state is instable against lattice distortions the chain-like compound $(\text{TaSe}_4)_2\text{I}$ undergoes a metal-insulator transition of Peierls type. This transition is associated with the appearance of an energy gap at the Fermi level and with the formation of charge density waves. Whereas the interesting non-linear transport properties of this material occurring below the transition temperature of $T_p = 263$ K were analyzed in many publications [1] the change of the electronic structure of this material during this transition was much less investigated. Therefore, this transformation is not understood in detail. Diffraction experiments have shown the development of a three-dimensional superstructure below 263 K, reflecting a static Peierls distortion associated with three-dimensional ordering [2,3]. Whereas the electronic transport properties below the transition temperature can be described in the framework of a charge density wave condensate, i.e. by collective phenomena, the transport properties above 263 K were attributed to metallic behaviour, i.e. to single electron excitations. Optical measurements at room temperature, however, have exhibited strong deviations of the reflectance spectra of $(\text{TaSe}_4)_2\text{I}$ from metallic behaviour at photon energies below the plasma edge [4]. Therefore, it seemed to be obvious to continue and to complete these earlier optical investigations by determining the polarized reflectance spectra of $(\text{TaSe}_4)_2\text{I}$ at different temperatures above and below the transition temperature.

2. Experimental

Single crystals of $(\text{TaSe}_4)_2\text{I}$ were grown by standard temperature-gradient furnace techniques. The size of the crystals was about $6 \times 1 \times 1$ mm³. They showed well-reflecting surfaces. The reflection measurements at room temperature and at higher temperatures were performed at near-normal incidence with a single-beam spectrometer, designed for the investigation of small samples. The low-Temperature spectra were obtained, using a Fourier transform spectrometer Bruker IFS 113v, equipped with a continuous-flow cryostat. The direction of polarization was parallel or perpendicular to the chain axis, respectively.

3. Results and discussion

Fig.1 shows the polarized reflectance spectra of $(\text{TaSe}_4)_2\text{I}$ in the energy range between 50 meV and 6 eV. The strong optical and electrical anisotropy of this material is well reflected by the room temperature data. For the electric field perpendicular to the chain axis the reflectivity is nearly constant, like in a typical insulator. For the electric field parallel to the chain axis a steep edge of the reflectivity near 1 eV is observed, at a first glance, similar to the plasma edge of a one-dimensional free-electron gas. At lower energy, however, the reflectance spectrum deviates significantly from the free-electron behaviour, represented by the dashed line. This deviation still remains even when the temperature of the crystals is increased close to the limits of chemical stability, well above the transition temperature of 263 K. When the crystal is cooled down to 15 K this deviation increases remarkably. The spectral distributions of the longitudinal optical conductivity, following from a Kramers-Kronig transformation of the reflectance spectra, are plotted in Fig.2. These conductivity spectra demonstrate more clearly the

Fig.1 - Polarized reflectance spectra $R_{\parallel}$ of $(\text{TaSe}_4)_2\text{I}$ in the metallic limit (dashed line), at 300 K and at 15 K; $R_{\perp}$ at 300 K (full lines).

Fig.2 - Longitudinal optical conductivity calculated from the reflectance spectra of Fig.1.

significance of the deviation of the experimental spectra from the free-electron behaviour: Even at high temperatures, well above the transition temperature of 263 K, no metallic state, i.e. no delocalized states at the Fermi level exist in $(\text{TaSe}_4)_2\text{I}$. Rather, a gap in the electronic excitation spectrum is present, manifesting that even at high temperature the free carriers are condensed into a charge density wave groundstate. Above 263 K, however, this charge density wave condensate shows no long-range order. It has the physical properties of a liquid. Therefore, the steep absorption edge, following from the joint density of states of a one-dimensional solid is smoothed out by tail states near the band edges. Below 263 K this "liquid" condensate crystallizes into a superlattice structure. Figs. 3 and 4 show a nearly continuous change of the optical spectra in the broad temperature range between 15 K and 300 K. By continuous narrowing of the longitudinal conductivity spectrum the shape, determined by the one-dimensional joint density of states, is approximated with decreasing temperature. Simultaneously, the gap

Fig.3 - Polarized reflectance spectra of $(\text{TaSe}_4)_2\text{I}$ at different temperatures (expanded scale)

Fig.4 - Longitudinal optical conductivity of $(\text{TaSe}_4)_2\text{I}$ at different temperatures.

Fig.5 - Evolution of the Peierls gap of $(\text{TaSe}_4)_2\text{I}$ with decreasing temperature (full lines), compared with the joint density of states of a one-dimensional solid (dashed-dotted lines).

energy increases slightly. If we take the value of 400 meV as the limit for $T = 0$ it follows from the relation

$$2 \Delta = 3.5 kT^{\text{MF}} \quad (1)$$

a value of $T^{\text{MF}} = 1370$ K for the mean field transition temperature. This may be the temperature, where the free carriers condense to a charge density wave "liquid". At the transition temperature $T_p = 263$ K this charge density wave "liquid" crystallizes to a static charge density wave superstructure.

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