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Indium doping-induced change in the photoconduction spectra of *o*-TaS_3

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ABSTRACT

Impurities and defects are known to affect the properties of the charge density wave (CDW) state but the influence of impurities on the density of states inside the Peierls gap remains largely unexplored. Here we present an experimental study of the effect of indium impurities on photoconduction spectra of CDW compound orthorhombic TaS_3. We use the temperature diffusion method to introduce indium into a sample from preliminary attached In contacts. The concentration of In after 23 h of diffusion is found to be nonuniform and strongly dependent on the distance to the contacts. The diffusion affects the spectral range 0.15–0.25 eV, increasing the photoconduction amplitude linearly with diffusion time. The optical gap value obtained from the measurements is $2\Delta = 0.25$ eV and the tail of states below 2Δ is associated with the impurities in agreement with the Tüttö–Zawadowski theory. Diffusion-induced modification of current–voltage characteristics and decrease of the Peierls temperature are also observed. Neither changes in photoconduction spectra nor in the Peierls transition temperature of the control sample with Au contacts are found.

1. Introduction

Impurities and defects strongly affect properties of the charge density wave (CDW) state in quasi-one dimensional (q-1D) conductors. The Peierls transition temperature, T_P and broad range of phenomena coupled to the pinning and sliding of the CDW depend on impurities [1].

However consistent understanding of the effect of impurities on the CDW gap is still lacking. This effect appears to be quite distinct from that in usual semiconductors. For example, STM study of $NbSe_3$ demonstrates that doping can either decrease (Fe) or increase (Co) the gap value 2Δ to the tens of percent already at dilute concentrations [2]. Discrete states inside the CDW gap were predicted for a single impurity site in 1D metallic chain and tail of states was predicted for a substantial concentration of weak-pinning impurities [3]. Intra-gap states in *o*-TaS_3 were observed in a recent photoconduction spectral study [4] but were not identified with impurities. A tail in bolometric response was observed [5] but the authors argued whether it originates from impurities or from other effects.

Investigation of gap features in relatively small samples of TaS_3 that are non-suitable for STM or ARPES techniques is possible however in photoconduction spectra study. A photoconduction spectrum close to fundamental absorption edge is defined mainly by electronic absorption spectrum of the sample which allows one to exclude phonon absorption crucial in bolometric response studies, as well as absorption by thermally excited electrons and holes. In this paper we report the results of the studies of the indium doping effect on the CDW gap in q-1D conductor *o*-TaS_3 investigated by means of the photoconduction spectroscopy.

2. Experimental

We employed the method developed by Gill [6] for $NbSe_3$ for introduction indium into *o*-TaS_3 samples. Namely, Gill found that heating of $NbSe_3$ with indium contacts for one hour at 120 °C increases the bulk concentrations of In by approximately 0.1 atomic % throughout the 2-mm length sample owing to high coefficient of In diffusion. Indium was presumed to intercalate the crystals.

We studied two samples of *o*-TaS_3 denoted below as samples #G and #Y one of which (sample #G) was the control sample. The sample #G was chosen from the batch synthesized by R.E. Thorne and the sample #Y was chosen from the batch of crystals grown in IRE RAS by direct reaction of high-purity Ta and S in a quartz tube at a

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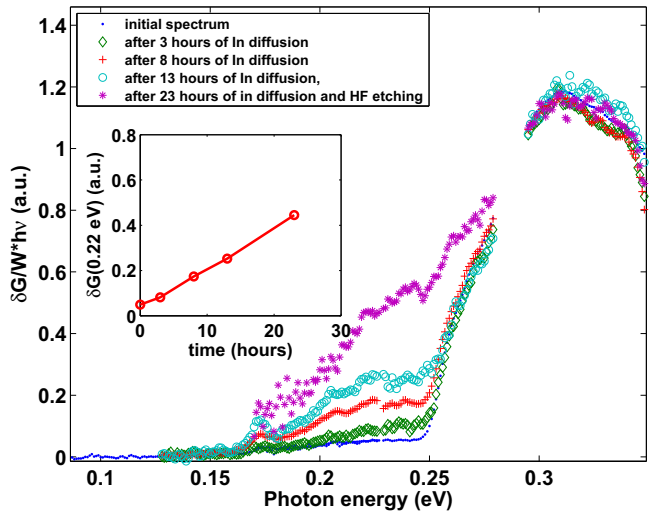

Fig. 1. Evolution of the photoconduction spectrum of the specimen of the *o*-TaS_3 with consequent In processing. Five spectra correspond to different time of In processing; *y*-axis shows photoconductivity normalized by power of incident light, beside these all spectra are normalized to unity at maximum for convenience. $T=40$ K, voltage applied to the sample is below $E_{th} \times l$ where l is the sample's length and E_{th} — threshold field for the onset of the CDW motion. Inset: the relative value of photoconductivity at 0.22 eV versus the total processing time.

temperature gradient 680–710 °C for 10 days. The sample #Y contacts were made of indium by the cold soldering. The width of each In contact was $d \sim 200$ μm, the distance between contacts — 387 μm, the sample cross-section — 2 μm^2. During the heating processing the sample #Y was kept at 120 °C under the constant Ar flow for 1 up to 10 h. Full data set which consists of photoconduction spectra, *IV* curve sets and temperature dependencies of resistance was measured between the processing procedures. In addition, we also performed heating in the air and did not found any difference in the character of spectral changes. Therefore the respective spectra are also included in the data set (see Fig. 1). The same effect of the heating in Ar atmosphere and on the air indicates absence of the noticeable contribution in photoconduction from the surface oxidation.

When the total duration of the processing reached 23 h we performed etching of the sample #Y in concentrated hydrofluoric acid (HF) [7] to get rid of possible surface states caused by possible surface oxidation. The procedure was to dip the sample in HF for 60 s then clean it in a flow of a distilled water. The full data set was collected before and after etching.

The control sample #G had the gold contacts deposited by the thermal evaporation and no indium was used for attachment of the sample to the measurement circuit. We applied the same heating processing and collected the full data set for the sample #G before and after the processing.

The temperature-dependent variation of conduction and *IV* curves were measured by the DC technique in two-contact configuration in the voltage-controlled regime. We used the same photoconduction measurements setup as in our earlier works [4]. It consists of light-induced conduction variation measurement by the standard lock-in technique in the two-contact configuration with the sample placed in cryostat in He heat-exchange gas at the normal pressure. The temperature was controlled with the accuracy of 0.1 K. All the photoconduction spectra presented in this work represent photoconductivity normalized by the number of incident photons, $\delta G\hbar\omega/W$, where $\delta G = \delta I/V$ is photoconduction, δI is measured photo-current, V, W, $\hbar\omega$ are the voltage, light intensity and photon energy respectively.

3. Results

3.1. Photoconduction spectra

Fig. 1 shows the set of photoconduction (PC) spectra obtained on different stages of the processing. The initial spectrum (empty circles) shows a tail of states starting at $\hbar\omega^* = 0.15$ eV followed by a sharp growth of photoconduction at $\hbar\omega = 0.25$ eV. The latter we ascribe to the Peierls gap edge for the reasons explained below. The gradual increase of the photoconductivity at photon energies $0.15\ \text{eV} < \hbar\omega < 0.25$ eV with growth of the total processing time with respect to photoconductivity at $\hbar\omega = 0.25$ eV is clearly seen in Fig. 1. The inset in Fig. 1 shows the dependence of the photoconduction at $\hbar\omega = 0.22$ eV on the total processing time. Processing shorter than 13 h affects only the amplitude of the photoconduction tail at low photon energies $\hbar\omega < 0.25$ eV but 23 h processing smears out the gap edge by $\delta\Delta \sim 50$ meV. Such a behavior is consistent with previous results for *o*-TaS_3 spectra: relatively thick fresh-cleaved samples demonstrate pronounced gap edge, i.e. photoconductivity drop at values close to $\hbar\omega = 0.25$ eV, whereas thin and/or old samples always show very smeared gap edge.

Changes in PC spectra proportional to the time of In introduction at $\hbar\omega < 0.25$ eV let us conclude that 0.25 eV corresponds to the band–band transition over the CDW gap 2Δ. But onset of the photoconduction is close to $\hbar\omega^* = 0.15$ eV matching the value obtained from the transport measurements for this particular sample $2\Delta_{tr} \approx 0.15$ eV where $\Delta_{tr} = 900$ K is resistivity activation energy, as well as reported transport values [8,9]. Such a discrepancy between the onset of PC and the sharp drop of PC, i.e. tail of states, is characteristic even for nominally pure *o*-TaS_3 PC spectra [4] and may include contributions from different effects. One possibility is the imperfect nesting [10,11] resulting in order parameter modulation in k-space and indirect gap $2\Delta_i$ with phonon-assisted transitions at $2\Delta_i < \hbar\omega < 2\Delta$ eV. The other contribution may arise from self-trapped states typical for q-1D systems [12]. In addition, Tüttö and Zawadowski obtained [3] that impurities in q-1D conductor in the weak-pinning limit would cause the region inside the gap to be filled by states if the distance between impurities is smaller than CDW amplitude coherence length ξ_0. This would shift the gap edge to the new value $2\Delta' = 2\Delta(1-t^2)^{1/2}$ where $t = T/v_F$ is impurity backscattering amplitude over the Fermi velocity. Considering $\xi_0 \sim 10$ nm [3] we obtain the corresponding concentration of impurities n_{imp} of the order $10^{18}\ \text{cm}^{-3}$–10^{-4} at% which is consistent with the values for nominally pure samples. Taking shifted gap edge value $2\Delta' = 0.15$ eV and direct gap value $2\Delta = 0.25$ eV one gets $t=0.6$ which is close to $t=0.7$ obtained in Ref. [5] and consistent with the case of weak pinning. We conclude that the observed photoconductivity increase with the In introduction corresponds to the latter case. However, the density of states obtained by considering both imperfect nesting and the modulation of the gap value in k-space gives remarkable fit to the spectral features at $\hbar\omega > 2\Delta$, see [15].

The curve plotted with stars in Fig. 1 corresponds to the photoconduction spectrum of the sample #Y etched in HF after 23 h of processing. One of the In contacts was replaced by a new one after the etching, so the resulted inter-contact distance l becomes 30 μm shorter ($l_{new} = 357$ μm). No changes in the spectra associated with etching or contact replacing were observed. However we detected small etching-induced decrease of the curvature of $\ln G(1/T)$ at the temperature range 50–100 K. Related type $G(T)$ change with decreasing of the sample thickness of *o*-TaS_3 whiskers was reported before [14]. The result of etching on *IV* curves corresponds to the decrease of conductance, both linear and nonlinear, obviously due to the cross-section area reduction. The absence of spectral changes is consistent with the statement that In is not confined to the surface [6].