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Charge-density waves physics revealed by photoconduction

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ABSTRACT

The results of photoconduction study of the Peierls conductors are reviewed. The studied materials are quasi-one-dimensional conductors with the charge-density wave: $K_{0.3}MoO_3$, both monoclinic and orthorhombic TaS_3 and also a semiconducting phase of NbS_3 (phase I). Experimental methods, relaxation times, effects of illumination on linear and nonlinear charge transport, the electric-field effect on photoconduction and results of the spectral studies are described. We demonstrate, in particular, that a simple model of modulated energy gap slightly smoothed by fluctuations fits the available spectral data fairly well. The level of the fluctuations is surprisingly small and does not exceed a few percent of the optical energy gap value.

1. Introduction

Despite of impressive development of modern experimental methods such as ARPES, Fourier spectroscopy, femtosecond spectroscopy, and scanning tunneling spectroscopy, more than 150 years old photoconduction remains to be very useful method for both material characterization and study of underlying physics. Application of this method for investigation of the quasi-one dimensional (q-1D) conductors with the charge density wave (CDW) provides a unique information on various aspects of very reach physics of the Peierls conductors (see [1] as a recent review). Here we present a brief overview of the modern state of research in this area.

The traditional definition of photoconduction as a phenomenon in which a material becomes more conductive due to absorption of electromagnetic radiation does not work in the case of q-1D conductors with the CDW where light absorption under certain conductions (temperature and voltage range) may make the material less conductive. So we will consider photoconduction as a phenomenon in which a material changes its conduction in any direction due to light absorption at a *constant* temperature. The latter condition is essential to distinguish photoconduction and the bolometric effect where conductance changes are caused by temperature variation caused by light absorption.

The underlying physical mechanisms of photoconduction are related to light-induced electronic transitions. Only those transitions contribute into conductance, which change the current carrier concentration or mobility. In this respect photoconduction study and dielectric spectroscopy or bolometric response study provide different information, because the latter are also sensitive to electronic transitions which do not change conductance.

We will use here the following notation: G is a sample conductance, $\delta G \equiv G(W) - G(0)$ is photoconductance, i.e. the conductance variation due to illumination, W is a light intensity at the sample position, I, V, $R \equiv 1/G$ and L are respectively the electric current, voltage, sample resistance and length, $E \equiv V/L$ is the electric field, applied to the sample, $2\Delta_{opt}$ and $2\Delta_{tr}$ are the optical and transport energy gaps, and D is the Gauss fluctuation dispersion. The spectral data discussed below are normalized to the flow of incident photons i.e. to the ratio $S(\hbar\omega) \equiv W/\hbar\omega$.

2. Experimental methods

Photoconduction study needs a light source optically coupled to a sample. In its simplest realization, a LED capable to operate at low-temperatures can be placed in the close vicinity of the sample. Special precautions should be undertaken to minimize the heating and capacitive coupling of the LED with the sample. Temperature dependence of the LED spectrum should also be taken into account in some special cases. As the LED-emitted light power is controlled by the current flowing through the LED, the light intensity control is also simple. This method was widely used for investigation of the temperature and time evolution of the photoconduction current in q-1D conductors [2–5].

Spectral study is a little bit more complex. Ogawa et al. [6] used short laser pulses (200 fs) generated by OPG-OPA (optical parametric generator and optical parametric amplifier) to study the electro-optical response of $K_{0.3}MoO_3$. In our experiments we used

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the grid monochromator IKS31 with a globar or quartz lamp (the choice depends on the spectral region) as a light source, the light was modulated mechanically and the photoconductance signal was measured by a lock-in amplifier [7–10]. Note that nonlinearity of photoconduction response, $\delta G(W)$, intrinsic to all Peierls conductors studied up to now complicate usage of advantages of Fourier spectroscopy.

3. Temperature and electric field dependences of photoconductance

To our knowledge photoconduction was studied in four inorganic q-1D materials: the blue bronze $K_{0.3}MoO_3$ and transition metal trichalcogenides: monoclinic and orthorhombic TaS_3, and also in NbS_3 (phase I). The first three materials are typical Peierls conductors with the Peierls transition temperatures $T_P = 180$ K for the blue bronze, 220 K for *o*-TaS_3, and 240 K and 160 K for *m*-TaS_3. NbS_3 (phase I) is considered as an anisotropic semiconductor with 1 eV optical gap value [1].

3.1. Temperature dependences of photoconductance

Fig. 1 demonstrates the difference between the bolometric and photoconduction responses in CDW conductors. It shows a typical set of temperature dependences of the photoconductance together with the temperature dependence of the ohmic conductance, $G(T)$, and its derivative, dG/dT, of a thick *m*-TaS_3 sample. Bolometric response, being proportional to the illumination-induced temperature increase ($\delta T = 3.4$ mK in this particular case), follows $(dG/dT)\delta T$ dependence, whereas the photoconductance depends on the temperature in a very different way. It is clear from this figure that a good thermal contact is critical for photoconduction study. We also found that the bolometric response is practically undetectable in much thinner samples. Note that dG/dT drops dramatically in the low-temperature region, whereas photoconductance remains almost constant. As a consequence, it is very difficult to study bolometric response of Peierls conductors at helium temperatures. It seems therefore that the first photoconduction spectrum of q-1D conductor was actually obtained by Herr et al. in 1986 in their low-temperature bolometric study [11].

Photoconduction in the studied CDW conductors is detectable in the low-temperature range only at $T \lesssim T_P/2$. Temperature dependence of photoconduction measured at fixed illumination intensity depends mostly on the temperature dependence of the relaxation time of the nonequilibrium current carriers, τ. In its turn, the relaxation time can be obtained from direct measurements of temporary response of photocurrent after switching the illumination on or off. The photoresponse kinetics was measured in blue bronzes by using the laser excitation [6] and in *o*-TaS_3 with LED excitation [2]. In both cases the millisecond time scale of the characteristic time, τ, was observed. It is known now that:

1. τ depends on the voltage applied and decreases with the voltage when it exceeds the threshold one for onset of nonlinear conduction [6];
2. τ follows the activation law at $T \gtrsim T_P/3$ [2];
3. τ depends on the light intensity in a way which corresponds to the collisional recombination mechanism [2], intensity-dependent relaxation times are observed in the low-temperature region at $T \lesssim T_P/4$ [2–4];
4. long-time logarithmic-type relaxation appears in the low-temperature region at $T \lesssim T_P/4$ [4].

Relatively long relaxation time observed in photoconduction measurements allows to consider the current carriers (electrons and holes) as well-defined physical objects justifying thereby the usage of the semiconductor model [12] for description of many properties of the Peielrs conductors. Note, however, that the initial and final energy states of optically excited electrons and holes may be different due to intrinsically high polarizability of crystal lattices of studied q-1D materials [13].

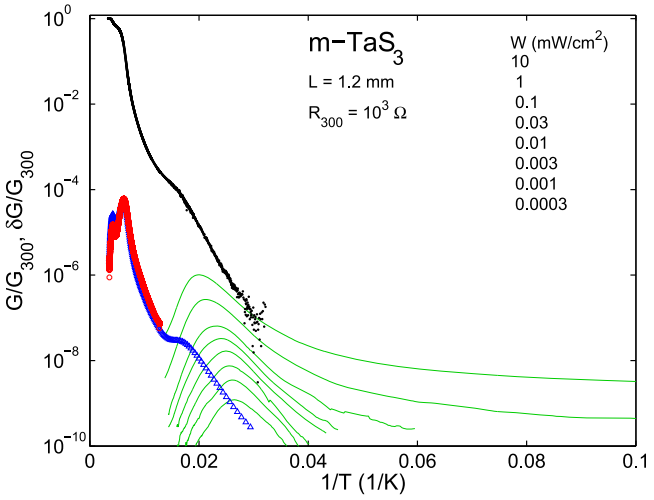

Fig. 1. Temperature dependences of conductance of a thick sample of monoclinic TaS_3 (points); $\delta T(dG/dT)$ (triangles); bolometric response at $W = 10$ mW/cm^2 (circles); a set of photoconductance dependences obtained at W values listed in the figure (lines). All the curves are normalized to G_{300}.

3.2. Effect of illumination on CDW kinetics

There is very interesting effect of illumination on the CDW kinetics. This effect was observed in the blue bronze, $K_{0.3}MoO_3$, where illumination-induced growth of the threshold field was found [6]. The effect was then reproduced and studied in details in *o*-TaS_3 [2,4]. It was shown that the effect results from the illumination-induced change of the screening which affects in its turn the elastic modulus of the CDW. The observed dependence, $E_T \propto G(W)^{1/3}$, corresponds to 1D pinning of the CDW.

Slow CDW motion (CDW creep) at $E \lesssim E_T$ suppresses phoco-conduction [2]. Negative photoconduction ($\delta G < 0$) is observed at $E > E_T$ [2,4,6] due to illumination-induced growth of E_T.

Surprisingly, a growth of photoconductance with the voltage applied can however be observed in some samples in the low-temperature region in the nonlinear conduction regime. In particular, such a growth was observed in both orthorhombic (see, e.g. Fig. 4 in Ref. [9]) and monoclinic modifications of TaS_3 (Fig. 2, see also [5]). Qualitatively, such a complex behavior corresponds to the competition between at least two physical mechanisms working in opposite directions. The first one is a mechanism of spatial separation of electrons and holes which complicates their recombination and is related to fluctuations of the chemical potential [4]. This mechanism smoothly disappears when the CDW starts to move in the electric field. The second one requires the presence of electronic states (impurities, defects, excitons) which are capable to capture electrons and provide their recombination, have relatively small excitation energy and can be depleted or destroyed by the electric field 10–100 V/cm. Electric-filed dependent energy states were really observed in the photoconduction spectra of *o*-TaS_3 [7], but their origin is still not entirely clear.