Fundamental absorption edge of the Peierls insulator of orthorhombic tantalum trisulfide

M. E. Itkis and F. Ya. Nad'
Institute of Radio Engineering and Electronics, Academy of Sciences of the USSR

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The spectral distribution of the response of orthorhombic TaS_3 is obtained. It is shown that a fundamental absorption edge at energies corresponding to the Peierls gap as well as a narrow absorption line at the center of the gap exist.

Many papers have been devoted to the study of various effects which are specific to inorganic quasi-one-dimensional conductors (see, for example, Ref. 1). However, the energy structure and the nature of the electronic excitations which determine the mechanism of the conductivity of these materials in the Peierls state are yet to be determined. The study of the spectral dependences of the optical properties can yield useful information for the resolution of these problems. The crystals of quasi-one-dimensional inorganic conductors, such as $NbSe_3$ and TaS_3, have the shape of filaments with transverse dimensions of $10\times 10\ \mu$m, which greatly complicates the investigations of optical absorption and reflection.

In this work we investigate the response of orthorhombic TaS_3, i.e., the relative change in the resistance $\Delta R/R$ under the action of radiation in the spectral range 3–22 μm at temperatures ranging from 90 to 320 K, both above and below the temperature of the Peierls transition $T_p \simeq 220$ K. The measurements were performed with a bias voltage on the specimen corresponding to fields lower than the threshold field E_T for the onset of motion of the charge density wave (CDW).[2–4] In the five specimens that we investigated, E_T varied from 0.3 to 1.5 V/cm.

In the entire temperature and spectral range investigated, including the microwave region (9.5 GHz), the response is, first of all, proportional to $d\ln R/dT$ and, second, it is shifted by 90° in phase relative to the incident radiation modulated at a low frequency (40–200 Hz). As the modulation frequency is increased, the response decreases in inverse proportion to it. In this case, however, it was not possible to separate out the component of the response which was in phase with the modulated radiation, which could correspond to some fast processes, for example photoconductivity. The time constant of the microwave response was 0.1 s. All of these results, as well as the data in Ref. 5, show that the response of TaS_3 crystals to the action of both IR and microwave radiation has primarily a bolometric character.

Figure 1 shows the spectral distribution of the response per unit incident power for specimen A with $E_T = 0.8$ V/cm($T = 100$ K). At all temperatures $T \lesssim T_p$, the response depends essentially on the energy of the radiation quanta. The magnitude of the response, but not the shape of its spectral distribution, depends on the thickness of the specimen d. The response was greater in thin specimens ($\sim 3\ \mu$m) than in thick specimens ($> 10\ \mu$m), i.e., apparently in thin specimens $\alpha d \simeq 1$ (α is the absorption

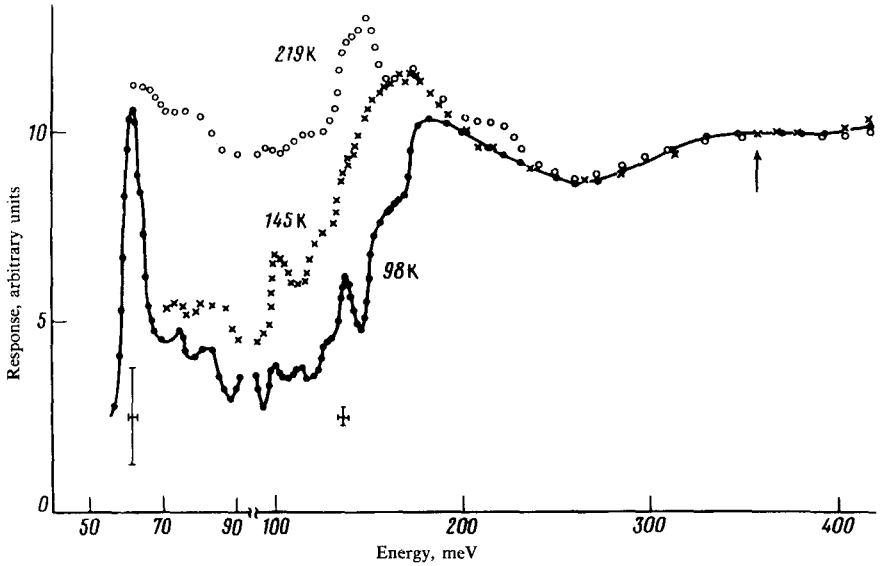

FIG. 1. Spectral distribution of the response of specimen A ($E_T = 0.8$ V/cm) at the temperatures indicated on the curves. The curves are drawn to scale at the point indicated by the arrow.

coefficient). The decrease in the response in a narrow spectral interval, the presence of narrow lines (see Fig. 2), and the dependence on the thickness show that the response is determined primarily by the p processes and absorption accompanying optical transitions, which are followed by relaxation accompanied by transfer of the excitation energy to the lattice, i.e., heating of the specimen.

It is evident from Fig. 1 that in the energy range 400–250 meV the magnitude of the response depends weakly on the energy of the radiation quanta for all temperatures. At low temperatures (the curve for 98 K) the spectral distribution of the response has two basic features. First of all, after the peak at $h\nu_1 \approx 184$ meV, the absorption with edge at $h\nu_2 \approx 125$ meV falls off considerably and, second, there is a narrow absorption peak at $h\nu_3 \approx 62$ meV with a fine structure appearing with increased spectral resolution. We note that $\nu_2 \approx 2\nu_3$. As the temperature is increased (Fig. 1), the peak at $h\nu_1$ moves toward lower energies and remains right up to the highest temperatures that we measured (320 K). In addition, the absorption increases continuously in the range of energies from ν_2 to ν_3.

Figure 2 shows the spectral distribution of the response of specimen B with a lower $E_T = 0.3$ V/cm for three temperatures $T < T_p$. Just as for specimen A, the absorption, whose edge—omitting the structure—lies near the 120 meV, falls off. Against the background of the decrease, there is a distinct structure in the form of sharp peaks at energies of 157, 136, and 100 meV, as well as lower peaks in the region 70–90 meV. An analogous structure was observed in all specimens investigated, in-

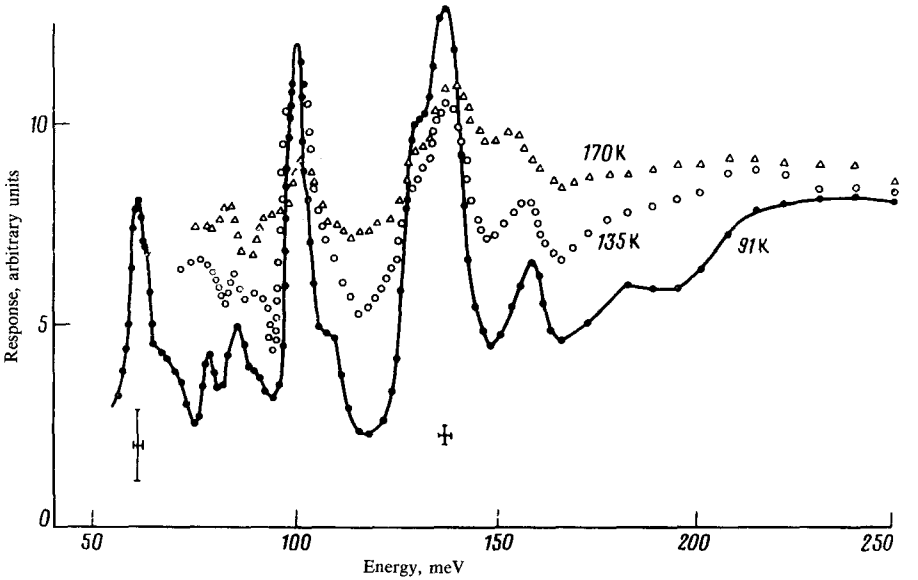

FIG. 2. Spectral distribution of the response of specimen B ($E_T = 0.3$ V/cm) at the temperatures indicated on the curves.

cluding in specimen A (Fig. 1), but in a weaker form (see also Ref. 5). For specimen B the peak at $h\nu_3 \approx 61$ meV remains, but its magnitude is relatively smaller than in specimen A with the higher value of E_T. The position of the peaks remains essentially unchanged as the temperature is increased up to 170 K, but their magnitude decreases and the structure is smeared. The observed structure is not a result of diffraction or interference, since the position of the peaks did not change in specimens with considerably different transverse dimensions.

As is well known, in orthorhombic TaS_3 in the temperature range 100–200 K an activation dependence of the conductivity with an activation energy $\Delta \approx 700$–800 K(60–70 meV) is observed.[2–4] The growth of the absorption that we observed at $h\nu_2 \approx 125$ meV is, in our opinion, due to optical excitations of electron-hole pairs from the ground state with CDW through the Peierls gap and corresponds to the fundamental absorption edge of orthorhombic TaS_3. The excitation energy that we obtained agrees well with the thermal energy of activation 2Δ. The smearing of the absorption curve near the edge and its structure are apparently related to the strong interaction of electronic excitations with phonons, corresponding to Peierls deformation of the lattice.[6] The growth of the absorption in the forbidden energy range with increasing temperature (Fig. 1) indicates a gradual transition from a gap to a pseudo-gap. The continued presence of the peak in the spectral curve near 150 meV up to a temperature of 320 K, considerably higher than the temperature of three-dimensional ordering T_p, apparently indicates that the singularities in the density of states corresponding to the

presence of the pseudo-gap remain at $T > T_p$. This result agrees with the observation of diffraction peaks, corresponding to a superlattice with $T > T_p$, in the electron-diffraction pattern.[7]

We associate the narrow peak at 62 meV with soliton states at the center of the forbidden band.[6] This is also supported by the frequency dependence of the conductivity,[8] which we observed in our previous measurements, and the existence of the finite density of states near the Fermi level at the center of the Peierls gap. Such soliton states can also be formed on defects in a crystal, as well as at boundaries separating the regions of commensurability. The fact that it is not possible to separate the photoconductivity against the background of the bolometric signal is due to the very short lifetime of optically excited electrons and holes as a result of their rapid relaxation (self-localization) in the soliton state over a time $\sim 10^{-13}$ s.[9]

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