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Low-temperature metallic conductivity in the semiconductor TISe having a chain structure

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Abstract. The results of experimental investigations of the electrical conductivity, magnetoresistance and Hall effect in the semiconductor TISe with a chain structure are presented. The measurements of electrical conductivity have been carried out in two directions, i.e. parallel and perpendicular to the crystal c axis (the chain orientation). Galvanomagnetic measurements were made in magnetic fields of up to 60 kOe at different orientations of the magnetic and electric fields.

The impurity conductivity is metallic in character with a negative magnetoresistance at low temperatures. We show that the low-temperature data can be explained by the model considering TISe as a disordered system with a low-dimensional conductivity near the percolation limit.

1. Introduction

The interest in the kinetic and galvanomagnetic properties of highly anisotropic semiconductors is due to the possible observation of low-dimensional effects. Because of the three-dimensionality of the electronic states in semiconductors with layer and chain structures [1,2], it is often supposed that the existence of low-dimensional effects is due to a specific type of defect in the crystalline structure of these semiconductors [3–5]. On the basis of only this hypothesis, i.e. on the basis of the existence of two-dimensional stacking faults, the main unusual transport and galvanomagnetic properties of $A^{III}B^{VI}$ layered semiconductors are the different conductivity mechanisms parallel and perpendicular to the plane of the layer [3], a two-dimensional cyclotron resonance effect [4] and the quantum Hall effect [5].

Although much work has been done on semiconductors with layer structures, few investigations have concerned semiconductors with a chain crystalline structure. In this paper we present the results of investigations on the temperature dependences of the resistivities in two directions in TISe single crystals in the 1.3-300 K temperature range as well as the magnetoresistance and Hall effect measurements.

2. Experimental details

Measurements of the resistivities were carried out using an alternating-current fourcontact method [6] in two directions (parallel and perpendicular to the crystal c axis (the chain direction)) in the temperature interval 1.3-300 K. The prepared specimens were in the form of rectangular plates with the chains lying in the plane of the plate. The indium contacts met the requirements discussed in [6].

Magnetoresistance and Hall measurements were performed in the 1.3-4.2 K temperature range in magnetic fields of up to 60 kOe. Only one direction of current (parallel to the c axis) was investigated in the galvanomagnetic measurements. The magnetic field was perpendicular to the chain direction. Special measurements of magnetoresistance were performed at different angles between the magnetic field and c axis.

3. Results

The most typical temperature dependences of ρ_{\parallel} and ρ_{\perp} in TISe single crystals are presented in figures 1-4. The data were obtained for different TISe crystals randomly chosen from various ingots prepared by various methods without special doping. As seen from figures 1-4, there is a small anisotropy in TISe which varies from sample to sample, including 'reverse' anisotropy (figure 1). There are three temperature intervals with specific temperature dependences for the resistivity: the 'high-temperature' interval 300-50 K; the 'intermediate-temperature' interval 50-4.2 K; the 'low-temperature' interval 4.2-1.3 K. As a rule, at high temperatures the resistivities (both ρ_{\parallel} and ρ_{\perp}) decrease with decreasing temperature according to a $\rho \sim T^{3/2}$ owing to a phonon scattering mechanism. In the intermediate-temperature range, exponential rises in ρ_{\parallel} and ρ_{\perp} are observed with decreasing temperature. The activation energy is in the range 3-6 meV, which is approximately equal to the activation energies of shallow acceptor levels in TISe.



Figure 1. Temperature dependence of resistivity for TISe crystal sample 26.

The low-temperature behaviour of resistivity in TISe is of special interest. Two types of behaviour in this temperature range were observed. In one case the resistivity rises with decreasing temperature with a low activation energy (about 1 meV) (figure 2)In the other case the resistivities remain almost unchanged at low temperatures (figure 3). Such 'metallic' behaviour can be observed from 2.5 to 5 K depending on the resistivity before the transition to the metallic regime; the lower the resistivity before the transition, the higher is the 'transition temperature'. In some



Figure 2. Temperature dependence of resistivity for TiSe crystal sample 6.



Figure 3. Temperature dependence of resistivity for TISe crystal sample 5.



Figure 4. Temperature dependence of resistivity for TISe crystal sample 21.

specimens with a metallic behaviour a hump is observed in the log $\rho_{\parallel(\perp)} = f(10^3/T)$ dependences (figure 4), as in the case of Ge [7].

A correlation exists between the electrical properties in the low-temperature region described above and the magnetoresistance measurements. Firstly, there is

a positive magnetoresistance (PM) in the first type of specimens at low temperatures, up to the maximum values of the applied magnetic fields. Secondly, the specimens with a metallic type of conductivity have a negative magnetoresistance (NM) in the metallic region and a PM at higher temperatures. As a rule, the temperature of inversion (from NM to PM) coincides with the temperature of 'metallization'. In particular, the inversion temperature in specimens with a hump corresponds to the maximum of the hump.

PM in all samples can be well described by $\Delta \rho / \rho \sim H^2$, i.e. the classic law. The field dependence of the NM depends on the temperature (figure 5). At 1.3 K there is a quadratic dependence of the NM on the magnetic field. At higher temperatures the NM begins to saturate with increasing magnetic field.



Figure 5. Field dependences of magnetoresistance at various temperatures (sample 5): curve 1, 4.20 K; curve 2, 3.77 K; curve 3, 3.60 K; curve 4, 3.34 K; curve 5, 3.08 K; curve 6, 2.82 K; curve 7, 2.07 K; curve 8, 1.30 K.



Figure 6. Field dependences of PM (curves 1, 3, 5, 7 and 9) (T = 4.20 K) and NM (curves 2, 4, 6, 8 and 10) (T = 1.30 K) at various mutual orientations of the electric field E and magnetic field H: curves 1 and 2, $H||n, H \perp E$; curves 3 and 4, $H^{n}n = 35^{\circ}, H \perp E$; curves 5 and 6, $H^{n}n = 55^{\circ}, H \perp E$; curves 7 and 8, $H^{n}n = 35^{\circ}, H^{n}E = 55^{\circ}$; curves 9 and 10, $H^{n}n = 55^{\circ}, H^{n}E = 35^{\circ}$. (*n* is the normal to the surface which contains the contacts.)

The field dependences of the magnetoresistance for different mutual orientations of the magnetic field and crystal axes are shown in figure 6. As is shown in figure 6, there is only a slow dependence of the PM on the crystal orientation, whereas the NM depends strongly on crystal orientation even for a fixed angle between the magnetic field and the crystal c axis (figure 6, curves 4 and 6). However, we could not find any definite law for the NM dependence on magnetic field orientation.

As mentioned above, Hall measurements were performed for only one geometry, i.e. with the magnetic field directed perpendicular to the electric field (c axis). The evaluated concentrations of free carriers were as follows. In samples with a metallic type of conductivity, $n = 10^{16}$ cm⁻³ (sample 5) and $n = 7 \times 10^{16}$ cm⁻³ (sample 21). In sample 26 with an activated type of conductivity (figure 1), n turned out to be 4×10^{16} cm⁻³ at 4.2 K and 6×10^{12} cm⁻³ at 1.3 K. The extremely small values of n obtained at 1.3 K for specimen 26 are due to background free carriers.

4. Discussion

Since the mechanisms of high- and intermediate-temperature conductivity in TISe seem rather clear, the interest is in the low-temperature conductivity. In the first type of specimen the low-temperature conductivity with a small activation energy is probably due to a hopping mechanism between impurity states. The metallic conductivity in the second kind of specimen needs detailed discussion.

Note that the concentration of impurities has not been obtained directly in the present work. Hall measurements in the low-temperature region give only a crude estimation of the impurity concentration. Nevertheless the values are very close to critical concentrations calculated from the measured activation energies of impurity states. Probably, the concentration of shallow impurities is very close to the critical values when metallic conductivity occurs.

The following experimental results are of importance.

(1) The values of metallic resistivities exceed by several orders of magnitude the 'allowed maximum' value of metallic resistivity in a three-dimensional case [8]. The 'maximum' value for two-dimensional metallic resistivity is also exceeded in some cases.

(2) There is no correlation between the metallic (or hopping) character of conductivity and the absolute value of resistivity in the low-temperature region. For example, the value of the metallic resistivity in specimen 5 (figure 3) is higher than that in specimen 6 (figure 2) with a hopping conductivity.

(3) There are high values of NM in the metallic region $(\Delta \rho / \rho \simeq 30-40\%)$.

The last fact can be explained by localization effects in a quasi-one-dimensional disordered system because the NM due to localization effects, even in a two-dimensional case, does not exceed 1-3% [9].

The results testify to the fact that the low-temperature conductivity in TISe crystals has a low-dimensional (most probably, one-dimensional) character. The question arises of how to explain the absence of any definite anisotropy of the conductivity, the common mechanism of the temperature dependence of conductivity in two directions (parallel and perpendicular to the c axis) and the orientational behaviour of the magnetoresistance in TISe crystals. We believe that all the above-mentioned data can be explained by the crystal structure of TISe supposing that at the given orientation of electric field (parallel or perpendicular to the c axis) the current has no definite (i.e. parallel or perpendicular to the c axis) direction. In real TISe crystals the accidental deviations of chains from the c axis as well as their termination seem possible.

Thus, one can consider TISe as a percolation system with quasi-one-dimensional trajectories which have no definite orientation in the crystal.

5. Conclusion

We conclude that the transport properties of TISe are determined by its crystal structure. In effect we observed the one-dimensional character of the conductivity in a disordered system with localization effects arising from the chain crystalline structure of TISe.

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