Nature of the conductivity anisotropy and distinctive features in the localization of electrons in layered indium selenide

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There is a temperature interval in which the conductivity in the direction transverse with respect to the layers in InSe results from a hopping conductivity with a variable hopping length, while the conductivity along the layers results from extended states of the conduction band. A model capable of explaining this unusual situation is discussed.

The theory of the hopping conductivity of uniform crystals does not allow a substantial anisotropy of the conductivity.[1] A pronounced anisotropy in the conductivity has been achieved in plastically deformed Ge samples, where the conductivity has been determined in one direction by the Mott law, while in a mutually perpendicular direction it has been determined by an impurity band which results from the "collection" of impurities at a dislocation. It is accordingly worthwhile to determine the nature of the low-temperature anisotropy in the conductivity of layered III–VI semiconductors, whose magnitude, $\sigma_{\parallel}/\sigma_{\perp} \approx 10^2$–$10^5$, cannot be explained on the basis of the present understanding of the band structure of these crystals[3] (here and below, the symbols $\parallel$ and $\perp$ indicate the directions with respect to the plane of the layer).

To solve the question of the nature of the anisotropy in the conductivity of layered crystals, we need data on the low-temperature behavior $\rho_{\parallel}(T)$ and $\rho_{\perp}(T)$. Data of this sort are not available for III–VI crystals because of the complexities of the

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corresponding experiments, which stem from the high ohmic resistance of layered semiconductors and —the most important point—the need to use special methods to study the temperature dependences $\rho_{\parallel}(T)$ and $\rho_{\perp}(T)$ in the case of a sample with a pronounced anisotropy which depends on the temperature. In the present experiments we used a four-probe method to measure the resistivities $\rho_{\parallel}$ and $\rho_{\perp}$ of indium selenide samples. The results were interpreted in accordance with Ref. 4, under the assumption that the potential electrodes are of a point nature and that the sample is infinite in the plane parallel to the c axis. The experimental capabilities were such that we were able to carry out measurements over the temperature interval 10–300 K. Resistance values $R < 10^6\ \Omega$ were measured within an error no greater than 10%. The curves of $\rho_{\perp}(T)$ and $\rho_{\parallel}(T)$ exhibit a high-temperature structural feature, which has been seen previously and which stems from a change in the scattering mechanism from a phonon mechanism (a scattering by homopolar optical phonons) to an impurity mechanism[5] and a manifestation of the temperature dependence of the electron density, as occurs in p-Ge (Ref. 6). For all of the samples studied, the plot of $\rho_{\parallel}(T)$ has an exponential region, $\rho_{\parallel} = \rho_{110} \exp(\epsilon_1/kT)$, at high temperatures (usually, 150–20 K), while at lower temperatures there is a saturation. The values of ϵ_1 for the various samples differ, lying in the range 10–30 meV, in agreement with the data of Ref. 5.

The dependence $\rho_{\perp}(T)$ is of particular interest. For an absolute majority of the InSe crystals studied, this dependence can be described by the Mott expression over a fairly wide temperature interval:

$$\rho_{\perp} = \rho_{10} \exp(T_0/T)^{1/4}, \qquad T_0 = \beta/kg(\mu)a^3,$$

where the value β depends on the dimensionality of the problem, k is the Boltzmann constant, $g(\mu)$ is the density of localized states at the Fermi level (ϵ_F), and a is the radius of states with an energy close to ϵ_F (Ref. 1). Figure 1 demonstrates the adherence to Mott's law for the samples from various lots. Our least-squares analysis of the experimental data on all the samples showed that the smallest mean square deviation

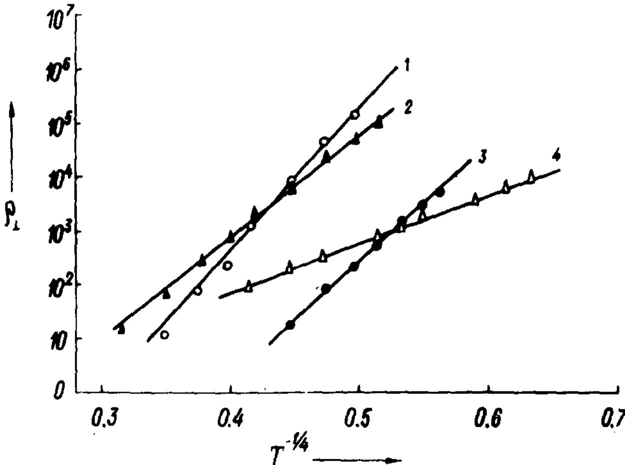

FIG. 1. Plot of $\log \rho_{\perp} = f(T^{-1/4})$ for various InSe samples. 1,2—Samples 3 and 9, not annealed; 3,4—samples 1 and 2, annealed.

(Δ) from a straight line $\rho_\perp = \rho_{\perp 0} \exp(T_0/T)^x$ ($x = 1/2$; $1/3$; $1/4$) was reached with $x = 1/4$. For sample 9 (Fig. 1), for example, we found $\Delta_{1/4} = 0.066$, $\Delta_{1/3} = 0.090$, and $\Delta_{1/2} = 0.136$. There thus exists a temperature interval within which the charge transport across the indium selenide layers occurs through a hopping of electrons between localized states whose energy lies in an energy band near the Fermi level, in the region of localized states. The width of this band decreases with decreasing temperature. The temperature interval in which this mechanism for the conductivity transverse with respect to the layers prevails differs from sample to sample. The indium selenide crystals subjected to an annealing exhibit a lesser anisotropy in their resistance and usually exhibit a Mott conductivity at low temperatures, $T \leqslant 50$ K (samples 1 and 2 in Fig. 1).

An unusual circumstance is of fundamental importance to an understanding of the nature of the conductivity anisotropy in layered crystals: The hopping conductivity across the layers of the InSe crystal occurs at the temperature at which there is an ordinary band conductivity along the layers ($\sigma_\parallel$). We should state that the data found in the present study, like the existence of a pronounced anisotropy in the conductivity of layered semiconductors in general, cannot be explained on the basis of arguments involving a uniform sample. As a model which might be capable of explaining the experimental data, we considered a layered crystal which contains regions of a disorder of the layers. In such regions, charge is transported exclusively through localized states in all directions. Each such region has a finite dimension d along the c axis, propagates over the entire area of the sample along its layers, and is responsible for the value of $\sigma_\perp$ and its temperature dependence. The component $\sigma_\parallel$, on the other hand, is governed by the existence of regions with an ordered arrangement of layers in the plane of the c axis, from contact to contact. Charge transport in these regions occurs through extended (band) states. On the basis of this model, the experimental results described above can be used to find the value of d. The maximum hopping length R_c at the lowest temperatures ($T_{\min}$) at which Mott's law still holds can be estimated on the basis of simple considerations[1]: $R_c/a = (3/8)(T_0/T)^{1/4}$. Taking the radius of the state to be the Bohr radius of an exciton in InSe, i.e., 50 Å, and adopting $\beta = 21$ (Ref. 1) for estimates, we can calculate the density of localized states, $g(\mu)$ and the value of R_c in InSe. The results for some typical samples are shown in Table I. If the disordered regions are to be capable of explaining the Mott conductivity, the condition $d \geqslant (4\text{–}5)R_c$ must hold. In view of the data in Table I, we should assume that the inequality $d \geqslant 1500$–3000 Å holds. The existence of these inhomogeneities cannot affect

TABLE I

№№ Sample	T_0, K	$g(\mu)$ eV$^{-1}\cdot$cm^{-3}	$T_{\min}$, K	R_c, Å
1	$6{,}7\times10^6$	$3{,}0\times10^{17}$	10	532
2	$2{,}1\times10^5$	$8{,}1\times10^{18}$	6	258
3	$1{,}9\times10^7$	$1{,}1\times10^{17}$	16	615
9	$3{,}6\times10^6$	$5{,}3\times10^{17}$	16	409

the results of electrical measurements if the dimensions of the electrodes are more than several tens of microns.

The results obtained in the present study contradict the theoretical arguments of Ref. 7 regarding the possibility of a one-dimensional localization in a three-dimensional crystal, based on the example of a layered semiconductor: According to those arguments, the behavior $\rho_\perp = \rho_{\perp 0} \exp(T_0/T)^{1/2}$ should be found in this case, but it is not found experimentally.

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