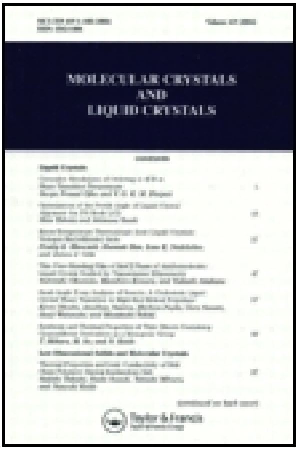

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INFLUENCE OF INTERCALATION ON THE ELECTROPHYSICAL PROPERTIES OF LAYERED SEMICONDUCTORS Bi_2Te_3 AND InSe

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Abstract The Li and Ba atoms were intercalated into the van der Waals gaps of Bi_2Te_3, solid solutions based on Bi_2Te_3 and β-polytype of InSe single crystals of n- and p-types. The temperature dependence of resistivity, the Hall effect and the Shubnikov- de Haas effect were investigated in host single crystals and after an inter calation. The intercalation of metallic atoms causes a change in carrier concentration and hence, the Fermi energy. The intercalated Bi_2Te_3 samples possess the same six-ellipsoidal Fermi surface as the host material 2D weak localization was observed in the host n-InSe which was suppressed by an intercalation.

INTRODUCTION

Bismuth telluride and indium selenide crystals belong to the family of layered semiconductors. Layered compounds are characterized by strong covalent bonds inside the layers and they have the predominantly van der Waals nature of interlayer bonds. The existence of van der Waals gaps allows one to inset guest atoms between layers. The influence of intercalation of metal atoms on electrophysical properties on InSe, for example, was studied for T>77K[1,2]. The influence of Li intercalation on the emission spectrum of γ-InSe was investigated in Refs.[2,3]. The influence of intercalation on Bi_2Te_3 was studied in Ref.[4]. Here we report on the influence of the intercalation with Ba and Li on the temperature dependence of the resistivity (4.2<T<300K) and on the magnetoresistance at T=4,2K (B<7T) of the β-InSe p- and n- type. We also investigated the energy spectrum of Bi_2Te_3 and solid solutions based on Bi_2Te_3 intercalated with Li and Ba with help of Shubnikov-de Haas effect.

SAMPLES AND EXPERIMENTAL TECHNIQUE

Single crystals of β-InSe (with the space symmetry group $D^4{}_{6h}$) and Bi_2Te_3 (with space symmetry group $D^5{}_{3d}$) were grown by the Bridgman method. The intercalation was performed by an electrochemical process. The number of intercalated atoms was calculated from the charge which flowed through the samples. During the measurements the current was directed in a basal plane along the c_2-axis and the magnetic field was applied perpendicular to the current along C_3-axis. A magnetic field up to 7 T was produced with help of a superconducting solenoid.

The host samples of InSe (n-type semiconductor) had a room temperature resistivity value of $\rho \approx 300$ Ohm cm. For synthesis of p-type InSe we doped InSe with 0.1 at.% Zn. The room temperature resistivity of the p-InSe samples equals $\rho \approx 3000$ Ohm cm.

RESULTS

With help of Ba or Li intercalation we can change the carrier concentration in layered semiconductors. The solid solutions $Bi_{0.5}Sb_{1.5}Te_3$ and $Bi_2Te_{2.75}Se_{0.25}$ were taken for investigations as the most important in thermoelectric devices. In p-type the concentration of holes decreases and in n-type the concentration of electrons increases after intercalation with metallic atoms. Some parameters of the samples at T=4.2K are shown in table 1. The sample 5 had p-type and the sample 8 had n-type conductivity. After measurements these samples were intercalated and investigated again as samples 6 and 9. We investigated SdH effect and angular dependence of the Fermi surface cross-sections of the host and intercalated Bi_2Te_3 crystals. The intercalated samples possess the same six-ellipsoidal Fermi surface as the host material.

In Fig. 1 we present the temperature dependence of the resistance of a host n-InSe sample (1), the same sample

TABLE 1 Parameters of samples at T=4.2K

N	composition	S Tesla	R_x (cm^3C^{-1})	$R_x\sigma$ ($cm^2V^{-1}s^{-1}$)	$\rho_{300}/\rho_{4.2}$
1	$Bi_{0.5}Sb_{1.5}Te_3$		+0.40	1900	24.4
2	$Bi_{0.5}Sb_{1.5}Te_3$<10^{18}Li>		+0.48	1450	19.4
3	$Bi_2Te_{2.75}Se_{0.25}$		-0.14	2200	18.6
4	$Bi_2Te_{2.75}Se_{0.25}$<10^{18}>		-0.10	2100	12.0
5	Bi_2Te_3	30±1	+0.50	7200	37.6
6	Bi_2Te_3<10^{18}Li>	26±1	+1.0	5600	29.0
7	Bi_2Te_3<10^{21}Ba>	24±1	+0.8	5800	26.8
8	Bi_2Te_3	25±1	-0.48	14000	39.4
9	Bi_2Te_3<10^{21}Ba>	30±1	-0.33	11100	37.0

S - extremal cross-section of the Fermi surface at $B||C_3$, $\rho_{300}/\rho_{4.2}$ - resistivity at T=300K devided to resistivity at T=4.2K, R_x - the Hall coefficient, $R_x\sigma=\mu_H$ - Hall mobility.

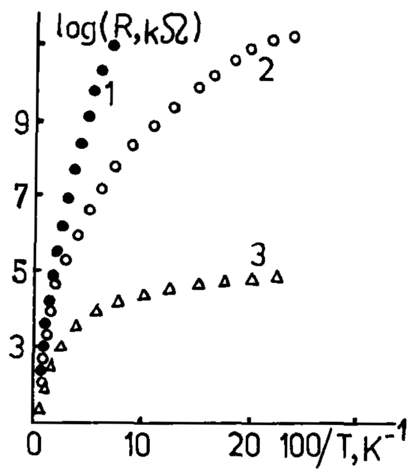
intercalated with Ba up to concentration of Ba atoms about $10^{20}cm^{-3}$ (2) and the same type of sample intercalated with Li with the same concentration (3). In the temperature range 100<T<300K we observed an activation behavior of the resistance with the activation energy $E_a\approx190$ meV. Resistivity is less in Ba_xInSe or Li_xInSe in the whole temperature range. The value of activation energy decreases from ≈190 meV to ≈170 meV.

We investigated also the influence of Ba or Li intercalation on electrical properties of p-InSe. In Fig. 2 we show the temperature dependence of the resistance for host p-InSe (curve 1), Ba (2) and Li (3) intercalated samples. A comparative study of n-InSe and p-InSe samples shows that Ba or Li intercalation enhances the n-character of the samples. For p-type Li_xInSe or Ba_xInSe, resistivity increases as x increases, due to the hole compensation as Li or Ba enters the lattice.

The positive transverse magnetoresistance observed in InSe for temperatures T>50K decreases as a result of cooling, and then became negative in low magnetic field rising in the absolute sense as a result of cooling to 4.2K. After the initial negative magnetoresistance a further increase in the magnetic field created a positive effect (Fig. 3, curve 1). The negative magnetoresistance has the following features: 1) it depends quadratically on the magnetic field in weak fields up to B≈0.01 Tesla; 2) lowering of T reduces the range of the quadratic dependence; 3) beginning from B≈0.03 Tesla the resistivity depended logarithmically on the magnetic field. After the intercalation the magnetoresistance becomes positive. The relative change in the resistance $\Delta R/R_0$ was very small for the intercalated samples (curve 2, Fig. 3).

DISCUSSION

The characteristic features of the magnetoresistance observed at T<10K in the host n-InSe samples are in full agreement with the theory of quantum corrections to the conductivity in the two-dimensional case [5], according to which the magnetoresistance should be quadratic in weak fields and logarithmic in strong fields. The quadratic dependence range should expand on increase the temperature, as observed experimentally. The results obtained indicate that at low temperatures the conductivity of our crystals was governed by the 2D electrons which exhibited weak localization, because of the capture of electrons by 2D defects in the basal plane, typical of $A^{III}B^{VI}$ layer crystals [6]. In n-type InSe at T<2K clear Shubnikov-de Haas oscillations were observed due to two-dimensional electrons present with a density of $2*10^{11}cm^{-3}$ [7].



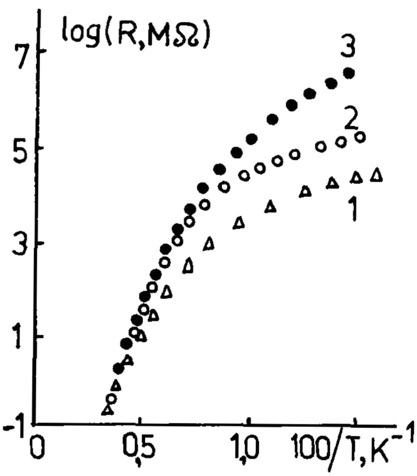


FIGURE 1 Dependence of the resistance (logarithmic scale) on the reciprocal of temperature: 1) n-InSe; 2) n-InSe<10^{20}Ba>; 3) n-InSe<10^{20}Li>.

FIGURE 2 Dependences of the resistance (logarithmic scale) on the reciprocal of temperature: 1) p-InSe; 2) p-InSe<10^{21}Ba>; 3) p-InSe<10^{21}Li>.

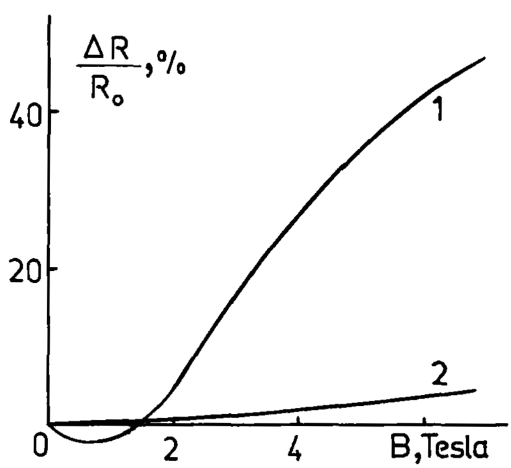


FIGURE 3 Dependence of the relative change in the resistance $\Delta R/R_0$ on magnetic field B at T=4.2 : 1) n-InSe, 2) n-InSe<10^{21}Ba>. R_0 is the resistance at B=0.

Ba or Li intercalation results in an increase of the free electron concentration in n-InSe and the weak localization regime disappeares. In Li_xInSe or Ba_xInSe samples we may observe only weak positive magnetoresistance (see Fig. 4), which is a typical for disordered metallic systems.

For p-InSe samples we observed an activation behaviour of the conductivity (see Fig. 3) with the energy of activation $E_a \approx 270$meV. For p-type Li_xInSe or Ba_xInSe the resistivity increases as x increase due to the hole compensation as Li or Ba enters the lattice.

At room temperature the change in conductivity due to intercalation is not so high as expected from the concentration of the intercalated atoms. It means that charge transfer from intercalated atoms to InSe matrix is not effective at this temperature. The same result was obtained by optical method for γ-InSe intercalated with Li [3].

In conclusion we may emphasize that the electrochemical reaction was reversible. Thus Li and Ba intercalated InSe or Bi_2Te_3 may be used in solid state ionic devices. The change of carrier concentration is a result of the Fermi level displacement owing to the charge transfer from the intercalate.

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