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SEMICONDUCTORS  
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## Conductivity Anisotropy of the $(\text{PbS})_{0.59}\text{TiS}_2$ Misfit Compound

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**Abstract**—A study is reported on the temperature dependence of the resistivity of the  $(\text{PbS})_{0.59}\text{TiS}_2$  misfit-layer compound in the commensurate and incommensurate basal-plane directions. The effect of the lattice incommensurability is shown to be equivalent to additional one-dimensional scattering from a neutral impurity.  
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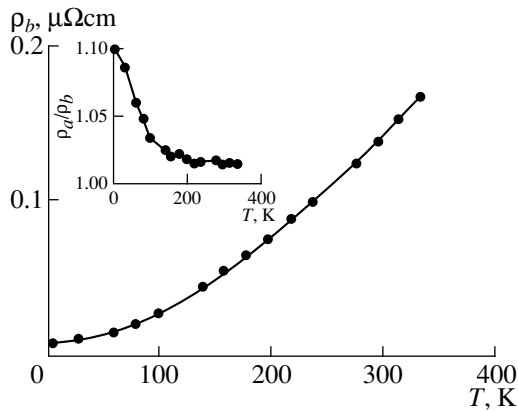
Materials with misfit layers (misfit compounds) with a common formula  $(MX)(TX_2)_n$ , where  $n \approx 1, 2$ ;  $M = \text{Pb, Sn, Bi, Ln}$ ;  $T = \text{Ti, V, Nb, Ta}$ ; and  $X = \text{S, Se}$ , may be considered as a set of  $MX$  and  $TX_2$  layers stacked in the order  $MX-TX_2-MX-TX_2\dots$  ( $n \approx 1$ ) or  $MX-TX_2-TX_2-MX-TX_2-TX_2-MX\dots$  ( $n \approx 2$ ) [1]. The fact that the structure of an  $MX$  fragment in a misfit material practically does not differ from that of the bulk  $MX$  crystal gives one grounds to consider these compounds as resulting from intercalation of a monomolecular  $MX$  layer into the  $TX_2$  matrix lattice. The axis perpendicular to the  $MX$  layer plane turns out to be a three-fold axis (the  $\{111\}$  axis in an  $MX$  crystal), so that the  $MX$  and  $TX_2$  layers have the same symmetry in the direction normal to the layer plane (the  $c$  axis). The difference between the unit cell parameters, however, makes the sublattices incommensurate. In materials with  $M = \text{Ln}$ , electrons are observed to transfer from the  $MX$  to the  $TX_2$  fragment, as in the case of conventional intercalation compounds, but in compounds with  $M = \text{Pb}$  and  $\text{Sn}$ , no change in the electron concentrations in both fragments compared to the bulk materials has been detected [1]. While the nature of the chemical bonding in the latter materials is still not fully understood, it is clear, however, that it is in this group of materials that one may expect the largest anisotropy in the properties, including superconductivity.

In the  $(\text{PbS})_{0.59}(\text{TiS}_2) \approx (\text{PbS})(\text{TiS}_2)_2 = \text{“PbTiS}_3\text{”}$  system, the  $\text{PbS}$  and  $TX_2$  fragments are observed to turn in such a way as to make their lattices commensurate in one of the directions ( $b$ ) while leaving them incommensurate in the direction normal to it ( $a$ ) [2]. This lowers the general symmetry to monoclinic (space group  $C2/m$ ) and permits one to expect a noticeable anisotropy of all properties, both in parallel and normal to the basal plane, and in the commensurate/incommensurate directions in the basal plane. Indeed, recent studies [3] of the

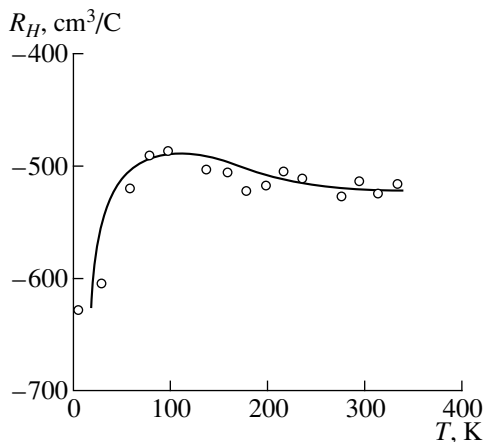
mechanical properties of  $(\text{PbS})_{0.59}\text{TiS}_2$  revealed a strong anisotropy; one cannot practically deform the lattice in the  $b$  direction because of the fact that it is extremely deformable in the incommensurate direction  $a$ .

There are practically no studies of the anisotropy of properties in the commensurate/incommensurate directions in the basal plane of misfit materials. The only work on this problem dealing with compounds of the  $(\text{LnS})_n\text{NbS}_2$  group [4] detected a weak anisotropy in conductivity,  $\sigma_a/\sigma_b = 1.19$  at  $T = 280$  K and  $\sigma_a/\sigma_b = 1.31$  at 4.2 K. This anisotropy is assigned to microcrack growth along the  $b$  direction. It was shown [3] that mechanical strains in  $(\text{PbS})_{0.59}\text{TiS}_2$  cannot give rise to crack development and, hence, this compound can serve as a convenient model object to study the effect of sublattice incommensurability on the behavior of charge carriers. The mean free path length of conduction electrons was estimated for a number of misfit materials [5, 6]. The values obtained agree well with one another and range from 9 to 11 Å, which is considerably in excess of both sublattice periods. The incommensurability (lack of periodicity) of the crystal potential can obviously substantially affect the carrier mobility. The present work studies the anisotropy of the electric properties of  $(\text{PbS})_{0.59}\text{TiS}_2$  in the commensurate and incommensurate directions.

$(\text{PbS})_{0.59}\text{TiS}_2$  single crystals up to  $15 \times 10 \times 0.01$  mm in size were grown by vapor transport reactions with a small excess of sulfur added as a carrier. The technique of single-crystal growth and characterization is described elsewhere [3]. The X-ray diffraction patterns of crushed single crystals and the calculated crystallographic parameters (DRON-1 UM,  $\text{CuK}_\alpha$  radiation, Ni filter) coincided with those quoted in [2]. The electronic properties were measured on samples devoid of mechanical defects, which are described in [3]. The Hall effect and resistivity measurements were per-



**Fig. 1.** Temperature dependence of the resistivity of  $(\text{PbS})_{0.59}\text{TiS}_2$  in the commensurate direction. The inset shows the temperature dependence of the ratio of resistivities in the incommensurate ( $\rho_a$ ) and commensurate ( $\rho_b$ ) directions.



**Fig. 2.** Temperature dependence of the Hall constant in the direction making  $45^\circ$  with the commensurate and incommensurate directions in the basal plane of  $(\text{PbS})_{0.59}\text{TiS}_2$ .

formed on samples  $10 \pm 3 \mu\text{m}$  thick and  $2 \times 2 \text{ mm}$  in size within the 4.2–350 K range. Contacts measuring  $0.1 \times 0.1 \text{ mm}$  were ultrasonically soldered with indium. Magnetic fields up to 14 T (Oxford Instruments) in Hall effect measurements were directed along the  $c$  axis, the potentials were measured along (110), and the measuring current was 1 mA. The resistivity was calculated by the technique of Montgomery [7]. The temperature dependence of the resistivity anisotropy was determined to within 0.5%.

The main experimental results obtained are displayed graphically in Figs. 1 and 2. The temperature dependence of the resistivity  $\rho$  in the commensurate ( $\rho_b$ ) and incommensurate ( $\rho_a$ ) directions measured for  $4.2 < T < 140 \text{ K}$ , is described by the  $\rho \sim \rho_0 T^2$  relation and, at higher temperatures, by  $\rho \sim \rho_0 T^{1.5}$ . This coincides with the behavior of the resistivity of  $\text{TiS}_2$  [8] with a slight excess of titanium,  $\text{Ti}_{1.05}\text{S}_2$ . The electron

concentration derived from the Hall constant is  $3 \times 10^{21} \text{ cm}^{-3}$ , which likewise coincides with the data quoted in [8] for  $\text{Ti}_{1.05}\text{S}_2$ . Thus, one may conclude that in the material under study, only the slightly intercalated  $\text{TiS}_2$  fragments account for the charge transport. This conclusion is in agreement with the results obtained for other  $M\text{S}(\text{TiS}_2)_n$  compounds ( $M = \text{Pb}, \text{Sn}$ ) [1] and permits one to associate the effect of the PbS fragment on the electronic properties with creation of the scattering electric potential only.

The resistivity anisotropy in the commensurate/incommensurate directions turned out to be small (see inset to Fig. 1), despite the strong anisotropy of the mechanical properties [3]. This can be attributed to a weak mutual coupling of the PbS and  $\text{TiS}_2$  structural fragments. It may be conjectured that the increase of resistivity in the incommensurate direction can be accounted for by the increase of the electron effective mass induced by the PbS incommensurate potential. Note that the  $\rho_a/\rho_b$  ratio substantially differs from unity only at low enough temperatures. Because states with an effective mass enhanced by the incommensurability of the potential should lie close to the conduction-band bottom [9], the vanishing of the anisotropy with increasing temperature can be assigned to electron excitation above the high-energy edge of these states. The same reason may account for the decrease of the Hall constant in absolute magnitude in the temperature domain with a noticeable anisotropy in conductivity (Fig. 2). The temperature at which the anisotropy disappears provides an estimate ( $\sim 0.01 \text{ eV}$ ) for the band width of the states which have grown “heavier.” This permits one to estimate the incommensurate potential  $V_0$  using the expressions for the mobility edge position  $\Delta E$  [9], structural data [10], and information on the conduction-band width  $B$  for  $\text{TiS}_2$  [11]:

$$V_0^2 = (2\Delta E(z-1)B)/z,$$

where  $z = 6$  is the coordination number of Ti atoms. Substituting  $B = 3.2 \text{ eV}$  yields the potential  $V_0 = 0.22 \text{ eV}$ . Thus, the effect of the structural incommensurability is comparable with that of randomly distributed impurities [12]. This conclusion correlates well with the temperature behavior of the carrier mobility, which was derived from the conductivity and carrier concentration calculated from the Hall constant. The difference between the mobilities in the commensurate and incommensurate directions is practically independent of temperature, which should be in the case of scattering from neutral impurities [13]. The high conductivity in the incommensurate direction permits one to exclude the scattering effect of randomly spaced intercalated atoms as a reason for carrier localization, which is observed in many intercalation compounds based on titanium dichalcogenides [14].

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## REFERENCES

1. G. A. Wiegers and A. Meerschaut, *Mater. Sci. Forum* **100&101**, 101 (1991).
2. A. Meerschaut, C. Auriel, and J. Rouxel, *J. Alloys Comp.* **183**, 129 (1992).
3. P. Panfilov, Yu. L. Gagarin, and A. N. Titov, *J. Mater. Sci. Lett.* **17**, 1049 (1998).
4. T. Taichi, Doctoral Dissertation (Kyoto Univ., 1993).
5. T. Kondo, K. Suzuki, and T. Enoki, *J. Phys. Soc. Jpn.* **64**, 4296 (1995).
6. T. Kondo, K. Suzuki, T. Enoki, *et al.*, *J. Phys. Chem. Solids* **57**, 1105 (1996).
7. H. S. Montgomery, *J. Appl. Phys.* **42**, 2971 (1971).
8. P. C. Klipstein and R. H. Friend, *J. Phys. C: Solid State Phys.* **20**, 4169 (1987).
9. N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon Press, Oxford, 1979).
10. J. L. Murray, *Bull. Alloys Phase Diagrams* **7**, 156 (1986).
11. A. Zunger and A. J. Freeman, *Phys. Rev. B* **16**, 906 (1977).
12. M. Inoue, M. Koyano, H. Negishi, *et al.*, *Phys. Status Solidi B* **132**, 295 (1985).
13. V. L. Bonch-Bruевич and S. G. Kalashnikov, *Physics of Semiconductors* (Nauka, Moscow, 1977).
14. A. Titov, S. Titova, M. Neumann, *et al.*, *Mol. Cryst. Liq. Cryst.* **311**, 161 (1998).

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