Thermoelectric Properties and Ferromagnetism of Diluted Magnetic Semiconductors Sb$_{2-x}$Cr$_x$Te$_3$

P. M. Tarasov, V. A. Kulbachinskii, and V. G. Kytn
Moscow State University, Vorob’evy gory, Moscow, 119992 Russia
e-mail: kulb@mig.phys.msu.ru

Abstract—Thermoelectric properties of single crystals of a new dilute magnetic semiconductor $p$-Sb$_{2-x}$Cr$_x$Te$_3$ are studied in the temperature interval 7–300 K. The temperature dependences of the thermal conductivity are measured. The Seebeck coefficient $S$ is found to increase upon doping with Cr. At low temperatures, a ferromagnetic phase with Curie temperature $T_C = 5.8$ K exists for a Cr concentration $x = 0.0215$, its easy magnetization axis being parallel to the crystallographic axis $C_3$. At $T = 4.2$ K, a negative magnetoresistance and anomalous Hall effect are observed; in strong magnetic fields, the Shubnikov–de Haas effect is manifested.

PACS numbers: 72.15.Jf, 75.50.Cc, 78.40.Fy
DOI: 10.1134/S1063776107070060

1. INTRODUCTION

In diluted magnetic semiconductors (DMSCs), an interesting manifestation of the indirect exchange interaction of magnetic ions is the emergence of ferromagnetism, which is observed only in samples with the $p$ type of conduction (see reviews [1–3]). Apart from academic interest in hole-induced ferromagnetism in DMSCs, this phenomenon has good prospects in applications for controlling various properties of semiconductors with the help of a magnetic field. In particular, new DMSCs based on thermoelectric materials of the Bi$_2$Te$_3$ and Sb$_2$Te$_3$ type have been discovered recently [4, 5].

Layered semiconductors of the Sb$_2$Te$_3$ type are characterized by a rhombohedral structure with symmetry axes $C_2$ and $C_3$ of the second and third order. The Sb$_2$Te$_3$ crystals always exhibit the $p$-type conduction with a high concentration of holes due to the high concentration of charged point defects predominantly of antistructural type; i.e., antimony atoms occupy the positions of tellurium atoms. The reason for the formation of such defects is the weak polarity of the Sb–Te bonds. Compound Sb$_2$Te$_3$ is a narrow-gap semiconductor with an indirect forbidden gap $E_g = 0.25$ eV (at 295 K) and $E_g = 0.26$ eV (at 4.2 K) [6]. The valence band consists of the upper band of light holes and the lower band of heavy holes, each of which is sixfold degenerate. It was shown that doping of bismuth telluride with iron increases the Seebeck coefficient of this material [7].

In this study, we investigate thermoelectric, galvanomagnetic, and magnetic properties of single crystals of the new dilute magnetic semiconductor $p$-Sb$_{2-x}$Cr$_x$Te$_3$, which possesses clearly manifested thermoelectric properties. In addition, we study the thermal conductivity and the Shubnikov–de Haas effect.

2. SAMPLES

Single crystals were grown by the Bridgman technique from the components taken in the stoichiometric proportion corresponding to the required composition Sb$_{2-x}$Cr$_x$Te$_3$. The ingots can be easily cleaved along the cleavage planes perpendicular to the $C_3$ axis (i.e., along the (0001) planes, which are usually parallel to the axis of the ampoule). The measuring samples with a characteristic size of $1 \times 0.5 \times 4$ mm were cut with the help of an electrical-spark machine. Electric contacts were soldered using the BiSb alloy.

The chromium content in specific samples was determined with the help of a JEOL 8621 electron microanalyzer after magnetic and electric measurements on the given sample. These measurements also proved that chromium is distributed uniformly in the sample. It was found that the Cr concentration amounts to 0.23 and 0.43 at % for the two doped samples studied using a SQUID magnetometer, which corresponds to $x = 0.0115$ and 0.0215 in the structural formula of Sb$_{2-x}$Cr$_x$Te$_3$.

The temperature dependences of the resistance, magnetoresistance, and Hall effect were measured using the standard four-probe method; the current was directed along the $C_2$ axis. To extract the Hall effect and magnetoresistance, the measurements were performed for two directions of the magnetic field. A magnetic field of up to 6 T was produced by a superconducting solenoid and was directed along the $C_3$ axis perpendicular to the layers. The Shubnikov–de Haas effect was...
Table 1. Crystal lattice parameters $a$ and $c$ of Sb$_2$–xCr$_x$Te$_3$ samples and unit cell volume $V$

<table>
<thead>
<tr>
<th>No.</th>
<th>$x$</th>
<th>$a$, nm</th>
<th>$c$, nm</th>
<th>$c/a$</th>
<th>$V$, nm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>–</td>
<td>0.42643(5)</td>
<td>3.0427(4)</td>
<td>7.136(2)</td>
<td>0.4792(1)</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>0.42638(8)</td>
<td>3.0433(5)</td>
<td>7.138(5)</td>
<td>0.4791(2)</td>
</tr>
<tr>
<td>3</td>
<td>0.035</td>
<td>0.42604(4)</td>
<td>3.0433(2)</td>
<td>7.143(3)</td>
<td>0.4784(1)</td>
</tr>
<tr>
<td>4</td>
<td>0.07</td>
<td>0.42576(6)</td>
<td>3.0432(3)</td>
<td>7.148(4)</td>
<td>0.4777(1)</td>
</tr>
</tbody>
</table>

measured in pulsed magnetic fields of up to 54 T with a pulse duration of 10 ms. Magnetic measurements were performed on the MPMS 5S SQUID magnetometer (manufactured by Quantum Design Co. Ltd.) in the temperature range 1.7–300 K and in magnetic fields of up to 5 T.

The covalent radii of antimony and chromium are $r$(Sb) = 0.140 nm and $r$(Cr) = 0.118 nm. Consequently, the lattice parameters must decrease when the relatively small Cr atoms replace the antimony atoms in Sb$_2$–xCr$_x$Te$_3$ solid solutions. To verify this assumption, we performed X-ray diffraction measurements, whose results are presented in Table 1. It can be seen that parameter $a$ decreases upon an increase in the Cr concentration in the samples, while parameter $c$ remains virtually unchanged. This leads to a decrease in the unit cell volume. Consequently, we can conclude that chromium atoms replace antimony atoms in the lattice.

3. RESULTS OF MEASUREMENTS AND DISCUSSION

Magnetic Properties

Magnetic susceptibility $\chi$ of the starting Sb$_2$Te$_3$ single crystal is diamagnetic and virtually independent of temperature; its value is $-8 \times 10^{-10}$ m$^3$/mol in the main crystallographic directions. The absolute value of $\chi$ increases with the Cr concentration in the samples. Figure 1 shows the magnetic field dependence of the magnetization of a sample with a Cr concentration of 0.43 at % at $T = 1.7$ K in magnetic fields $B$ oriented along the $C_3$ and $C_2$ axes. The Curie temperature was $T_C = 5.8$ K (0.43 at % Cr) and $T_C \approx 3$ K (0.23 at % Cr). The hysteresis loop for $B \parallel C_3$ is narrow with a coercive force of about 15 mT, while the saturation magnetization corresponds to $3.8\mu_B$ per Cr ion. These results indicate the existence of ferromagnetism in the Cr-containing samples and match the temperature dependences of the magnetic susceptibility, which obey the Curie–Weiss law with a positive paramagnetic Curie temperature. For the magnetization measured along $B \parallel C_2$, the width of the hysteresis loop increases to 70 mT, but field $B = 2.5$ T turns out to be insufficient for attaining saturation of magnetization. Analogous results were also obtained by a sample with a Cr concentration of 0.23 at %.

The origin of ferromagnetism is associated with indirect exchange interaction of Cr ions via holes. According to estimates, the exchange interaction constant is 0.19–0.22 eV nm$^3$ for a $g$ factor of $g = 2$ and for experimentally obtained values of $S = 3/2$ for Cr and $T_C = 5.8$ K [8]. This value is on the same order of magnitude as that calculated for (Mn)GaAs [9].

Galvanomagnetic Properties

The resistivity $\rho$ for all samples decreases with temperature and attains saturation at low temperatures. In the temperature range 150–300 K, dependences $\rho(T) \propto T^m$ are observed with an exponent of $m = 1.2$. The deviation from $m = 1.5$ typical of phonon scattering is probably associated with additional scattering of holes from ionized impurities and the temperature dependence of the effective mass in this temperature range. The mobility decreases upon doping with chromium. The resistivity in doped samples increases also due to additional scattering of holes from localized magnetic moments of Cr ions. The latter circumstance is confirmed by the presence of negative magnetoresistance $\rho(B)$ in weak magnetic fields, which is associated with suppression of the spin-dependent scattering. The presence of the Cr magnetic impurity led to the anomalous Hall effect in the samples under investigation [4].
The Hall coefficient in all samples is positive and increases with the chromium content, indicating a decrease in the hole concentration. The donor effect of chromium is associated with its influence on the polarity of bonds. The weak polarity of the Sb–Te bonds is responsible for the presence of a large number of antistructural defects in the lattice (Sb atoms substitute Te atoms). Doping with Cr changes the polarity of bonds, leading to a change in the concentration of charged point defects and, hence, in the hole concentration. Chromium atoms mainly substitute Sb atoms in the lattice (Sb atoms substitute Te atoms) and, hence, in the hole concentration.

Electronegativity of bonds. The weak polarity of the Sb–Te bonds is responsible for the presence of a large number of antistructural defects in the lattice. In the case of Sb$_2$–Cr$_2$Te$_5$ crystals, the lattice parameters of Sb$_2$Te$_5$ are $a = 0.42643(5)$ nm and $c = 3.0427(4)$ nm, while for a sample with a Cr concentration of 0.043 at %, these parameters are $a = 0.402602(4)$ nm and $c = 3.0431(3)$ nm. The increase in the bond polarity upon the substitution of Cr for Sb reduces the probability of antistructural defect formation.

Shubnikov–de Haas Effect

The ellipsoidal nonparabolic band model correctly describes the energy spectrum of the upper valence band of Sb$_2$Te$_5$ crystals. The dispersion relation corresponding to this model has the form

$$\frac{2m_0E}{\hbar^2} = \alpha_{11}k_1^2 + \alpha_{22}k_2^2 + \alpha_{33}k_3^2 + \alpha_{23}k_2k_3,$$

(1)

The principal axes of six ellipsoids of the upper valence band are inclined in the mirror plane at an angle $\theta$ relative to crystallographic axes; i.e., in the $k$ space, we have

$$k_1 = k_1', \quad k_2 = k_2' \cos \theta - k_3' \sin \theta,$$

$$k_3 = k_3' \sin \theta + k_3' \cos \theta.$$

Consequently, the constant-energy surface in terms of the principal axes can be described as

$$\frac{2m_0E}{\hbar^2} = \alpha'_{11}(k_1')^2 + \alpha'_{22}(k_2')^2 + \alpha'_{33}(k_3')^2,$$

(3)

where $\alpha_{11} = \alpha'_{33}$, $\alpha'_{22} = \alpha'_{33}$, $\alpha_{22} = \alpha_{33}$, $\alpha_{22} \alpha_{33} = \alpha_{22} \alpha_{33} - (\alpha_{22})^2, \tan 2\theta = -2\alpha_{22}/(\alpha_{22} + \alpha_{33})$, and $\alpha_{ij} = m_i/m_j$ are the components of the reciprocal effective mass tensor in the principal axes of the ellipsoid, which depend on energy due to a slight deviation of the spectrum from parabolicity. Let us consider one of the six ellipsoids of the Fermi surface and introduce the following notation: $a$, $b$, and $c$ are the principal axes of the ellipsoid and $S_a$, $S_b$, and $S_c$ are its extreme cross sections. One of the axes of each of the two ellipsoids centered in the $xz$ plane is parallel to the coordinate plane $y$ ($C_2$). The principal axes of the ellipsoids are inclined at an angle $\theta$ to the crystallographic axes in the $xz$ ($C_1C_2$) plane. The values of the semiaxes of the ellipsoid can be expressed as

$$a = \frac{\sqrt{2m_0E/\alpha_{11}}}{\hbar}, \quad b = \frac{\sqrt{2m_0E/\alpha_{22}}}{\hbar},$$

$$c = \frac{\sqrt{2m_0E/\alpha_{33}}}{\hbar}.$$

(4)

Angle $\theta$ in (Bi$_{1-x}$Sb)$_2$Te$_3$ crystals is known only up to $x = 0.6$ [10] and, by extrapolation, amounts to approximately $48^\circ$ for Sb$_2$Te$_5$. This value of $\theta$ was used for mixed Bi$_{1-x}$Sb$_x$Te$_3$ crystals studied here. With the help of simple transformations, we obtain the following expressions for the areas of extreme cross sections of the ellipsoid:

$$S_a = \pi cb = \frac{2\pi m_0E_F}{\hbar^2}\frac{1}{\sqrt{\alpha_{11}' \alpha_{33}' \alpha_{33}'}}$$

$$S_b = \pi ac = \frac{2\pi m_0E_F}{\hbar^2}\frac{1}{\sqrt{\alpha_{11}' \alpha_{22}' \alpha_{33}'}}$$

$$S_c = \pi ab = \frac{2\pi m_0E_F}{\hbar^2}\frac{1}{\sqrt{\alpha_{11}' \alpha_{22}' \alpha_{22}'}}.$$

(5)

We denote by $S_H$ the cross section of the ellipsoid by a plane passing through its center and perpendicular to the magnetic field vector directed along the $z$ ($C_3$) axis. It would be interesting to find the area $S_H$ of the cross section by a plane perpendicular to the direction of the magnetic field vector as a function of the angle $\varphi$ formed by this vector with the $z$ ($C_3$) axis. In this case, the six ellipsoids can be conditionally divided into two groups: two ellipsoids lie in this plane, while the remaining four ellipsoids are located symmetrically outside this plane. In view of the symmetry, the ellipsoids in each group are equivalent (i.e., their cross sections $S_H$ are identical for any $\varphi$). For a nonzero value of angle $\varphi$, the areas of the first-group ellipsoid cross sections are given by

$$S_H = \left[(\cos(\varphi + \theta)/S_a)^2 + (\sin(\varphi + \theta)/S_a)^2\right]^{-1/2},$$

(6)

where $\varphi$ is the experimental value of the angle between the direction of the magnetic field vector and the $z$ ($C_3$) axis and $\theta$ is the angle between the axes of the ellipsoids.
The cross-sectional area $S_H$ of the Fermi surface can be found using the expression for the frequency of Shubnikov–de Haas oscillations $F = [\Delta(1/B)]^{-1}$:

$$S_H = \frac{2\pi e F}{\hbar} = \frac{2\pi e}{h\Delta(1/B)}$$

$$= \frac{2\pi m_0 e F}{\hbar^2 \sqrt{\alpha_{22} \alpha_{33} \sin^2 \theta + \alpha_{11} \alpha_{22} \cos^2 \theta}}.$$  

(8)

The volume of an ellipsoid can be expressed in terms of quantities $\alpha_{ij}$, $\theta$, and $S_H$:

$$V = \frac{4}{3} \pi abc \left(\frac{S_H S_{ab} S_{bc}}{\pi}\right)^{1/2} = \frac{4}{3} \sqrt{\frac{\pi}{S_H}} \times \left[\frac{\alpha_{11} \alpha_{22} \alpha_{33} \sin^2 \theta + \alpha_{11} \alpha_{22} \cos^2 \theta}{\sqrt{\alpha_{11} \alpha_{22} \alpha_{33}}}\right]^{3/2}.$$  

(9)

In this case, the hole concentration in the upper valence band is given by

$$P = \frac{2}{6V} \left(\frac{2\pi}{e}\right)^3.$$  

(10)

Frequencies $F$ of the Shubnikov–de Haas oscillations for Sb$_{2-x}$Cr$_x$Te$_3$ single crystals with band parameters $\alpha_{11} = 2.26$, $\alpha_{22} = 32.5$, and $\alpha_{33} = 11.6$, which were used earlier for calculations of Sb$_2$Te$_3$ [11, 12], were used to calculate the values of hole concentration $P$ in the upper valence band and Fermi energy $E_F$ (Table 2).

The values of light-hole concentration $p_{SdH}$ calculated using the Shubnikov–de Haas effect were compared with the relevant Hall concentrations $1/eR$. It can be seen from Table 2 that the values of $p$ are always smaller than the corresponding values of $1/eR$, which indicates the filling of the second lower valence band for such high concentrations of holes. However, it follows from the results of the above experiments that no oscillations of magnetoresistance from the lower band of heavy valence holes were observed even in strong magnetic fields, which is undoubtedly associated with high values of the effective masses of holes in this band.

### Table 2. Parameters of Sb$_{2-x}$Cr$_x$Te$_3$ samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$F$, T</th>
<th>$E_F$, meV</th>
<th>$P$, $10^{19}$ cm$^{-3}$</th>
<th>$\rho_{42}$, $\mu\Omega$ cm</th>
<th>$\rho_{300}$, $\mu\Omega$ cm</th>
<th>$\mu_{42}$, m$^2$/V s</th>
<th>$1/eR_H$, $10^{19}$ cm$^{-3}$</th>
<th>Cr, at %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb$_2$Te$_3$</td>
<td>54.7</td>
<td>103.6</td>
<td>3.4</td>
<td>38.8</td>
<td>260</td>
<td>0.103</td>
<td>12.5</td>
<td>0</td>
</tr>
<tr>
<td>Sb$<em>{1.99}$Cr$</em>{0.0115}$Te$_3$</td>
<td>43.4</td>
<td>82.2</td>
<td>2.3</td>
<td>142</td>
<td>437</td>
<td>0.029</td>
<td>8.3</td>
<td>0.23</td>
</tr>
<tr>
<td>Sb$<em>{1.98}$Cr$</em>{0.0215}$Te$_3$</td>
<td>46.2</td>
<td>87.5</td>
<td>2.6</td>
<td>106</td>
<td>314</td>
<td>0.066</td>
<td>9.9</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Note: $F$ is the Shubnikov–de Haas oscillation frequency; $E_F$ is the Fermi energy; $P$ is the hole concentration obtained from the Shubnikov–de Haas effect; $\rho_{42}$ and $\rho_{300}$ are the resistivities at $T = 4.2$ and $300$ K, respectively; $\mu_{42}$ is the mobility at $T = 4.2$ K, and $1/eR_H$ is the Hall concentration of holes.
Thermoelectric Properties

We measured the temperature dependence of the Seebeck coefficient $S$; the thermopower increases with temperature (Fig. 3). In the temperature range 10–15 K, the $S(T)$ dependence has a peak corresponding to the thermal conductivity peak (Fig. 4) and associated with phonon drag.

It can be seen from Fig. 3 that the thermopower of Cr-doped samples at $T > 100$ K considerably exceeds the thermopower of an undoped sample.

In the case of a quadratic dispersion relation and an isotropic relaxation time, the Seebeck coefficient in the impurity conduction region and for an arbitrary degeneracy has the form [13]

$$\alpha = \frac{k_B}{e} \left( \frac{(2r + 5)F_{r+3/2}(\xi)}{e} - \frac{(2r + 3)F_{r+1/2}(\xi)}{e} \right),$$  

where $k_B$ is the Boltzmann constant, $e$ is the electron charge, $r$ is the scattering parameter, $\xi = E_F/k_B T$, $E_F$ is the Fermi energy, and $F_s(\xi)$ is the Fermi integral defined as

$$F_s(\xi) = \int_0^\infty \frac{x^s}{\exp(x - \xi) + 1} dx.$$  

Using the experimental dependences $S(T)$ (Fig. 3), the Fermi energies calculated using the Shubnikov–de Haas effect, and formulas (11) and (12), we calculated the temperature dependences $r(T)$ of the scattering parameter. The Fermi integral (2) was evaluated numerically. Figure 5 shows the $r(T)$ dependences for two $Sb_{2-x}Cr_xTe_3$ samples. It can be seen that, at temperatures below 100 K, parameter $r$ approaches the value $r = -1/2$, which is typical of scattering from acoustic phonons ($r = -3/2$ for scattering from ionized impurities and $r = 1/2$ for scattering from polar optical phonons [14]).

Thus, a new dilute magnetic semiconductor $Sb_{2-x}Cr_xTe_3$ is investigated and the temperature dependences of the Seebeck coefficients and thermal conductivity are measured. Doping of $p$-$Sb_{2-x}Cr_xTe_3$ crystals with chromium increases their thermopower, but the thermal conductivity changes insignificantly. For such an insignificant concentration of the doping impurity, phonon scattering also typical of undoped samples plays the major role in the temperature range 77 K < $T < 300$ K.

REFERENCES


13. B. M. Gol’tsman, V. A. Kudinov, and I. A. Smirnov, Semiconducting Thermoelectric Materials Based on Bi₂Te₃ (Nauka, Moscow, 1972) [in Russian].


Translated by N. Wadhwa