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TRANSPORT PROPERTIES OF CdIn$_2$S$_4$ AND CdIn$_{2(1-x)}$Cr$_{2x}$S$_4$
SINGLE CRYSTALS

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Abstract. — Several transport properties have been studied on CdIn$_2$S$_4$ single crystals with different degree of deviation from stoichiometry. The electrical resistivity at room temperature spreads from an order of $10^{-3}$ $\Omega$-cm to $10^4$ $\Omega$-cm corresponding to the degree of excess sulphur. The Hall coefficient also spreads from an order of $10^{-1}$ cm$^3$/C to $10^5$ cm$^3$/C. All the samples exhibited n-type conduction.

The energy gap at 0 K was determined from the electrical measurements to be 2.2 eV. The temperature dependence of the Hall mobility and the sign of the Nernst coefficient indicate that the scattering of carriers are mainly due to the acoustic mode of lattice vibrations and the ionized impurities in the high and low temperature range, respectively. The anisotropy of the magnetoresistance effect was studied. It is suggested that the minima of the conduction band are located at points along the [100] directions in $k$ space. The density-of-states effective mass of electrons was determined to be 0.19 $m_e$ from the Seebeck and the Hall measurements. The thermal conductivity was measured from 4 K to 300 K and analyzed by Callaway's formalism.

Transport studies were also made on CdIn$_{2(1-x)}$Cr$_{2x}$S$_4$ for 0 < $x$ < 0.02. It was found that the Cr atoms substituted for In atoms produced a deep acceptor level at 0.7 eV below the conduction band. The substituted Cr ions cause resonance type phonon scatterings at about 2.5 K and about 30 K.

Introduction. — The ternary compound CdIn$_2$S$_4$ is a photosensitive semiconductor crystallizing in a cubic spinel structure. Its optical properties have been studied by several workers. However, a difficulty of growing the large and homogeneous single crystal had been preventing them from a detailed investigation of the transport properties until recent years. Recently, we have succeeded in growing large and homogeneous single crystals of CdIn$_2$S$_4$ with different degree of deviation from stoichiometry and have made preliminary study on the transport properties [1], [2], [3]. The work presented here is the result of more detailed measurements of the transport properties of CdIn$_2$S$_4$ single crystals than have been made previously. Effect of Cr ions substituted for In ions in CdIn$_2$S$_4$ on the transport properties will also be presented. Such a study will provide a foundation for the study of the ferromagnetic semiconducting spinel.

1. Experimental procedure. — Stoichiometric amounts of the components with or without excess sulphur were sealed into an evacuated quartz tube and heated to about 500°C at a rate of 50°C per day. After the tube was held at this temperature for about one week, the temperature was again raised to about 1 250°C at the same rate as before and maintained for one day. Then the tube was cooled down to room temperature at the same rate as that for heating. Oriented crystals were grown from the ingots by the horizontal or vertical Bridgman process. Single crystals as large as about 150 mm x 4 mm x 10 mm were obtained. X-ray diffraction analysis revealed the spinel structure having
the lattice constant in accordance with the published data. The crystal grows preferentially in the [111] or the [110] direction. The Cr-doped samples were cut out of the single crystals grown from the melts having composition of CdIn$_{1-x}$Cr$_x$S$_4$ with $x = 0.000$ - $0.02$. The solid solubility was confirmed by X-ray analysis in the compositional range studied. The susceptibility and the paramagnetic resonance measurements provided evidence that chromium substituted for indium in the lattice.

Electrical and thermal measurements were made by the conventional method using a potentiometer or a vibrating reed electrometer.

2. Experimental results and analysis. -- 2.1 Electrical properties. — 2.1.1 CdIn$_2$S$_4$. — The electrical resistivity $\rho$ and the Hall coefficient $R_H$ are plotted against the reciprocal temperature in figure 1 and figure 2, respectively for a series of samples having different compositions. The samples cut from a crystal grown from a melt with stoichiometric composition are designated as ST-1 and that from a melt with excess sulphur as ES-1, where 1 is a sample number. It can be seen that the electrical resistivity at room temperature spreads from an order of $10^{-3}$ Ω-cm to $10^4$ Ω-cm corresponding to the degree of excess sulphur. The Hall coefficient also spreads from an order of $10^{-1}$ cm$^3$/C to $10^6$ cm$^3$/C. As the sulphur excess in the melt is increased the electrical resistivity and the Hall coefficient increase. The sign of $R_H$ is negative for all the samples in the temperature range studied. From a slope of the resistivity curve in the temperature range which can be regarded as an intrinsic region, the energy gap at 0 K was determined as 2.2 eV.

Figure 3 gives the temperature variation of the Hall mobility $\mu_H$. In the high temperature range $\mu_H$ varies as $T^{-3/2}$ indicating that the scattering is mainly due to the acoustic mode of lattice vibrations. In the low temperature range $\mu_H$ is nearly constant for ST-samples, while it increases with the rise of the temperature for ES-samples. These results indicate that the ionized impurity scattering is predominant in this temperature range for all the samples. In order to confirm these conclusions the Nernst coefficient was measured in the temperature range between 80 K and 700 K. It was found that the Nernst coefficient was negative in the low temperature range and positive in the high temperature range. These results are consistent with the mobility data. From an analysis of the mobility data at low temperature using the Brooks-Herring's formalism [4], [5], the density of the ionized impurities was found to be the order of $10^{19}$ cm$^{-3}$ for the all samples. This fact indicates that the high-resistive samples are highly compensated by acceptors.

In order to obtain some information about the band structure of CdIn$_2$S$_4$, angular dependence of the
TRANSPORT PROPERTIES OF CdIn$_2$S$_4$ AND CdIn$_{2(1-x)}$Cr$_2$xS$_4$ SINGLE CRYSTALS C3-79

2.1.2 CdIn$_{2(1-x)}$Cr$_x$S$_4$. CdIn$_{2(1-x)}$Cr$_x$S$_4$ is a system of solid solutions between CdIn$_2$S$_4$ and CdCr$_2$S$_4$ which is known as a ferromagnetic semiconducting spinel. Electrical measurements were made on the samples of $x = 0.002$ and 0.01. Composition and specification of the samples are summarized in Table I. The samples RS-1 and 2 are the as-grown samples and RS-3 - 6 are the annealed ones. Figures 5 and 6 show $\rho$ and $R_H$, respectively as a function of

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition $x$</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS-1</td>
<td>0.01</td>
<td>as-grown</td>
</tr>
<tr>
<td>RS-2</td>
<td>0.01</td>
<td>as-grown</td>
</tr>
<tr>
<td>RS-3</td>
<td>0.01</td>
<td>RS-2 annealed at 300 °C for 1 hour</td>
</tr>
<tr>
<td>RS-4</td>
<td>0.01</td>
<td>RS-3 annealed at 500 °C for 48 hours</td>
</tr>
<tr>
<td>RS-5</td>
<td>0.002</td>
<td>annealed at 300 °C for 1 hour</td>
</tr>
<tr>
<td>RS-6</td>
<td>0.002</td>
<td>RS-5 annealed at 500 °C for 54 hours</td>
</tr>
</tbody>
</table>

The magnetoresistance relative to the direction of the magnetic field on the oriented samples was measured at 300 K. The magnetoresistance $\Delta \rho/\rho$ was confirmed to be proportional to the square of the magnetic field intensity. Angular dependence of $\Delta \rho/\rho$ are shown in figure 4a and b for the current directions of the [110] and the [001], respectively. From an analysis using a phenomenological theory developed by Seitz [6], it is suggested that the minima of the conduction band are located at points along the [100] directions in $k$ space. The Seebeck coefficient was also measured between 100 K and 700 K and combined with the Hall data, the density-of-states effective mass was determined to be 0.19 $m_0$, where $m_0$ is the mass of electron in free space.

Fig. 3. — Hall mobility of CdIn$_2$S$_4$ single crystals as a function of absolute temperature.

Fig. 4. — Weak-field magnetoresistance at 300 K as a function of magnetic field orientation. (a) Sample current in the [110] direction and the magnetic field is rotated in the (110) and the (001) plane. (b) Sample current in the [001] direction and the magnetic field is rotated in the (110) plane.

Fig. 5. — Electrical resistivity of CdIn$_{2(1-x)}$Cr$_x$S$_4$ single crystals as a function of inverse absolute temperature. Compositions and specifications are given in table I. Dashed lines are the data for CdIn$_2$S$_4$.
of the Hall curve in the high temperature range exhibits an activation energy of about 0.7 eV which is not observed in pure CdIn₂S₄ and remain invaried for annealing. It may be said that chromium substituted for indium in CdIn₂S₄ lattice acts as a deep acceptor the level of which lies about 0.7 eV below the conduction band. Figure 7 shows the Hall mobility as a function of inverse absolute temperature. Comparing with the result of the undoped samples which is shown in figure 3, it can be said that chromium ions have pronounced effects on the mobility such as lowering the absolute value and increasing the temperature variation at low temperatures.

2.2 THERMAL CONDUCTIVITY. — The thermal conductivity of CdIn₂S₄ was measured from 4 K to 300 K and plotted in figure 8 as a function of the temperature. The sample used is ES-1. The electronic part of the thermal conductivity can be neglected in the temperature range studied. The solid line in the figure represents Callaway’s equation [7],

\[ \kappa = \frac{k}{2 \pi^2 \tau} \left( \frac{kT}{\hbar} \right)^3 \int_0^{\theta_0/T} \tau^{-1} x^4 e^x \, dx, \]

(1)

\[ \tau^{-1} = A \omega^3 + B \omega^2 T \exp(-b/T) + v/L, \]

(2)

with \( \theta_0 = 200 \) K,

\[ A = 1 \times 10^{-43} \text{s}^3, \quad B = 9 \times 10^{-18} \text{s.deg}^{-1}, \]

\[ b = 40 \text{ K} \quad \text{and} \quad v/L = 8 \times 10^6 \text{s}^{-1}. \]

In eq. (1) and (2) \( k \) is the Boltzmann constant, \( v \) the average sound velocity, \( \hbar \) the Planck constant divided by \( 2 \pi \), \( \theta_0 \) the Debye temperature, \( \omega \) the phonon angular frequency and \( L \) is the characteristic length of the sample. The values of the parameters \( A, B \) and \( b \) are reasonable from a physical point of view. A large value

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**Fig. 6.** Hall coefficient of CdIn₂(1-x)CrₓS₄ single crystals as a function of inverse absolute temperature. Compositions and specifications are given in table I. Dashed lines are the data for CdIn₃S₄.

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**Fig. 7.** Hall mobility of CdIn₂(1-x)CrₓS₄ single crystals as a function of absolute temperature. Compositions and specifications are given in table I. Dashed lines are the data for CdIn₃S₄.

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**Fig. 8.** Lattice thermal conductivity as a function of absolute temperature for sample ES-1. The solid line is a fit of Callaway’s equation to the data.
of \( v/L \) compared with the value deduced from the sample dimension which is about \( 8 \times 10^5 \text{ s}^{-1} \) may be due to existence of internal boundaries in the sample.

These phonon energies may correspond to the separation of Cr ions in the crystalline host.

The density-of-states effective mass for the conduction band is 0.19 m,.

The anisotropy of the magnetoresistance effect indicates that minima of the conduction band are located at points along the [100] directions in \( k \) space.

The chromium substituted for indium in \( \text{CdIn}_2\text{S}_4 \) acts as deep acceptor of which lies 0.7 eV below the conduction band and has a pronounced effect on the carrier scatterings.

These phonon energies may correspond to the separation between the energy levels of the d-shell electrons of Cr ions in the crystalline host.

The temperature variation of the electrical resistivity of \( \text{CdIn}_2\text{S}_4 \) single crystals in the intrinsic range shows that the energy gap at 0 K is 2.2 eV. The anisotropy of the magnetoresistance effect indicates that minima of the conduction band are located at points along the [100] directions in \( k \) space.

The density-of-states effective mass for the conduction band is 0.19 m,.

The chromium substituted for indium in \( \text{CdIn}_2\text{S}_4 \) acts as deep acceptor of which lies 0.7 eV below the conduction band and has a pronounced effect on the carrier scatterings.

The lattice thermal conductivity of \( \text{CdIn}_2\text{S}_4 \) single crystal in the temperature range from 4 K to 300 K can be satisfactorily explained by the Callaway's theory.

The chromium ions substituted for indium ions in \( \text{CdIn}_2\text{S}_4 \) lattice produce additional phonon scatterings of resonance type. This may be caused by the phonon assisted transitions between energy levels of the d-shell electrons.

Acknowledgments. — The authors would like to thank Prof. Kimura and Mr. Kobayashi of Tokai University for performing the paramagnetic resonance study on our samples of \( \text{CdIn}_{1-x} \text{Cr}_x \text{S}_4 \). They are also much indebted to Mr. Ueno for help with the experiments.

3. Conclusions. — The temperature variation of the electrical resistivity of \( \text{CdIn}_2\text{S}_4 \) single crystals in the intrinsic range shows that the energy gap at 0 K is 2.2 eV. The anisotropy of the magnetoresistance effect indicates that minima of the conduction band are located at points along the [100] directions in \( k \) space.

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