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Investigation of the electrical properties of thallium monosulphide single crystals

A T Nagat
Physics Department, Faculty of Science, Qena, Egypt

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Abstract. The preparation and electrical properties of thallium monosulphide single crystals are reported in the present work. Measurements of electrical conductivity and Hall coefficient were performed over the temperature range 215–415 K. The study was carried out with the current flowing parallel to the *c* axis and the magnetic field direction perpendicular to the *c* axis. The crystals obtained had p-type conductivity with a hole concentration of $1.18 \times 10^{10}\,\mathrm{cm}^{-3}$ at room temperature. Conductivity and Hall mobility at 300 K were evaluated as $5.01 \times 10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ and $2511.89\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ respectively. The energy-gap width was found to be 1.37 eV. An anomalous behaviour of the temperature dependence of Hall mobility was noticed.

1. Introduction

The structure of TlSe and TlS crystals is the same; they both have D_{4h}^{18} symmetry and contain four formula units per unit cell (Belousov *et al* 1985). The metal atoms in such compounds can have different valences, namely Tl^+ and Tl^{3+} atoms from repeated fragments of the $[Tl^{3+}S_2]^-$ type, which are arranged as chains elongated along the crystallographic *c* axis. The Tl^+ atoms provide ionic binding between neighbouring chains. In the thallium chalcogenide system with sulphur, several binary compounds have been identified (Itoga and Kannewurf 1971). Probably the most known and best studied is Tl_2S. The melting of Tl_2S takes place congruently, but TlS melts by a peritectic reaction below 540 K (Fedorov and Machuev 1972). The unit cell parameters of thallium sulphide (TlS) as reported by Demishev *et al* (1988) are $a = 0.777$ nm and $c = 0.679$ nm. Very little work has been done on the preparation and crystal structure of such compounds. Very few reports are found in the literature concerning electrical transport and related properties. Measurements of the Hall effect and electrical conductivity, which generally give more precise and straightforward information on carrier density, mobility, energy gap, the position of the impurity level in addition to the conductivity type, are the subject of the present investigation.

2. Sample preparation and measurements

High quality TlS single crystals have been grown from melt in our laboratories by the Bridgman method. The growth method and the experimental apparatus have been described in detail by Hussein and Nagat (1989). The purity of the materials used was as follows: Tl, 99.9999% and S, 99.999%. Stoichiometric quantities of the constituent elements, 17.031 g Tl and 2.672 g S, representing 86.4385% thallium and 13.5615% sulphur were used as starting materials. The appropriate amounts were first sealed in quartz ampoules at a pressure of 10^{-5} Torr. The lower end of the ampoule was tapered in order to favour crystal growth at a single point. The usual precautions were taken throughout this investigation to prevent oxide formation on the ingot material. In the first procedure the tube was placed in a three-stage tube furnace in which a controlled temperature gradient was maintained. The mixture was heated above the melting point and maintained for several hours with periodic agitation to ensure thorough mixing of the constituents. The ampoule is allowed to move at a constant rate of 1.7 mm h^{-1} through the stationary furnace. At least two weeks growth are necessary to obtain TlS single crystals. The resulting ingot appears grey-black in colour and the freshly cleaved surfaces have a reflective lustre. The single-crystallinity of this material was verified by means of x-ray diffraction. Single crystal samples for all electrical measurements were selected from the ingot material. The specimens were ground and polished thoroughly using diamond pastes to obtain mirror-like surfaces. Typical dimensions for the rectangular samples were $9.1 \times 3.6 \times 2.0$ mm^3. Silver paste was used as an ohmic contact. The ohmic nature of the contacts was verified by recording the current–voltage characteristics. The conductivity and Hall coefficient were measured by a compensation method in a special cryostat with a conventional DC-type measurement system. Control measurements were taken to check the linear dependence of the voltages on the current and of the Hall voltage on the modulus of the magnetic field strength. The Hall voltages were measured by reversing the current and the magnetic field directions and taking the appropriate averages. The measurements were performed under vacuum in a cryostat especially designed for mounting between the polar expansions of an Oxford 177 electromagnet. The designed cryostat allows measurements to be made in a wide range of temperature. Keeping liquid nitrogen in the inner jacket of the cryostat enables the temperature to be kept below 300 K, while supplying a current to a small resistance heater keeps the temperature above 300 K. For Hall measurements the magnetic field was perpendicular to the crystallographic *c* direction and along the [110] direction with a magnitude of 0.5 T. In all measurements the applied current direction was parallel to the crystallographic *c* axis of the sample. Electrodes for simultaneous Hall and conductivity measurements at the same temperature were attached to the TlS sample in the usual four-probe configuration on the fresh surfaces. In both the conductivity and Hall measurements in TlS, the maximum temperature was kept considerably below the melting point in order to ensure that there would be no crystal decomposition and loss of the chalcogenide constituents. The temperature of investigation was in the range 215–415 K.

3. Results and discussion

The results presented in the figures are for thallium monosulphide single crystals with room-temperature conductivity of 5.01×10^{-6} Ω^{-1} cm^{-1}. Figure 1 shows the temperature dependence of the electrical conductivity. The complete temperature range can be subdivided into three regions; below transition, transition region and above the transition. These regions are shown quite clearly in figure 1. With increasing temperature the electrical conductivity first increases, reaches a transition region at 337.6 K, then

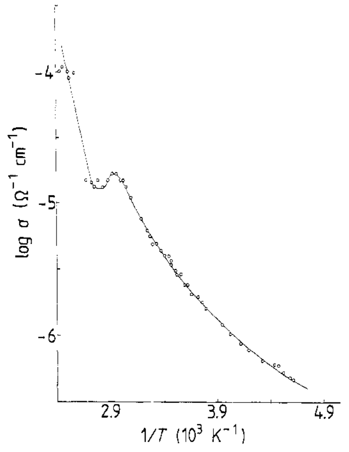

Figure 1. Temperature dependence of the electrical conductivity of TlS single crystals.

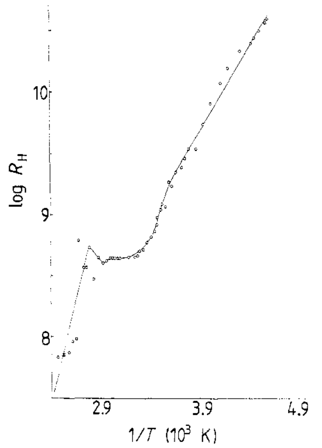

Figure 2. Variation in Hall coefficient with temperature for TlS.

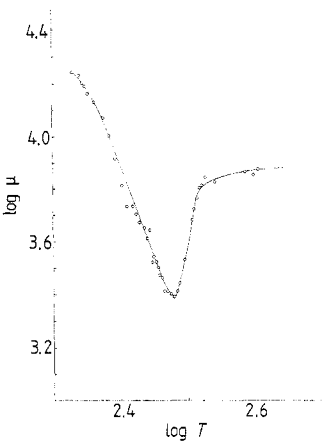

Figure 3. Behaviour of the Hall mobility in TlS as a function of temperature.

passes through a minimum and rises again. This pattern of change in the electrical properties is due to the appearance of impurity and intrinsic conductivity respectively and to the variation of the hole mobility and concentration with temperature. The fall in the electrical conductivity is due to a decrease in mobility, since the carrier density ($N_A - N_D$) in this temperature region remains practically constant until the intrinsic region is reached. At temperatures above the transition point, the conductivity rises rapidly. The temperature dependences exhibit a transition from a region of lower slope to one of higher slope. The slopes of the curve increase with increasing temperature, and are higher at higher temperatures because of the carriers being excited from the extended state of the valence band into the conduction band. The width of the forbidden zone, as calculated from the slope of the curve in the high-temperature region, was found to be 1.37 eV. Figure 2 shows the variation in the Hall coefficient with temperature for TlS. A positive sign of R_H is indicative of holes being the major contribution to the conductivity. It is of the usual type for semiconductors. Calculation of the forbidden-band width from these graphs gives a value of 1.37 eV. Little information on the Hall coefficient of TlS is available in the literature since electrode problems prevent some authors (Itoga and Kannewurf 1971) from obtaining Hall data for TlS. The width of the forbidden zone as deduced from Hall measurements is in reasonable agreement with that deduced from the conductivity data. Figure 3 shows the behaviour of the Hall mobility in TlS as a function of temperature. The temperature dependence of the Hall mobility of the current carriers at high temperatures ($300 \leqslant T \leqslant 350$) is represented by $\mu_H \simeq T^{8.33}$, while at $T > 350$ the Hall mobility is nearly constant. At low temperatures ($215 \leqslant T \leqslant 300$), $\mu_H \simeq T^{-6.78}$. The high values of the exponent n in the relation $\mu_H \simeq T^n$ and its sign suggest that the scattering mechanisms of the carriers should differ from that in semiconducting single-crystal materials. In contrast to the usual behaviour of semiconductors the Hall mobility was observed to decrease with temperature in the low-temperature range, while it increases with temperature in the high-temperature range. This behaviour is fairly contradictory compared with that of typical semiconducting materials. This anomalous behaviour cannot be explained by the usual theory of semiconductors. Hall mobility behaviour of the higher resistivities in TlS may be due to a change in the transport mechanism between localised states either within the energy gap or in the regions close to the bottom of the conduction band or to the top of the valence band. However, there is a need for more work on the role of the mobility behaviour with temperature before any definite conclusions can be drawn from this type of measurement. Clearly, charge-carrier mobility in our material is much higher among other semiconducting material from the group $A^{III}B^{VI}$. The highest value of mobility that has been calculated in our measurement is 17 782.8 $cm^2\,V^{-1}\,s^{-1}$ at 215 K, while the lowest value of mobility is 2454.7 $cm^2\,V^{-1}\,s^{-1}$ at room temperature. The values for hole concentration and diffusion coefficient for holes were calculated to be $1.18 \times 10^{10}\ cm^{-3}$ and 62.8 $cm^2\,s^{-1}$, respectively.

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