Electrical properties of the ternary compound Cu_2GeSe_3

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We report in this work the temperature dependence of the electrical resistivity and the Hall effect on p-type Cu_2GeSe_3in the temperature range from 80 to 300 K and under a magnetic field of 15 kG. The data is analysed assuming the two-band conductivity model, that is, the impurity band and the valence band. Employing this model we were able to obtain the temperature dependence of the ratio between the charge carrier concentrations in both bands. From the analysis of the carrier concentration in the valence-band $p_v$and the impurity-band p_a, the ionization energy is estimated to be around 26 meV. The mobility temperature dependence is analyzed by taking into account the scattering of charge carriers by acoustic phonons, polar optic phonons and thermally activated hopping. From the analysis, the activation energy is estimated to be around 18 meV.

Keywords: Semiconductors; new materials; electrical properties.

En este trabajo presentamos la dependencia de la resistividad eléctrica y el coeficiente de Hall del compuesto Cu_2GeSe_3 tipo-p,en función de la temperatura desde 80 hasta 300 K y bajo un campo magnético de 15 kG. Los resultados son analizados considerando el modelo de conductividad de dos bandas, esto es, la banda de impurezas y la banda de valencia. Utilizando este modelo, obtenemos la dependencia de la razón de las concentraciones de portadores de carga en ambas bandas, en función de la temperatura. Del análisis de la concentración de portadores en la banda de valencia p_v y la banda de impurezas p_a, la energía de ionización determinada es aproximadamente 26 meV. La dependencia de la movilidad con la temperatura es analizada tomando en cuenta los diferentes procesos de scattering de los portadores de carga con los fonones acústicos, fonones ópticos polares y hopping térmicamente activado. Del análisis, la energía de activación determinada es aproximadamente 18 meV.

Descriptores: Semiconductores; nuevos materiales; propiedades eléctricas.

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1. Introduction

Ternary compounds belonging to the Cu_2-Ge-VI_3 (VI = S, Te, Se) family present potential applications as photovoltaic and acustooptic devices in the near-infrared region of the spectrum [1]. These materials posses a low melting point [2], which decreases as the atomic number, atomic weight and radius of the anion increase. One of the potential candidates is Cu_2GeSe_3. Single crystal diffractometry [3] indicates that this material crystallizes in the orthorhombic system. The structure determined by the X-ray powder diffraction technique belongs to space group Imm2 and with unit cell parameters of: a = 11.860(3) Å, b = 3.960(1) Å, c = 5.455(1) Å. The compound melts in the 760-788°C range [4-8]. Recent studies by X-ray diffraction in polycrystalline samples [8] confirm previous results reported in reference [3].

Previous studies of the electrical properties [9] point out that Cu_2GeSe_3exhibits a semiconductor behavior at liquid nitrogen and a metallic one at room temperature. From the analysis of electrical measurements in a p-type sample, Endo *et al.* [10] found a carrier concentration of approximately 10^{19} cm^{-3} and a carrier mobility of 0.5 cm^2/V·s at room temperature. From the analysis of the hole concentration in the valence band as a function of temperature they concluded that the p-type conductivity is due to shallow acceptor states with an energy activation of about 0.02 eV. On the other hand, from the Hall and Sebeeck effect measurements, they obtained an effective mass ratio of 0.94. However, the empirical procedure with a transcendental equation employed by diverse authors [10-13] is cumbersome and subjected to misinterpretations in the parameters, and does not take into account the compensated and uncompensated situations.

In order to determine the quality as a semiconductor, we enterprise in this work a study of the electrical properties of Cu_2GeSe_3. A complete and detailed study of the carrier concentration in as-grown and un-doped samples of Cu_2GeSe_3 was performed between 80 and 300 K at 15 kG. Hot probe studies lead to a p-type sample, a result confirmed by the Hall Effect measurements. Carrier statistics and the two-band model appropriate for non-degenerate p-type semiconductors were used in order to calculate the Fermy energy and the hole concentration in the valence and impurity bands. In the deduction of the equations, no empirical procedures were employed to obtain the carrier concentration.

1.1. Hole concentration and Fermi Energy Calculations

The electric neutrality equation for a p-type semiconductor is:

$$p_v + p_a - n_c - n_d = N_a - N_d \tag{1}$$

Considering a partial compensation at low temperatures such that all donor levels are ionized, we can assume that

$n_c \ll p_v$ and $n_d = 0$; then Eq. (6) becomes:

$$p_v + p_a = N_a - N_d \tag{2}$$

This equation determines in the two-band model the concentration of holes in the valence band and in the impurity band, p_v and p_a, respectively. Therefore, under a partial compensation we obtain:

$$e^{E_f/K_BT} = \frac{2p_v}{(N_a - N_d - p_v)} e^{E_a/K_BT}$$

Multiplying this expression by p_v it is obtained that:

$$p_v^2 + \left(\frac{N_v}{2} e^{-E_{ai}/K_BT}\right) p_v - \frac{(N_a - N_d)}{2} N_v e^{-E_{ai}/K_BT} = 0 \tag{3}$$

where: $E_{ai} = E_a - E_v$ represents the activation energy for the acceptor levels.

Resolving Eq. (3), we have for the hole concentration in the valence band:

$$p_v = \frac{N_v}{4} e^{-E_{ai}/K_BT} \left[\sqrt{1 + \frac{8(N_a - N_d)}{N_v} e^{E_{ai}/K_BT}} - 1\right] \tag{4}$$

To determine the Fermi energy we resolved Eq. (4) to obtain:

$$E_f = E_a - K_BT \ln\left[\frac{1}{4}\left(\sqrt{1 + \frac{8(N_a - N_d)}{N_v} e^{E_{ai}/K_BT}} - 1\right)\right] \tag{5}$$

In order to determine the hole concentration in the impurity band we replace Eq. (4) into Eq. (2) to obtain:

$$p_a = (N_a - N_d)\left[1 - \frac{N_v}{4(N_a - N_d)} e^{-E_{ai}/K_BT} \times \left(\sqrt{1 + \frac{8(N_a - N_d)}{N_v} e^{E_{ai}/K_BT}} - 1\right)\right] \tag{6}$$

2. Experimental

The compounds were synthesized by direct fusion of the constituent elements and weighed in their proper stoichiometric relations inside vacuum-sealed quartz ampoules [8]. The composition and the stoichiometry were verified by EDX chemical analysis. The homogeneity was corroborated measuring several and different portions along the ingot. The average composition obtained is represented by the following values: Cu: 1.81 (± 0.9%), Ge: 1.05 (± 0.9%), and Se: 3.14 (± 1.0%). It can be appreciated that the stoichiometry is close to the 2:1:3 ideal relation; therefore, the samples present a small deviation represented by a Cu deficiency with respect to Ge (Cu/Ge = 1.72) and an excess of anions over cations (Se/metal = 1.05).

Employing the Van der Pauw technique [11], the resistivity and the Hall Effect were measured from 80 to 300 K under a magnetic field of 15 kG. Indium solder contacts were attached onto a clean and polished surface that was previously flux etched. The contacts were completely ohmic as deduced from the I-V characteristic taken from 1 to 20 mA, at 80 K and at room temperature.

3. Results and discussion

Figure 1 shows the resistivity as a function of the inverse of temperature. At low temperatures below 150 K, the compound presents a behavior characteristic of an extrinsic semiconductor, while at high temperatures between 150 and 300 K, the material behaves as a metal. This semiconductor-metal shift is known as a Mott transition [12], and it is ascribed to a shallow impurity band near the valence band. The intrinsic region is never reached.

For this reason, a model similar to Friszsche's model was used to fit the data, that is, a semiconductor-like and a metal-like expression were combined to obtain:

$$\rho = \rho_0 \frac{T}{T_0} + \rho_1 e^{E_1/K_BT} \tag{7}$$

In this formula we have assumed only one activation energy E_1.

The value for the activation energy obtained from a fit to the resistivity in the low temperature region was E_1=7.4meV, which corresponds to 0°C resistivity of $\rho_0 = 0.124\ \Omega$·cm.

Figure 2 shows the Hall coefficient as a function of the inverse of temperature. In this figure, a maximum around 90 K is observed. This maximum is characteristic of an impurity band near the valence band [13]. No sign inversion in the Hall coefficient was observed; this justifies the use of the two-band conduction model in the determination of the carrier concentrations under the presence of an impurity band.

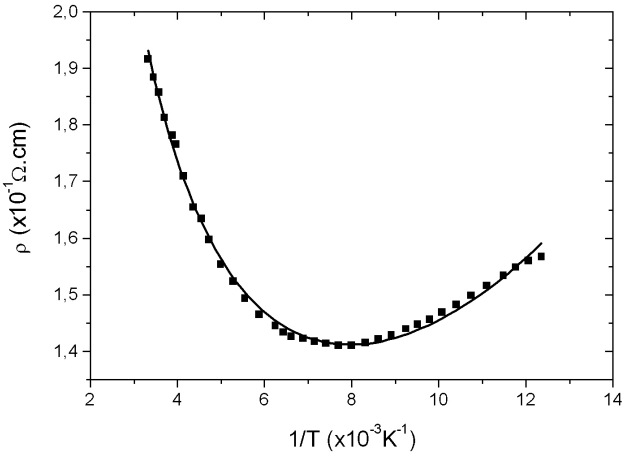

FIGURE 1. Temperature dependence of the resistivity (the best fit is indicated by a continuous line).

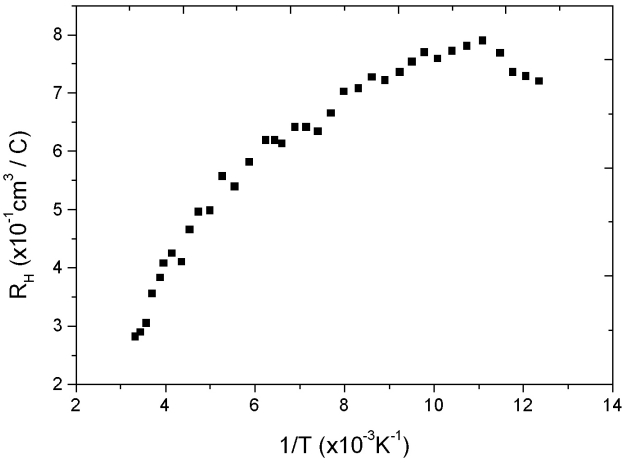

FIGURE 2. Temperature dependence of the Hall coefficient.

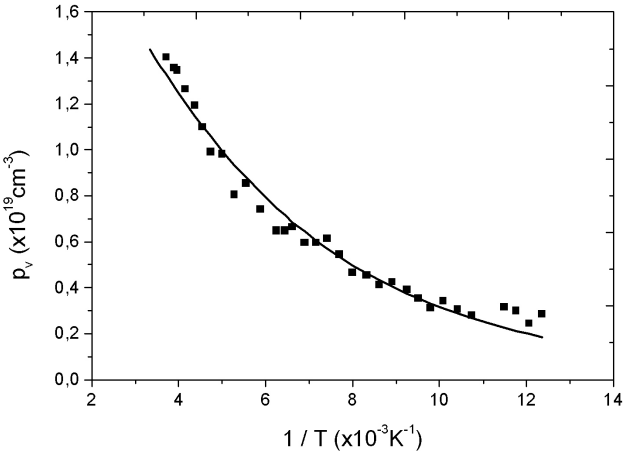

FIGURE 3. Temperature dependence of the hole concentration in the valence band.

From Eq. (2) it can be demonstrated that:

$$p_v = \frac{(N_a - N_d)}{(1+c)}c \tag{8}$$

$$p_a = \frac{(N_a - N_d)}{(1+c)} \tag{9}$$

where $c = p_v/p_a$ is the hole concentration ratio.

When a noticeable number of holes from the valence band along with a similar number from the impurity band are accessible, it can be proved that the Hall coefficient, in the case of this mixed conduction due to two types of carriers and for low magnetic fields, if $b = \mu_v/\mu_a$, is defined as the mobility ratio, then, can be written as:

$$R_H = \frac{(1+c)}{e(N_a - N_d)}\frac{(1+cb^2)}{(1+cb)^2} \tag{10}$$

As the impurities are exhausted at high temperatures, a minimum value in the Hall coefficient is reached and eq. (10) becomes:

$$R_{Hexh} \cong \frac{1}{e(N_a - N_d)} \tag{11}$$

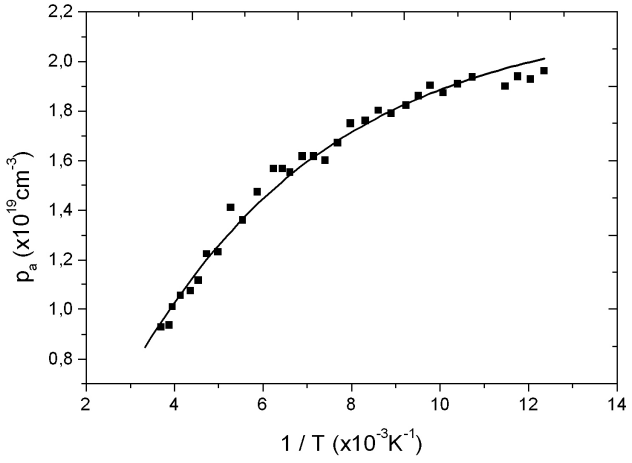

FIGURE 4. Temperature dependence of the hole concentration in the impurity band.

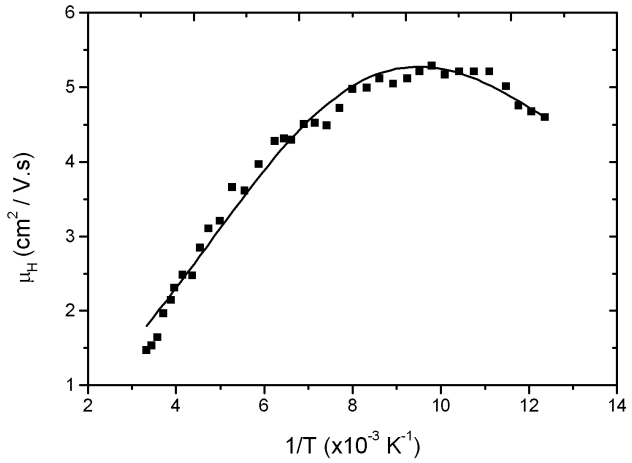

FIGURE 5. Mobility temperature dependence.

The maximum value forR_H occurs when $c = 1/b$, therefore:

$$\frac{R_{H_{máx}}}{R_{H_{exh}}} = \frac{(b+1)^2}{4b} \tag{12}$$

Equation (12) allows us to determine b; assuming it as a constant, then we can determine c. Later, we can obtain the experimental values for the concentrations $p_v$and p_a. The results are shown in Figs. 3 and 4 along with the best fits obtained employing Eqs. (4) and (6). From eq. (11) one can obtain the acceptor concentration in excess over the donor concentration defined as $N_a - N_d = 2.214 * 10^{19} cm^{-3}$. The activation energies obtained from the fits for the acceptors levels in the valence and impurity bands were 29 meV and 26 meV, respectively.

The mobility as a function of the inverse of the temperature is shown in Fig. 5. This behavior is usually well explained using standard scattering processes. Thus, at low temperatures, neutral and ionized impurities dominate, according to the Mott model [14]. The Erginsoy and Brooks-Herring models are not suitable. At high temperatures, acoustic phonons ruled by the usual acoustic deformation potential

model and optical polar phonons ruled by a phenomenological model of the form$\mu_{op} \propto (e^{\theta/T} - 1)G(\theta/T)$ are appropriate.

To fit the data we used the Matthiessen rule as well as a density $\rho = 5.6g/cm$ and sound velocity $v \approx 4\times10^5$ cm/s [4] as constant parameters. To avoid parameter dependency, we define: $C_{ac} = m^{*5/2}E_{ac}^2$ and $E_d = x_d/\theta^{1/2}$. Thus, using $C_{ac},\ \mu_0,\ W, E_d,\ \theta\ and\ m^*$ as adjustable parameters, the following values are obtained: activation energy $W = 18\ meV$, hopping factor $\mu_0 = 0.46$, effective mass $m_h^* = 0.82$, and phonon characteristic temperature $\theta = 328$. From the redefined parameters, the deformation potential $E_{ac} = 26.3\ eV$ and the effective dielectric constant $x_d = 1.1$ were obtained.

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1. L.K. Samantha, *Phys Stat. Solidi (a)* **100** (1987) K93.
2. L.I. Berger and V. Prochukhan, *Ternary Diamond-Like Semiconductors* (Consultans Bureau, NY 1969).
3. E. Parthé and J. Garín, *Monastsh. Chem.* **102** (1971) 1197.
4. E.P. Rogarocha, A.N. Melikhova, and N.M. Panasenco, *Neorg. Mater.* **11** (1975) 839.
5. E.G. Zhukov *et al.*, *Zh. Neorg. Khim.* **29** (1984) 1897.
6. B.J. Fernández, J.A. Henao, and J.M. Delgado, *Cryst. Res. Technol.* **31** (1996) 65.
7. I.D. Olekseyuk, L.V. Piskach, O.V. Parasyuk, O.M. Mel'niyk, and T.A. Lyskovetz, *J. Alloys Compds.* **298** (2000) 203.
8. M.A. Villarreal *et al.*, *Rev. Mex. Fís.* **49** (2003) 198.
9. B.J. Fernández, G. Marcano, and D.B. Bracho, III Latin American Workshop Magnetism, Magnetics Materials and their Applications, Mérida-Venezuela, 280 (1995).
10. S. Endo, I. Sudo, and T. Irie, *Jpn. J. Appl. Phys.* **10** (1971) 218.
11. L.J. van der Pauw, *Philips Res. Rep.* **13** (1958) 1.
12. N.F. Mott, *Physics Today* **31** (1978) 42.
13. O.V. Emelyanenko, T.S. Lagunova, D.N. Nasledov, and G.N. Talalakin, *Fiz. Tverd. Tela (Leningrad)* **7** (1965) 1315 [*Sov. Phys. Solid State.* **7** (1965) 1063].
14. M. Cutler and N.F. Mott, *Phys. Rev.* **181** (1969) 1336.