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Carrier Scattering Mechanisms in GaS_{0.5}Se_{0.5} Layered Crystals

Systematic dark electrical resistivity and Hall mobility measurements have been carried out in the temperature range 150–400 K on *n*-type GaS_{0.5}Se_{0.5} layered crystals. The analysis of temperature dependent electrical resistivity and carrier concentration reveals the extrinsic type of conduction with a donor impurity level located at 0.44 eV, donor and acceptor concentrations of 3.4×10^{17} and 4.1×10^{16} cm⁻³, respectively, and an electron effective mass of 0.41 m_0 . The Hall mobility is limited by the electron-phonon short-range interactions scattering at high temperatures combined with the ionized impurity scattering at low temperatures. The electron-phonon short-range interactions scattering mobility analysis reveals an electron-phonon coupling constant of 0.25 and conduction band deformation potential of 5.57 eV/Å.

Keywords: GaS_{0.5}Se_{0.5} crystals, resistivity, Hall mobility, scattering mechanisms

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1. Introduction

Due to the quasi two-dimensional crystal structure with strong covalent bonds in two dimensions and only weak interaction of the van der Waals type in the third direction parallel to the *c*-axis, layered semiconducting compounds like GaSe, InSe, GaS, and GaS_{*x*}Se_{1-*x*} are candidates for the future opto-electronic devices production. Furthermore, these compounds have large optical non-linearity. Therefore they are promising materials for the production of optical switching devices (SINGH et al.) and photodetectors (ADDUCI et al.; MEKHTIEV et al.).

Literature concerning the preparation, electrical and optical properties of GaS_{*x*}Se_{1-*x*} layered crystals are relatively poor. Most of the reported data are focused on the study of the optical and electrical properties as a function of *x*. The room temperature electrical and optical properties of GaS_{*x*}Se_{1-*x*} have been investigated in details (SCHLÜTER et al.; DE BLASI, GALASSINI et al. 1983 ; MANFREDOTTI et al. 1978; MANFREDOTTI et al. 1975). However, -up to our knowledge- no works have been done to study the temperature dependent dark electrical resistivity and Hall mobility of these crystals.

In our previous publication (AYDINLI et al.) we have reported the photoluminescence (PL) spectra of GaS_{0.5}Se_{0.5} crystals in the temperature range of 15–170 K and observed two bands located at 585 nm and 640 nm in the PL spectra. This study allowed us to suggest a simple energy diagram that explains the recombination process in the crystals. Besides, we have studied the phonon modes dominated in the crystals by means of polarized Raman scattering and infrared reflection (IR) spectra (GASANLY et al.).

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In this work, we have measured the temperature dependence of dark electrical resistivity and Hall mobility for GaS_{0.5}Se_{0.5} mixed crystals. These measurements allowed us to identify the impurity levels and to determine the acceptor and donor impurity concentrations, the carrier effective mass and the carrier scattering mechanisms of the crystals studied.

2. Experimental details

GaS_{0.5}Se_{0.5} single crystals were grown by the modified Bridgman method using high purity elements (99.999%). For each crystal ingot, several samples have been investigated. They were gently cleaved from the ingots and had typical dimensions of 0.5×0.5 cm², and thickness ranging from 0.1 to 0.2 cm along the *c*-axis. Sample electrodes were established by painting the electrode area with silver paste using suitable masks (van der Pauw shaped). The ohmic nature of contacts was confirmed by the *I-V* characteristics. The *I-V* characteristics were found to be ohmic for low voltages ($V < 25$ V) and were found to be independent of the reversal applied bias. The dark temperature dependent resistivity and Hall mobility measurements were done in the temperature range of 150 - 400 K using a Lake Shore automated Hall measuring system. The system is composed of Keithley 485 Pico-ammeter, Keithley 220 programmable current source, Keithley 2182 nano-voltmeter, Lake Shore 450 Gaussmeter, Lake Shore 340 temperature controller and ARS 8200 closed-cycle refrigerator. The system is connected to an Edwards EXC 120 turbo-molecular vacuum pump (10⁻⁵ Torr) and the sample is located in a Lake Shore 665 magnet. The Hall mobility was measured at several magnetic fields in the range of 0.1-1.0 T.

3. Results and discussion

The results reported here are the representatives of the repeated measurements on a series of reproducible samples of GaS_{0.5}Se_{0.5} crystals. The sign of the Hall coefficient (R_h) in all the studied temperature range (150-400 K) indicates that the crystal exhibits *n*-type conductivity. The ratio of length to width of the samples is ~1.2, thus no corrections are made for the shortening effect of the current electrodes. The crystals exhibit a dark electrical resistivity (\mathbf{r}), Hall mobility (μ) and carrier concentration (n) of $(5.2 \pm 0.1) \times 10^4 \Omega \text{ cm}$, $(80 \pm 6) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $(1.5 \pm 0.1) \times 10^{12} \text{ cm}^{-3}$ at room temperature, respectively. The values of n and μ measured here are higher than those reported in literature (DE BLASI, GALASSINI et al. 1983; MANFREDOTTI et al. 1978). The difference in the previous and current reported results may be attributed to the crystalline nature and disorder degree in the crystals. The low mobility and high resistivity values reported in literature were attributed to the high degree of structural disorder in the crystals. Thus, the high values of the above parameters obtained here indicate the better crystalline nature of the crystals.

To deduce the dominant scattering mechanisms and identify the impurity levels in GaS_{0.5}Se_{0.5} layered crystals, the temperature dependence of dark electrical resistivity and Hall mobility measurements were carried out in the temperature regions of 150-400 K. Figure 1 illustrates the variation of electrical resistivity as a function of reciprocal temperature. It is clear from the figure that the electrical resistivity increases with temperature decreasing at high rate above 200 K, below which the \mathbf{r} -T dependence is weak.

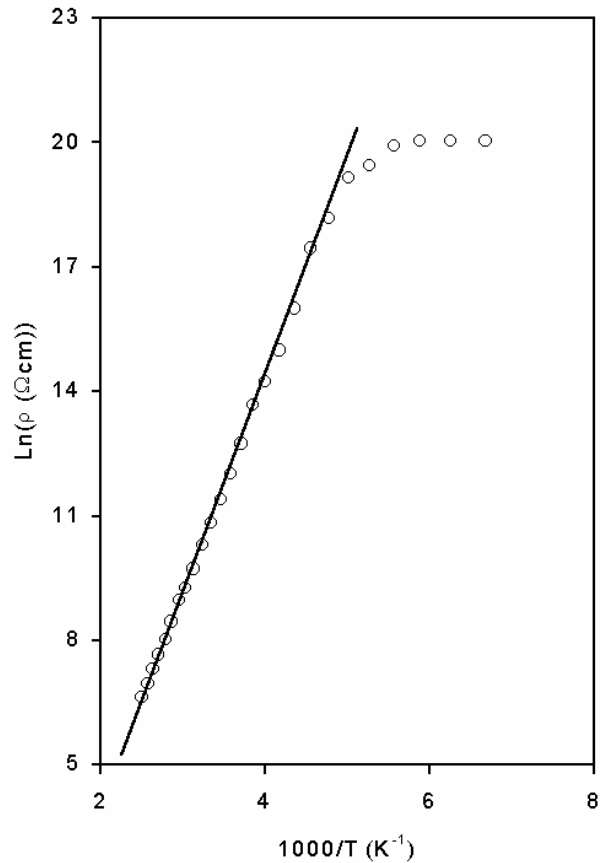


Fig. 1: Variation of the electrical resistivity as a function of reciprocal temperature for $\text{GaS}_{0.5}\text{Se}_{0.5}$ crystals.

The measured data of \mathbf{r} -T dependence are found to follow the relation,

$$\mathbf{r} = \mathbf{r}_0 \exp \left(\frac{E_d}{kT} \right), \quad (1)$$

where \mathbf{r}_0 is the pre-exponential factor and E_d is the donor energy level. As illustrated in Fig. 1, in the temperature region of 400-200 K, the \mathbf{r} -T variation was found to follow Eqn. (1), with a donor energy level $E_d = (0.44 \pm 0.02)$ eV. The value of E_d suggests the extrinsic conductivity due to impurity carriers, as will be confirmed later from the Hall data. The obtained energy level may be ascribed to the native structural defects such as Ga, S or/and Se interstitial or vacancies and strain induced defects, which exist in the $\text{GaS}_{0.5}\text{Se}_{0.5}$ layered crystals. Similar donor level was also reported for n -type GaS single crystals (DE BLASI et al. 1981). It is worth noting that, the fitting procedure was carried out by a special high-convergence minimization program that uses the x^2 method. The errors in the data were evaluated to be 2-10 %. Typical best fit for the experimental data is illustrated in Fig. 1.

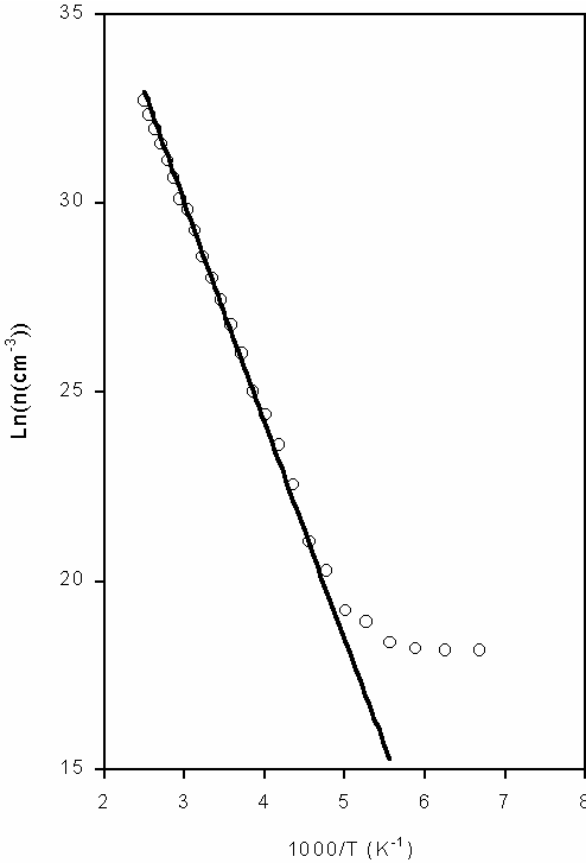


Fig. 2: Variation of carrier concentration with reciprocal temperature for GaS_{0.5}Se_{0.5} crystals.

The temperature dependence of carrier concentration, n , of GaS_{0.5}Se_{0.5} crystals calculated from the relation $n = 1/eR_h$ is illustrated in Fig. 2. The figure shows the strong decrease of n from $1.6 \times 10^{14} \text{ cm}^{-3}$ at 400 K to $1.7 \times 10^8 \text{ cm}^{-3}$ at 200 K. Below this temperature, the n - T variation is weak, indicating the degeneracy of carriers in the samples. In temperature region above 200 K, the temperature dependence of carrier concentration is analyzed by using the single donor - single acceptor model in which the dependence of carrier concentration on temperature is given by (BLACKMORE p. 134),

$$\frac{n(n + N_a)}{N_d - N_a - n} = \mathbf{b} N_c \exp \left(-\frac{E_d}{kT} \right), \tag{2}$$

where \mathbf{b} is the degeneracy factor, N_c is the effective density of states of the conduction band, N_a and N_d are the acceptor and donor impurity concentrations, respectively, presented in the crystals. Assuming both types of impurities to be present in the crystals and using the three-dimensional expression for N_c , the temperature dependence of n in Eqn. (2) could then be rewritten as,

$$n = \frac{2(N_d - N_a)}{1 + \frac{N_a}{b N_c} \exp(E_d/kT) + \left[\left(1 + \frac{N_a}{b N_c} \exp(E_d/kT) \right)^2 + \frac{4(N_d - N_a)}{b N_c} \exp(E_d/kT) \right]^{1/2}} \cdot (3)$$

By substituting the degeneracy factor $b = 2$ and $E_d = 0.44$ eV, which is the value of donor ionization energy calculated from the resistivity measurement in the extrinsic region, a computer numerical analysis was handled using Eqn. (3). The best fitting curves to the experimental data, obtained from the temperature-dependent Hall effect measurements, is represented by the solid line in Fig. 2. As a result of this fitting procedure, data regressions provide the determination of the acceptor and donor concentrations in addition to the carrier effective mass ratio. The values of N_d , N_a , and m_e/m_0 -the electron effective mass ratio- were found to be $3.4 \times 10^{17} \text{ cm}^{-3}$, $4.1 \times 10^{16} \text{ cm}^{-3}$ and 0.41, respectively. The value of N_a reported here coincides with the value calculated for $\text{GaS}_{0.4}\text{Se}_{0.6}$ crystals (MANFREDOTTI et al. 1978). The correctness of the obtained value of $m_e = 0.41 m_0$ is confirmed by calculating the electron effective mass from the relation, $M^{-1} = m_e^{-1} + m_h^{-1}$ with M -the reduced effective mass- being $0.23 m_0$ (ABDULLAYEVA et al.) and m_h -the holes effective mass in the crystals- being $0.52 m_0$ (MANFREDOTTI et al. 1978). It should also be noted that the plot of $\ln(n) - T^{-1}$ reveals a donor level of $E_d = (0.44 \pm 0.02)$ eV which coincides with the value obtained from the electrical resistivity measurements. The fitting parameters obtained from the single donor - single acceptor model are used to evaluate the ionized impurity scattering mobility (\mathbf{m}) as it will be shown later through the mobility analysis.

The Hall mobility calculated from the relation $\mathbf{m} = \mathbf{s} / ne$ (see Fig. 3) was found to decrease with increasing temperature for $T > 200$ K. In the temperature region below 200 K the Hall mobility increases with temperature increase. The temperature dependence of Hall mobility illustrated in Fig. 3 follows the relation $\mathbf{m} \propto T^{-g}$, with $g \sim 1.6$ above 200 K. This behavior is an indication of the domination of thermal lattice scattering in this temperature region. Below 200 K, the \mathbf{m} -T dependence become very weak indicating the domination of ionized impurity scattering in the low temperature region. The \mathbf{m} -T dependence observed in the $\text{GaS}_{0.5}\text{Se}_{0.5}$ crystals is similar to that reported for layered structured materials like GaSe and InSe (SCHMID, VOITCHOVSKY; MANFREDOTTI et al. 1977; DE BLASI, MICOCCI et al. 1983; QASRAWI et al.), where the mobility-temperature dependence was observed to be limited by ionized impurity scattering combined with the electron-phonon short-range interactions scattering. To check the validity of this behavior in the crystals under study, a detailed theoretical and numerical analysis were handled and discussed.

The temperature dependence of Hall mobility above 200 K is interpreted using the electron-phonon short-range interactions mobility given by SCHMID as,

$$\mathbf{m}_{ep} = \frac{e}{m_e} \int_0^{\infty} \mathbf{t}(u) u^{3/2} \exp(-u) du \quad (4)$$

with $u = \frac{E}{kT}$. $E = \frac{\hbar^2 \mathbf{k}^2}{2m_e}$ is the energy of a nearly free electron and $\mathbf{t}(u)$ the average

scattering time. This integral is solved numerically. An approximate solution is also given by SCHMID. The best fit of the mobility of GaS_{0.5}Se_{0.5} layered crystals was achieved using the electron-phonon short-range interactions in three dimensions where the solution of the above integral takes the form,

$$m_{ep} = \frac{e \hbar \sqrt{\hbar\omega}}{3 \sqrt{p} m_e g^2 (kT)^{3/2}} \tag{5}$$

Here, $\hbar\omega$ is the optical phonon energy and g^2 is the electron-phonon coupling constant given as,

$$g^2 = \frac{e^2 m_e^{3/2}}{2 \sqrt{2} p \hbar MN (\hbar\omega)^{3/2}} \tag{6}$$

where e is the deformation potential, M is the reduced ionic mass and N is the number of cells per unit volume.

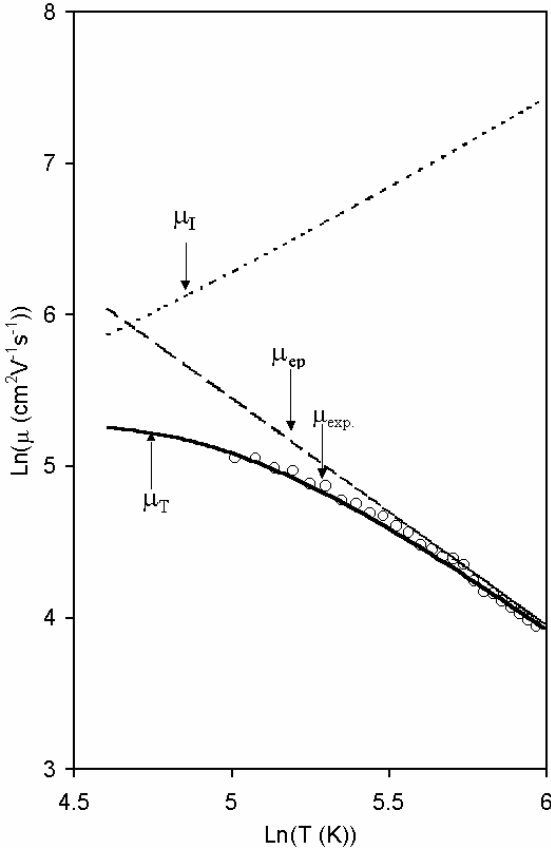


Fig. 3: Variation of $Ln(\mu)$ as a function of $Ln(T)$ for GaS_{0.5}Se_{0.5} crystals.

In computing the electron-phonon short-range interaction scattering mobility, the value of $m_e = 0.41 m_0$, obtained from the carrier concentration analysis, and $\hbar\omega = \hbar c\mathbf{n} = 0.029$ eV were used. Here $\mathbf{n} = 240 \text{ cm}^{-1}$ is the frequency of the most intensive longitudinal optical mode observed through IR measurements (GASANLY et al.). Thus, the only fitting parameter in Eqn. (5) is the electron-phonon coupling constant g^2 . The best fit to the experimental data of Hall mobility illustrated in Fig. 3 above 200 K reveals a coupling constant $g^2 = 0.25 \pm 0.05$. The value of g^2 reported here coincides with the values found in layered structured crystals like GaSe and InSe (SCHMID, VOITCHOVSKY; MANFREDOTTI et al. 1977; DE BLASI, MICOCCI et al. 1983). By substituting, the value of $g^2 = 0.25 \pm 0.05$, $m_e = 0.41m_0$, $M = 0.23 m_0$, $\hbar\omega = 0.029$ eV, and the value of N calculated assuming hexagonal structure with a lattice parameters of $a = 3.671$ and $c = 15.719 \text{ \AA}$ (AYDINLI et al.) into Eqn. (6), the deformation potential was calculated as $(5.57 \pm 0.10) \text{ eV/\AA}$. This value is in good agreement with the theoretical calculated values 5.65 and 5.80 eV/\AA for GaS_{0.5}Se_{0.5} and GaSe crystals, respectively, (SCHLÜTER et al.), and with the value 5.2 eV/\AA obtained from the Hall mobility analysis for GaSe crystals (SCHMID, VOITCHOVSKY). It is worth noting that in this fitting procedure, the ratio of Hall to drift mobility was taken to be unity, and the theoretically obtained m_p data agree will with that measured as could be seen from Fig. 3.

The ionized impurity scattering mobility (m_i) is given by the Brooks-Herring equation (PUTLEY). The temperature dependence of m_i is calculated from

$$m_i = \frac{3.28 \times 10^{15} e_s^2 T^{3/2}}{(N_a + N_d) \left(\frac{m_e}{m_0} \right)^{1/2} \left[\ln(b+1) - \frac{b}{b+1} \right]} \tag{7}$$

where

$$b = \frac{1.29 \times 10^{14} \left(\frac{m_e}{m_0} \right) e_s T^2}{N^*} \tag{8}$$

N^* is the effective screening density and given by,

$$N^* = n + \frac{(n + N_a) (N_d - N_a - n)}{N_d} \tag{9}$$

Using the values of N_d , N_a and m_e/m_0 obtained from the single donor-single acceptor model analysis and the value of the static dielectric constant, $\epsilon_s = 10.2$, obtained from IR measurements on the GaS_{0.5}Se_{0.5} crystals (GASANLY et al.), the ionized impurity scattering mobility was calculated and illustrated in Fig. 3.

The ionized impurity scattering mobility and the electron-optical phonon short-range interactions scattering mobility are related to give the combined mobility m_r through the relation,

$$\frac{1}{m_r} = \frac{1}{m_{ep}} + \frac{1}{m_i} \tag{10}$$

Using Eqn. (10), the total mobility was evaluated and plotted in the same figure. The calculated theoretical m_i agrees with that obtained from the Hall effect experiments. Similar type of mobility behavior was reported for GaSe single crystals (MANFREDOTTI et al. 1977; SCHMID, VOITCHOVSKY) and for InSe in single crystal and thin film forms (DE BLASI, MICOCCI et al. 1983; QASRAWI et al.).

4. Conclusions

The electrical resistivity and Hall mobility measurements in the temperature region 150-400 K for GaS_{0.5}Se_{0.5} layered crystals indicate that, the crystals exhibit extrinsic *n*-type conductivity. The temperature dependencies of electrical resistivity and carrier concentration predict the existence of the donor level located at (0.44 ± 0.02) eV below the conduction band. The single donor-single acceptor model analysis on the temperature dependence of carrier concentration reveals an electron effective mass of $0.41 m_0$ and donor and acceptor impurity concentrations of 3.4×10^{17} and 4.1×10^{16} cm⁻³, respectively. The Hall mobility is found to be limited by the scattering of electron-phonon short-range interactions at high temperatures and by the ionized impurity scattering at low temperatures. The data analysis reveals an electron-phonon coupling constant of 0.25 ± 0.05 . and a deformation potential of (5.57 ± 0.10) eV/Å.

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