Some physical properties of Ga$_2$Te$_5$ single crystals

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Single crystals of Ga$_2$Te$_5$ were prepared by a special modified Bridgman technique. Measurements of the electrical conductivity and Hall effect between 268 and 503 K were carried out on Ga$_2$Te$_5$ samples, in two crystallographic directions (parallel and perpendicular to the C-axis). The Hall coefficient is positive and varies with the crystallographic direction. A unique mobility behaviour and strong anisotropy in the carrier mobility was observed. Also, the present investigation involves the thermoelectric power measurements of Ga$_2$Te$_5$ samples, in the wide range, from 170 to 511 K, when the direction of the temperature gradient is parallel to the layer planes. The combination of the electrical and thermal measurements in the present investigation makes it possible to find various physical parameters such as, carrier mobilities, effective masses of free charge carriers ($m^*_p$, $m^*_n$), diffusion coefficient ($D_p$, $D_n$) and diffusion length ($L_p$, $L_n$), as well as the relaxation time ($\tau_p$, $\tau_n$) and to reveal the general behaviour of this semiconductor.

1 Introduction

Crystalline materials with a high anisotropy of physical properties have attracted ever-growing attention recently. Of particular interest in this connection are, the ($A^{VI}$ $B^{V}$-type) semiconductors compounds. Characteristic of these crystals is the existence of great number of diverse structural types, very different in their physical properties. Ga$_2$Te$_5$ is a chalcogenide binary compound. The phase diagram of Ga-Te system has been investigated by differential thermal analysis and direct observation of melting points under control to pressures (10$^{-1}$,10$^{3}$ mm-Hg)$^{1,2}$. The earlier phase diagram determination was compiled by Hansen & Anderko$^3$ based on experimental results of Klemm & Vogt$^4$, who identified two compounds GaTe and Ga$_2$Te$_5$, and expected that another poly-telluride would exist in the Te-rich regions of many countries, because the longest thermal arrest was observed at 75 %Te. Newman et al.$^1$ reported two other compounds, Ga$_2$Te$_3$, GaTe$^5$ to be unstable at room temperature by X-ray analysis. Alapini et al.$^2$ published results obtained from DTA and X-ray studies which were in agreement with those of Klemm & Vogt$^4$ (GaTe, Ga$_2$Te$_3$, Ga$_2$Te$_5$) and are stable compounds.

After Antonopoulis et al.$^6$ identified another compound Ga$_2$Te$_3$ by electron microscope, four stoichiometric compounds GaTe, Ga$_2$Te$_3$, Ga$_3$Te$_5$, and Ga$_4$Te$_{13}$ were accepted and confirmed by recent DTA works done by Blachnik & Irl$^7$, and by Tschirner et al.$^8$. The new phase diagram of Ga-Te system reported by Levinsky et al.$^9$.

The Ga$_2$Te$_5$ crystal structure has a Pearson symbol (t14) and space group (I4/m) (by Okamoto et al.$^{10}$, Deiseroth & Amann$^{11}$ found that Ga$_2$Te$_5$ contains chains of trans-edge-sharing GaTe$_5$-tetrahedra and additional Te-atoms according to the formulation Te[GaTe$_5$]$_2$ and ($a$=792.9 pm, $b$=792.9 pm and $c$=685.5 pm). The gallium compound forms a body-centered tetragonal structure, in which infinite chains [GaTe$_5$]$_n$ of edge-linked GaTe$_5$-tetrahedra and held together by inter-chain Te atoms in a square-planar coordination of Te atoms from the four surrounding chains.

Deiseroth & Amann$^{11}$ studied the polymorphism structural relations and homogeneity ranges of M$_2$Te$_5$ (M = Al, Ga, In). Electronic structure of semiconducting compounds (Re$_2$Te$_5$, Ga$_2$Te$_5$, K$_2$SbTe$_5$) studied by Bullet$^{12}$. The three crystal structures have in common Te in a quasi-planar environment of four Te neighbours.

In the present work, the authors intend to investigate the electrical conductivity, Hall effect and their temperature dependence, and also thermoelectric power phenomena of Ga$_2$Te$_5$ compounds. From this study, the main physical parameters could be determined, such as the energy...
gap, the depth of the impurity level, the Hall coefficient, conductivity type, the diffusion coefficient, the diffusion length, the scattering mechanism of the charge carriers and their concentration, the mobility, the effective mass and the life time of both majority and minority carriers.

![Graph](image)

**Fig. 1** — Temperature dependence of the electrical conductivity of Ga$_2$Te$_5$.

2 Experimental Procedure

2.1 Crystal growth

High quality Ga$_2$Te$_5$ single crystals have been grown from melt by the Bridgmann method. The growth method and the experimental apparatus have been described in detail elsewhere$^6$. The purity of the materials used was as follows: Ga (99.999 %, Aldrich) and Te (99.999 %, Aldrich). Stoichiometric quantities of the constituent elements (2.324 g Ga and 10.6333 g Te) representing 17.935 % Ga and 82.064 % Te were used as starting materials. The appropriate amounts were first sealed in quartz ampoules at a pressure of (10$^{-4}$ Torr). The quartz ampoule is washed with pure alcohol and hot distilled water, then coated with a thin layer of graphite to prevent contamination of the charge on the internal surface of the ampoule. Individual components were weighed using electric balance, which characterized with sensitivity equal to (10$^{-5}$ g) (Sartorius Mark). The reaction vessel was heated to about 814 K, under thorough agitation, to ensure complete mixing of the components, the ampoule was held in the hot zone of a three zone tube furnace for about 24 h, then was allowed to be drawn at a very low rate (1.2 mm h$^{-1}$) to enter the middle zone, where the crystallization temperature of the compound is reached. This temperature is 754 K according to the phase diagram reported$^6$. Finally, the ampoule enters the last zone in the furnace, where the temperature is below the melting point. Such a process requires at least 15 days to be performed. The resulting single crystal obtained by the above procedure was 2 cm in length and 1.5 cm in diameter. The results of X-ray analysis, which was done at the Central Metallurgical Research and Development Institute (CMRDI, Egypt) revealed the presence of a good crystalline phase without any secondary phases.

![Graph](image)

**Fig. 2** — Temperature dependence of the anisotropic factor for Ga$_2$Te$_5$. 

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2. J. to cleavage plane
3. Mn. J.
4. Cl
5. J.
6. J. to cleavage plane
7. 6. II to cleavage plane
8. 1.9
9. 2.4
10. 3
11. 6. 10.3 / T(K)
12. 3.4
13. 3.9
14. 3.5
15. 1.0-1.5-2-2.5-3-3.5
16. 1.9
17. 2.4
18. 29
19. 10-2
20. 1.0-1.5-2-2.5-3-3.5
21. 1.9
22. 2.4
23. 29
24. 10-2
2.2 Measuring technique

For studying the electrical conductivity and Hall effect, the sample was prepared in a rectangular shape. In this way, the length of the sample was made three-times its width to avoid Hall voltage drop. After polishing processes, the sample’s dimensions were 11.95 x 3.5 x 1.1 mm³. Referring to current, the optic axis, coinciding with the C-axis of the crystal and the applied magnetic field with the symbols J, C and H, respectively, one can sum up the conditions of the measurements when the current was parallel to the C-axis as (\(J||C,LH\)) and when the current flows perpendicular to the C-axis as (\(J\perp C||H\)). Measurements were done with the help of a pyrex glass cryostat, which was designed by the authors for this purpose, and a sensitive potentiometer (UJ33E mark). The cryostat is used as a holder, evacuated container for liquid nitrogen (in case of low measurements) and a support to the electric heater (for high temperature measurements). By using Edward rotary pump, one can evacuate the cryostat (\(10^{-3}\) Torr), for protecting the sample from the water vapour condensation and oxidation. Copper-constantan thermocouple was used for measuring the environment temperature of the sample. The silver paste was used as an ohmic contact by pointing the cleaved cherry red sample. An intermediate magnetic field (\(\approx 5\) k gauss) supplied from Oxford electromagnet (N117 type) was used.

In the thermoelectric power (TEP) measurements, an evacuated calorimeter (\(-10^{-3}\) Torr) was used to protect the sample from oxidation and water vapour condensation at high and low temperatures, respectively. The calorimeter has two heaters. The outer heater (the external source) discharges its heat slowly to the specimen environment. The inner heater (connected to the lower end of the crystal) was made purposely to
control properly, the temperature and its gradient along the specimen.

Fig. 5 — The relation between $\alpha$ and $(10^3/T)$ for Ga$_2$Te$_5$.

The TEP is calculated at different temperatures by dividing the magnitude of the thermo-voltage difference across the crystal by the temperature difference between the hot and cold ends, where the thermo-voltage was measured also, by a sensitive potentiometer (UJ33E mark).

3 Results and Discussion

3.1 Electrical conductivity and the Hall coefficient

Interesting physical phenomenon in layer semiconductor Ga$_2$Te$_5$ includes a strong anisotropy of electrical conductivity, the anisotropy of electrical properties are investigated in great detail, and particularly, the changes in Hall coefficient and Hall mobility, as well as electrical conductivity ($\sigma$) of Ga$_2$Te$_5$ in the temperature ranges, extending from 268 to 503 K are dealt with. Fig. 1 gives the temperature dependence of electrical conductivity parallel ($\sigma_r$) and perpendicular ($\sigma_\perp$) to the layers of Ga$_2$Te$_5$ single crystal, where intrinsic region in this sample appears at 384 K for ($\sigma_r$) and at 377 K for ($\sigma_\perp$). The transition region lies in the temperature range 333-384 K for ($\sigma_r$) and 357-377 K for ($\sigma_\perp$). The energy gap assessed from the graph of $\log(\sigma) = F(10^3/T)$ is $\Delta E_{\text{g}1} = 1.77$ eV and $\Delta E_{\text{g}2} = 0.46$ eV.

The value of $\Delta E_{\text{g}1} = 1.77$ eV agrees with the values obtained from electronic structure calculations ($\Delta E_{\text{g}} = 1.7$ eV) by Bullitt$^{12}$. The room temperature conductivity of this sample is $5.8 \times 10^{-4}$ ohm$^{-1}$ cm$^{-1}$ parallel to the cleavage plane and $(13 \times 10^{-4}$ ohm$^{-1}$ cm$^{-1}$) perpendicular to the cleavage plane. Fig. 1 shows that the conductivity perpendicular to the layers plane differs from that parallel to it, suggesting a great anisotropy. Fig. 2 illustrates an examination of the anisotropy of the electrical conductivity at all the temperature range of investigation. The ratio ($\sigma_\perp/\sigma_r$) seems to be fairly constant and equals 25.52. Presence of such anisotropies can be attributed partly or wholly assignable to inter-layer macroscopic defects and/or planes of precipitates, as...
studied by G A Gamal et al.\textsuperscript{15} Fig. 3 shows the relation between log \((R_\text{II}T^2)\) and \((10^7T)\). This curve divided into two regions, the first part at low temperature where \(R_\text{II}T^2\) and \(R_\text{II}T^3\), grow slowly with respect to the temperature region and reaches a maximum value of \(3 \times 10^{16}\) at 388 K and \(1.26 \times 10^6\) at 388 K, respectively. This region indicated the extrinsic region and from this region the position of the acceptor level was calculated to be \(\Delta E_a = 0.33\) eV and \(\Delta E_{a+} = 0.19\) eV. The second region is above 388 K. In this region, a rapid decrease was observed as the temperature increases for \(R_\text{II}T^2\) and \(R_\text{II}T^3\). This region indicated the intrinsic region and from this region, the energy gaps were calculated as \(\Delta E_a = 1.79\) eV and \(\Delta E_{a+} = 0.47\) eV. These values are in agreement with that deduced from the conductivity data. The Hall coefficient at room temperature \((R_\text{II})\) is evaluated as \((20 \times 10^3/\text{cm}^3)\) and \((R_\text{II})\) as \((23 \times 10^3\text{ cm}^3)\). Hence their ratio comes out to be \(R_\text{II}/R_\text{II} = 0.0115\). It is possible to notice that, \(R_\text{II}\) is higher in magnitude than \(R_\text{II}\) in the temperature range under study. The positive sign of the \(R_\text{II}\) values signifies that Ga\textsubscript{2}Te\textsubscript{5} has a p-type nature over the entire temperature range of the investigation. Fig. 4 shows the temperature dependence of charge-carrier mobility. The Hall mobility is calculated by using the values of conductivity and Hall coefficient from the relation \(\mu = R_\text{II}/\pi\). From this curve, one can distinguish three regions. In the first region, at low temperature \((275-354\text{ K})\), the mobility \((\mu_\text{II})\) increases with temperature, obeying the law \((\mu \propto T^2)\). Such a behaviour is characteristic of a scattering mechanism of the charge carriers with ionized impurities. The second region extends from 354 to 484.5 K, the mobility \(\mu_\text{II}\) has a nearly constant value with increase of temperature until 384.5 K, which corresponds to the transition region. After that, the third region begins. At high temperature ranges \((384-501\text{ K})\), the mobility \(\mu_\text{II}\) decreases with increasing temperature, according to the law \((\mu \propto T^{3.5})\). This leads to the assumption that, lattice-scattering dominates and the impurity concentration has little effect on the mobility.

For the mobility \((\mu_\text{II})\) has the same behaviour. In the temperature range 268-360 K, the mobility \(\mu_\text{II}\) increases with temperature, obeying the law \((\mu_\text{II} \propto T^{3.5})\). This leads to the assumption that, scattering caused by the ionized and un-ionized acceptor atoms. In the high temperature range 360K-501 K, the mobility \(\mu_\text{II}\) decreases with increasing temperature according to the law \((\mu_\text{II} \propto T^{-5.5})\). This behaviour leads to phonons scattering. At room temperature, Hall mobility along the layers \((\mu_\text{II})\) is equal to 5011.8 cm\(^2\)/Vs and that normal to the layers \((\mu_\text{II})\) is equal to 309.3 cm\(^2\)/Vs.

From Hall coefficient data, the charge-carrier concentration calculated by using the relation \(R_\text{II} = (p/e)\), where \(p\) is the hole concentration and \(e\) the electron charge. The carrier concentration at room temperature calculated from \(R_\text{II}\) and \(R_\text{III}\) values was \(3.09 \times 10^{12} \text{ cm}^{-3}\) and \(2.69 \times 10^{12} \text{ cm}^{-3}\), respectively. The variation of the values of the carrier concentration along and perpendicular to the C-axis gives a good evidence of the strong anisotropy of the Ga\textsubscript{2}Te\textsubscript{5} single crystals and its interesting semiconductor properties.

3.2 Thermoelectric power (TEP)

Gallium chalcogenides have interesting thermoelectric properties and have many practical applications\textsuperscript{16}. This study may be the first investigation of TEP for Ga\textsubscript{2}Te\textsubscript{5}. Measurements of thermal emf of Ga\textsubscript{2}Te\textsubscript{5} crystals were carried out when the direction of the temperature gradient is parallel to the layer planes. Measurements covered the temperature, ranging from 170 to 511 K.

The room temperature thermoelectric power value for Ga\textsubscript{2}Te\textsubscript{5} sample amounted to be 50 \textmu V/K.

The behavior of thermoelectric power with temperature in the intrinsic range can be described by the equation of Laue\textsuperscript{17}:

\[
\alpha = -\frac{K}{e} \left[ \frac{b-1}{b+1} \left( \frac{\Delta E}{2KT} \right) \right] + \frac{1}{2} \ln \left( \frac{m_e}{m_p} \right)^{3/2}
\]

where, \(K\) is the Boltzmann constant, \(b\) the ratio of the electron to hole mobilities, \(\Delta E\) the energy gap width, and \(m_e\), \(m_p\) the effective masses of electrons and holes, respectively. This relationship shows that, a plot of \(\alpha\) in the intrinsic range, as a function of the reciprocal of absolute temperature, is a straight line as shown in Fig. 5. The slope of the linear part of this dependence is used to estimate the ratio of the electron and hole mobilities. Taking \(\Delta E \approx 1.77\) eV (as obtained from the electrical conductivity and Hall effect data), the ratio \(b = \frac{\mu_e}{\mu_p}\) is found to be 1.71. Since \(\mu_e = 5011 \text{ cm}^2/\text{Vs}\), then we
can evaluate $\mu_e = 8570$ cm$^2$/Vs. Another important parameter can be deduced with the aid of the obtained values of $\mu_e$ and $\mu_h$ using the famous Einstein relation\textsuperscript{16} that is, the diffusion coefficient for both majority and minority carriers (holes and electrons), at room temperature, can be evaluated to be $D_n = 125.2$ cm$^2$/s and $D_p = 214.25$ cm$^2$/s, respectively. From the intersection of the curve, the ratio between the effective masses of both electrons and holes can be evaluated to be $(m'_n/m'_p) = 1.93 \times 10^{-5}$ and assume that, this ratio does not vary with temperature.

Since $\alpha$ has a positive sign over the entire temperature range of investigation, the sample's majority carriers are the holes, i.e., Ga$_2$Te$_3$ crystal exhibits p-type conductivity, which is in good agreement with the results reported from Hall effect data. The observed large values of thermoelectric power in Ga$_2$Te$_3$ samples at low temperature indicate drag of carriers by phonons.

Another important relation was suggested for application in the extrinsic region\textsuperscript{\textsuperscript{17}}:

$$\alpha = \frac{K}{e} \left[ 2 - \ln \left( \frac{\rho h^3}{2(2\pi m'_p KT)^{3/2}} \right) \right]$$  

Fig. 6 shows the dependence of TEP on carrier concentration, for a given Ga$_2$Te$_3$ sample, as has been seen, $\alpha$ decreases linearly with the increase of the carrier concentration in the low carrier density region. Calculation of the effective mass of holes from the intersection of the curve yields the value $(m'_p = 82.5 \times 10^{-24}$ kg$)$.

Combining these values with the above-mentioned results for the ratio $(m'_n/m'_p)$, one obtains an effective mass of electrons $(m'_n = 1.5 \times 10^{-24}$ kg$)$.

The mean free time between collisions can be estimated to be $\tau_e = 2.58 \times 10^{-11}$ s and $\tau_h = 8.03 \times 10^{-11}$ s. By using the values of diffusion coefficient and the mean free time, the diffusion length for both charge carriers can be determined. The values of the diffusion length for electrons and holes are found to be $L_e = 4.15 \times 10^{-2}$ cm and $L_h = 5.58 \times 10^{-2}$ cm, respectively.

References