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# Peculiarities Of The Anisotropic Properties Of Electrical Conductivity And Hall Mobility Of $In_4se_3$ Crystals

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***Abstract*—Simple, durable and new crystal growth method was used for the present investigation by which enabled us to grow these unique crystals of $In_4Se_3$.**

**Temperature variation of electrical conductivity in two crystallographic directions (σ// and σ⊥) of In4Se3 crystals has been measured. We extend our work to cover Hall Effect phenomenon. Accordingly the Hall mobility behavior and the scattering mechanism were discussed. The energy gap and ionization energy are estimated as an important physical constant for the first time for this new compound.**

***Keywords—$In_4Se_3$, crystal growth, anisotropy, Hall mobility, electrical conductivity, scattering mechanism.***

## I. INTRODUCTION

Great attention has been paid to the properties of both crystals and thin films of the InSe system due to their importance in different applications. Amorphous and polycrystalline InSe films exhibit a fairly large photovoltaic effect similar to that for metal dichalcogenides (TMD), and attempts have already been made to utilize them as solar cells [1-3]. Owing to the low-dimensional structure these materials have also been used in the area of electrochemical devices and they have been proposed as positive electrodes in microbatteries [4-8], for example, in lithium microbatteries [8]. Anisotropic properties of semiconductors are associated with its layered structure with strong covalent bonding [9] in the layer and weak Van Der Weals bonding between the layer as in $Bi_2Te_3$ [10]. Photosensitivity of $In_4Se_3$ single crystals has been studied experimentally in two crystallographic axes [11]. $In_4Se_3$ layered semiconductor crystals' surfaces have been studied with application of Auger electron spectroscopy (AES) [12]. The basic features of the surface layer information at thermal oxidation of the native cleavage surface on $In_4Se_3$ layer crystal have been investigated [13]. Photosensitivity anisotropy of $In_4Se_3$ single crystals has been studied experimentally [14].

The effect of Se vacancy on the electronic and thermoelectric properties of $In_4Se_3$ has been investigated by first-principles calculations [15]. It was found that $In_4Se_3$ compound could be synthesized by mechanical alloying of the elemental powders mixture only for 3h. The density and microstructure of $In_4Se_3$ compound could be improved by increasing HP temperature or pressure. A maximum power factor of 533μWm-1K-2 was obtained for the $In_4Se_3$ sample hot pressed at 450°C under a pressure of 120MPa [16].

Literature survey reveals that the anisotropic electrical properties and Hall Effect of $In_4Se_3$ nanocrystals have not been reported so far. The present work aims to study the electrical conductivity and the mobility of the prepared $In_4Se_3$ crystals.

## II. EXPERIMENTAL TECHNIQUES

### *A. A. Crystal Growth*

A mixture of Indium and Selenium in correct stoichiometric proportions was used to produce $In_4Se_3$ 10.995 g (65.97 %) of Indium (purity 99.9999 %) and 5.672 g (34.03%) of Selenium (purity 99.9999 %), the chemicals were obtained from Aldrich. The chemicals were placed into a sealed evacuated tube held at 550 $^0$C [17]. We used for growth of single crystals of $In_4Se_3$ a new method which illustrated in fig.1. This technique is very simple and produces high quality crystals. Due to the absence of the motor vibrations and the growth rate can be controlled easily.

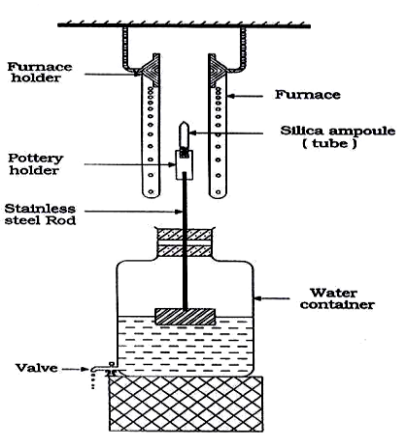


Fig. 1. Home-made modification of Bridgeman furnace.

*B. B. Electrical Conductivity and Hall Effect Measurements*

A sample of 6×2×2 $mm^3$ dimensions was prepared directly using a gentle cleavage from the product version ingot this is because the product crystal is of layer crystal. The sample in this way has length of three times its width (to avoid Hall voltage drop as recommended by Isenberg [18]. The sample was placed in an evacuated Pyrex cryostat. The cryostat end finger has an isolated electric heater (for high-temperature measurements) and can be immersed in a liquid nitrogen dewar flask (for low-temperature measurements). A variac transformer was used for adjusting the required ambient temperature, which was measured by K-type thermocouple. If *ab* is the crystal layer plane and *c* is the direction perpendicular to both *a* and *b*, then the measuring condition can be summarized as follows: *a* is the current direction, *b* is the magnetic field direction and *c* is the developed Hall voltage. The magnetic field value was 5000 G in this experiment. It was supplied from a PHEWE (Germany) electromagnet. In the present work, D.C conductivity and Hall measurements were performed as the method recommended by ASTM (F67).The silver conducting paste was employed as an Ohmic contact and its Ohmic nature was checked by recording the I-V characteristics in both forward and reverse bias directions. The potentiometer type (UJ33E-England) was used for measuring Hall voltage.

## III. Result and Discussion

The dc electrical conductivity was measured at a wide range of temperatures extending from 220 up to 455 K showing semiconducting behavior. Because $In_4Se_3$

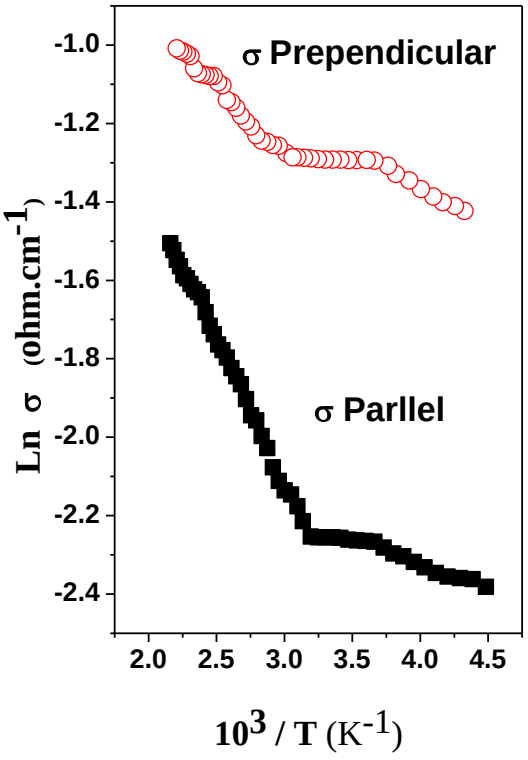


Fig. 2. Variation in σ// and σ⊥ with temperature.

behaves as anisotropic semiconductor [14]; the present work deals with measuring the conductivity in two crystallographic directions. The σ// was measured in the direction parallel to the crystallographic *C*-axis and σ⊥ was measured in the direction perpendicular to the crystallographic *C*-axis. As demonstrated in Fig 2 $\sigma_{//}$ is higher than $\sigma_{\perp}$ ($\sigma_{//}$ at room temperature = $51x10^{-3}$ $\Omega^{-1}cm^{-1}$, $\sigma_{\perp}$ at the room temperature = $5x10^{-3}$ $\Omega^{-1}cm^{-1}$. The general mode of σ variation against temperature is typically as other semiconductor behaviors.

At high temperatures semiconductors possess an intrinsic electrical conductivity due to thermal activation of carriers across the gap separating the valence and the conduction bands. The intrinsic region for σ// is extending from 325 to 455 K and for σ⊥ the intrinsic region is extending from 325 K to 460 K. As evident in Fig 2 the conductivity is sharply increases due to the excitation of charge carrier from the valance band to the conduction band where there is rapid increase in the total current density. In the intrinsic region the following equation can be applied:

$$\sigma = \sigma_0 \exp(-\Delta E_g / 2KT) \quad (1)$$

where $\Delta E_g$ is the energy gap and $\sigma_O$ is the pre-exponential factor.

The value of $\Delta E_g$ $\sigma_{//}$ $\Delta E_g$ = 0.2 eV and for $\sigma_{\perp}$ $\Delta E_g$ = 0.3 eV according to equation 1. This disagreement between $\Delta E_g$// and $\Delta E_g$⊥ is usual in semiconductors where Garret [19] pointed out that there is no guarantee that the energy gap should be the same along different crystal directions.

As result of the large activation energy $E_g/2$, the intrinsic carrier concentration decreases with temperature. At low temperatures it becomes less than the concentration contributed by impurities. In this region the conduction is entirely determined by the nature and concentration of impurities, and is therefore called extrinsic. $\sigma_{//}$, $\sigma_{\perp}$ are extended from 220 K to 270 K the dc conductivity increases as a result of the liberation of the ionized acceptor and their transition from the impurity level. The dependence in this temperature range follows the relationship:

$$\sigma = \sigma_0 \exp(-\Delta E_a / 2KT) \quad (2)$$

where, $\Delta E_a$ is the ionization energy and *K* is Boltezman constant.

From equation (2) the values of $\Delta E_a$ were estimated, $\sigma_{//}$ $\Delta E_a$ = 0.07 eV and $\sigma_{\perp}$ $\Delta E_a$ = 0.05 eV.

The transition region, for σ// is extending from 275 to 325 *K* and for $\sigma^{\perp}$ the transition region is the same. The second part (275 K - 325 K) where the steepness is different, this indicates the appearance of the transition region. Since this region is not flat and not parallel to the *X*-axis, this argued to nature of σ which depends mainly on the charge carrier concentration and their mobility. Hence the middle region corresponds to impurity, or extrinsic conductivity. This region lies between the impurity saturation temperature and the temperature of intrinsic conductivity. In this range all the impurity atoms are ionized but no noticeable excitation of intrinsic carriers take place. Because of that the carrier concentration remains approximately constant and equal to the impurity concentration n = Nd, therefore in this region the temperature dependence of the conductivity is determined by the temperature dependence of carrier mobility. If the principle carrier scattering mechanism inside this region is the scattering on thermal lattice vibration, which causes the mobility to fall with temperature, then specific conductance will also diminish with the of temperature. But if the principle mechanism is impurity or imperfection scattering, then specific conductance will increase with temperature.

The anisotropy of the electric conductivity parallel and perpendicular to the *C*-axis is mainly attributed to variation of the carrier mobility in the two directions. However one cannot exclude the presence of two dimensional-defects between the layers of the semiconductor as concluded from the structure work done on this crystal.

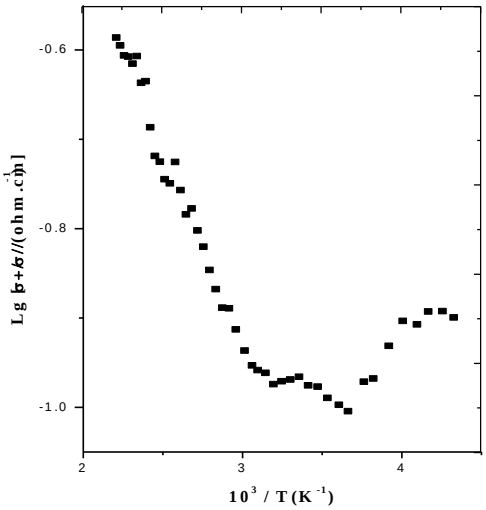


Fig. 3. Shows the temperature dependence of anisotropic factor ($\sigma^{\perp}/\sigma//$)

Fig. 3 shows the temperature dependence of the anisotropic factor (the ratio ($\sigma//$ / $\sigma\perp$)). This curve is divided into three regions as the same as the general behavior of σ against temperature.

The extrinsic region is extended between 230 K and 275 K; the transition region from 275 K to 325 K and from 325 K to 455 K represented the intrinsic region.

This behavior satisfies the following equation:

$$\sigma_{//} / \sigma_{\perp} = A \exp(-\Delta E_g / 2KT) \quad (3)$$

where A is in the order of the value ($m^*_{//} / m^*_{\perp}$).

From equation (3) the energy gap value was estimated 0.2 eV. Also A = 2.3 eV.

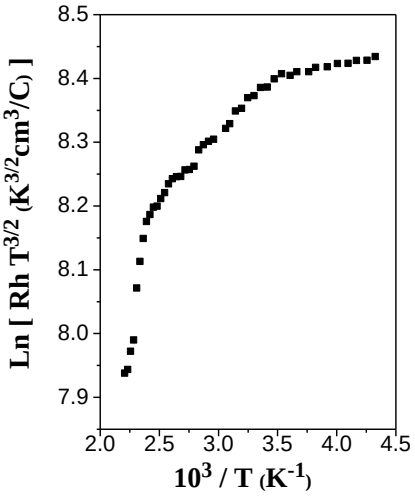


Fig. 4. Relationship between $R_H T^{3/2}$ and $10^3/T$.

The anisotropic ratio has a general mode of variation similar to the electrical conductivity. In a previous work during investigate in GaTe [20] the

anisotropic ratio was temperature independent. However in 1972 Schmid and Mooser [21] observed that the conductivity anisotropy in GaSe of the form:

$$\sigma_{//} / \sigma_{\perp} \alpha \exp(-\Delta E_g / 2KT) \quad (4)$$

In the present work, the compound $In_4Se_3$ behaves like the last formula i.e. it follows Schmid's model.

As for the importance of Hall Effect work in the field of solid state and especially in semiconductors, the present investigation is extended to cover this unique phenomenon.

In the same temperature range i.e., the variation of the Hall coefficient against temperature was carried out is illustrated in fig.4. This was done on the basis of the relationship:

$$R_H T^{3/2} \alpha \exp(-\Delta E_g/2KT) \quad (5)$$

Fig.4 represented the relationship between $R_H T^{3/2}$ and $10^3/T$, which can be divided into three different parts.

Some estimated values on the basis of the above relationships are presented in the corresponding range as follows:

| Region | Temp K | |
|---|---|---|
| *Extrinsic* | *230 to 275* | $\Delta E_a = 0.04$ *eV.* |
| *Transition* | *275 to 360* | |
| *Intrinsic* | *360 to 455* | $\Delta E_g = 0.32$ *eV* |

Table 1 estimated values on the basis of the above relationships are presented in the corresponding range.

These values are in good agreement with those obtained from the electrical conductivity measurements.

It must be noticed that Hall coefficient is an isotropic against temperature in the both crystallographic directions i.e. it is a scalar quantity.

The Hall mobility was examined in two crystallographic directions and is illustrated in fig.5 where we can observe that the general mode of $\mu_{//}$ and $\mu_{\perp}$ have the same variation. It is observed that the values of $\mu_{//}$ are much higher than those of $\mu_{\perp}$, this means that μ is an anisotropic. For instance at room temperature $\mu_{//}$ =1995 ($cm^2$/v.sec). Where it is for $\mu_{\perp}$ at same temperature equals 229 ($cm^2$/v.sec).

Fig.5 can be divided into three categories: From 230 to 275 (extrinsic region) μ grows with temperature increase. At this part where the mobility has a positive temperature coefficient the relationship between μ and T obeys the relationship:

$$\mu_{//} \alpha T^{1.5} \quad (6)$$

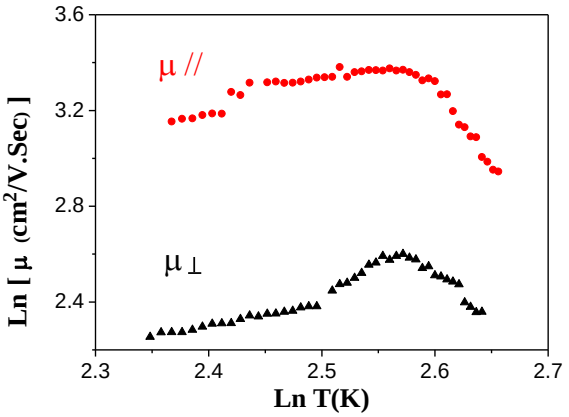


Fig. 5. Hall coefficient is an isotropic against temperature in both crystallographic directions.

Based on this relationship we consider the effect of impurities as the main reason for the scattering mechanism in this range.

From 280 to 360 the Hall mobility seems to be fairly constant. This corresponds to the transition region. From 360 to 455 we notice that there is another rate of decreasing of μ with temperature increase. Here the temperature coefficient is negative at high temperature range μ follows the relationship:

$$\mu_{//} \alpha T^{-6.8} \quad (7)$$

This indicates that the scattering mechanism in this compound is not similar to conventional semiconductor materials. This high exponent leads to the assumption that the classical theories of semiconductors can not be used for understanding the real scattering mechanism of the charge carriers in this crystal. Hence more efforts must be done for understanding the definite reason for this behavior.

The relationship between μ and T in the intrinsic range of temperature justifies the following relationship $\mu_{\perp} \alpha T^{-3.8}$. Such dependence leads to the assumption that a high density of stoichiometric vacancies and creation defects are presented. In the low temperature range (extrinsic), the mobility obeys the power low $\mu_{\perp} \alpha T^{1}$. Based on this, we consider that the effect of impurities is the main reason for scattering mechanism in this range.

## IV. CONCLUSIONS

The anisotropy of the electrical conductivity was observed and discussed. Narrow band gab crystal In4Se3 (The energy gap was found to be 0.28 eV and the ionization energy 0.053 eV) was introduced for applications. The dependence of anisotropic factor on temperature was found to be similar to dependence of electrical conductivity. The anisotropy of Hall mobility was also studied and discussed. The anisotropy of Hall mobility was also studied and discussed. The scattering mechanism in the low temperature range is attributed to the effect of impurities. The scattering mechanism in the high temperature range is attributed

to the effect of high density of stoichiometric vacancies and creation of defects.

REFERENCES

[1]T. T. Nang, T. Matsushita, M. Okuda, and A. Suzuki, Jpn. J.
Appl. Phys. 16, 25 (1977).
[2]K. Ando and A. Katsui, Thin Solid Films 76, 141 (1981).
[3]J. P. Guesdon, B. Kobbi, C. Julien, and M. Balkanski, Phys. Stat. Sol. (a)
102, 327 (1987).
[4]C. Julien, I. Samaras, M. Tsakiri, P. Dzwonkowski, and M. Balkanski,
Mater. Sci. Eng. B 3, 25 (1989).
[5] C. Julien, M. Massot, P. Dzwonkowski, J. Y. Emery, and M. Balkanski,
Infrared Phys. 29, 769 (1989).
[6] M. Balkanski, C. Julien, and J. Y. Emery, J. Power Sources 26, 615
(1989).
[7] I. Samaras, C. Julien, M. Balkanski, J. R. Akridge, and M. Balkanski
(Eds.), Solid State Microbatteries, NATO ASI Series, Ser. B 217, 293
(1990).
[8] C. Julien, A. Khelfa, N. Benramdane, J. P. Guesdon, P. Dzwonkowski, I.
Samaras, and M. Balkanski, Mater. Sci. Eng. B 23, 105 (1994).
[9] C. Julien, I. Samaras, M. Tsakiri, P. Dzwonkowski, and M. Balkanski, *Mater. Sci. Engng.* B3, 25, (1989).
[10] J. Nagao, M. Ferhat, E. Htta and K. Mukasa, *phys. stat. sol. (b),* 219, 347, (2000).
[11]P.V. Galiy, A.V. Musyanovych, T.M. Nenchuk, *J. of Electron Spectroscopy and Related Phenomena,* 142, 121, (2005)
[12]I. M. Belyukh, V. M. Demkiv, T. M. Kavych, V. I. Savchin and V. P. Stakhira, *J. of Poverkhnost Fizika Khimiya Mekhanika*. 12, 1, (1994).
[13] V. M. Gritsyuk, B. M. Galochkin, O. V. Rarenko and A. I. Strebezhev. *J. of Proceedings of SPIE – The International Society for Optical Engineering*. 5065, (2003).
[14] V.P. Savchin, Functional materials, 1998, Vol.5, No. 2.
[15]Dong Bao Luo, Hai Gang Si, Yuan Xu Wang Journal of Alloys and Compounds Volume 589, 15 March 2014, Pages 125–13
[16]Gen Li, Junyou Yang* , Jiansheng Zhang, Ye Xiao, Shuanglong Feng, Ming Liu, Jiangying Peng, Procedia Engineering 27 (2012) 163 – 169
[17] H. Natter, M. Schmelzer, M. S. Loffler, C. E. Krill, A. Fitch & R. Hempelmann, *J. Phys. Chem. B*, 104, 2467, (2000).
[18] I. Isenberg, B. R. Russell and R. F. Greene, *Rev. Sci. Inst.*, 19, 685, (1948).
[19] C. G. B. Garret, Organic Semiconductors, in N. H. Hannay, ed.Semiconductors, Reinhold, New Yourk, (1959).
[20] G. A. Gamal, M. N. Nassary, S. A. Hussien, A. T. Nagat, *Cryst. Res. Technol*. 27, 629, (1992).
[21] M. Shmid and PH. E. Mooser, *phys. Rev.* B12, (1975