

phys. stat. sol. (b) **61**, 533 (1974)

Subject classification: 6; 20.1; 22.7

Physikalisches Institut der Universität Würzburg

Optically Active Lattice Vibrations in Bi_2Se_3

By

H. KÖHLER and C. R. BECKER

The preparation of Bi_2Se_3 single crystals with low free carrier densities allowed an investigation of the lattice vibrations to be carried out from the reflectivity of cleavage planes at nearly normal incidence of the radiation ($\mathbf{E} \perp \mathbf{c}$). The experimental results can be explained with two classical oscillators, whose eigenfrequencies occur at 92 and 69.5 cm^{-1} . The static dielectric constant was determined to be 100 ± 10 for $\mathbf{E} \perp \mathbf{c}$.

Die Präparation von Bi_2Se_3 -Einkristallen mit niedriger Konzentration freier Ladungsträger erlaubte die Untersuchung der Gitterschwingungen aus dem Reflexionsvermögen von Spaltflächen bei nahezu senkrechter Inzidenz der Strahlung ($\mathbf{E} \perp \mathbf{c}$). Die Meßergebnisse können mit zwei klassischen Dispersionsoszillatoren erklärt werden, deren Eigenfrequenzen bei 92 und $69,5 \text{ cm}^{-1}$ liegen. Die statische Dielektrizitätskonstante wurde zu 100 ± 10 für $\mathbf{E} \perp \mathbf{c}$ bestimmt.

1. Introduction

Bismuth selenide crystallizes in a layer-type structure belonging to the space group $R\bar{3}m$, as is also the case for the semiconductors Bi_2Te_3 , Sb_2Te_3 , and their solid solutions. However, Bi_2Se_3 is more difficult to prepare than Bi_2Te_3 . The non-stoichiometric composition of the crystals normally produces high free-carrier concentrations.

A reduction in free-carrier concentration by doping with impurity atoms is possible in Bi_2Te_3 , but not to a significant extent in Bi_2Se_3 and Sb_2Te_3 . Low-carrier densities of about 10^{17} cm^{-3} were achieved in Bi_2Te_3 by doping with iodine [1], respectively excess tellurium in the melt. Whereas, to our knowledge, the lowest free-carrier concentration achieved in p- Sb_2Te_3 is of the order of magnitude of some 10^{19} cm^{-3} . Even though the doping on n-type, as-grown Bi_2Se_3 with impurity atoms is ineffective, a higher selenium content in the melt has been used to obtain carrier densities down to $4 \times 10^{16} \text{ electrons/cm}^3$.

The smaller the free-carrier concentration the smaller their contribution to the optical constants, which more readily allows the influence of the optically active lattice vibrations to be ascertained. However, the cleavage — normal to the trigonal c -axis — of crystals with low carrier concentrations is difficult in order to achieve high quality optical surfaces. A mechanical or chemical polish of surfaces with good optical quality is impossible at the present. Since reflection measurements are most conveniently carried out under nearly normal incident conditions, the electric field vector \mathbf{E} is parallel to the crystal surface and therefore perpendicular to the trigonal axis ($\mathbf{E} \perp \mathbf{c}$) for cleavage planes under experiment. Thus, only optically active modes which involve movements of the atoms normal to the c -axis may be observed with normal incident radiation, i.e. the conditions of the present measurements.

The electronic band structure of n- and p-type Bi_2Te_3 has been well known for a long time [2 to 7] because of its easier preparation. Besides that, investigations of Bi_2Te_3 advanced more rapidly as a result of its outstanding thermo-

electric properties which made the crystals more attractive for thermoelectric cooling. Because Bi_2Se_3 has the same symmetry and almost identical lattice spacings, similar properties were expected. It was found, however, that the electronic properties of the conduction bands differ appreciably from each other [8, 9]. Valence band parameters in Bi_2Se_3 are still unknown, because of the difficulty incurred in preparing p-type material.

The elastic constants for Bi_2Te_3 [10] and specific heat values for Bi_2Te_3 and Bi_2Se_3 [11] have been determined. From the specific heat data, Debye temperatures were calculated for temperatures between 1.4 and 90 K. From a comparison of Debye temperatures near absolute zero, θ_0 , almost identical force constants for Bi_2Te_3 and Bi_2Se_3 were concluded [11], and hence, correspondingly similar lattice dynamics were expected. The Debye temperature at high temperatures, which is equal to 200 and 154 K for Bi_2Se_3 and Bi_2Te_3 , respectively, permits one to estimate averaged longitudinal optical frequencies of 139 and 107 cm^{-1} , respectively. Thus slightly higher eigenfrequencies are expected for Bi_2Se_3 in comparison with Bi_2Te_3 . However, in spite of the above mentioned similarities, the lattice vibration contributions to the long wavelength dielectric constant may differ in the two cases because of a different degree of polarizability of the crystal lattices.

A rigid ion calculation involving only first and second nearest neighbour forces [10] has been made using measurements of the elastic constants of Bi_2Te_3 between 4.2 and 300 K. However, the departure of the experimental elastic constants for Bi_2Te_3 from those obtained from the Debye theory already at $T \approx \approx \theta/300$ indicates the presence of either strong polarizabilities or a significant contribution from atoms more distant than first and second nearest neighbours. The extraordinarily high value for the static dielectric constant of Bi_2Te_3 [1] in comparison with Bi_2Se_3 supports the former.

The eigenfrequencies calculated for Bi_2Te_3 using the above mentioned lattice model [10], were only of the correct order of magnitude [1] as one would also expect to be the case for a similar calculation for Bi_2Se_3 .

The primitive unit cell contains five atoms and, therefore, 15 degrees of freedom are allowed whose irreducible representation at $k = 0$ is

$$\Gamma_5^1 = 2A_{1g} + 3A_{1u} + 2E_g + 3E_u,$$

where $A_{1u} + E_u$ are the acoustic modes. The remaining $2A_{1u} + 2E_u$ are optically active for $\mathbf{E} \parallel \mathbf{c}$ and $\mathbf{E} \perp \mathbf{c}$, respectively. The second-order symmetric tensor representation $2A_{1g} + 2E_g$ yields the Raman-active lattice vibrations.

2. Experimental

Experimentally, several crystals with low carrier densities were investigated. The reflectivity of cleavage planes was measured at nearly normal incidence with

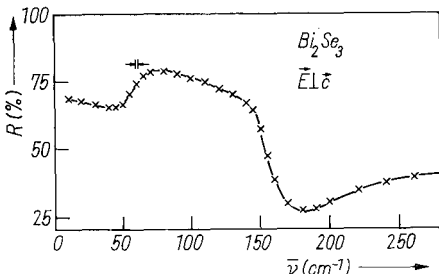
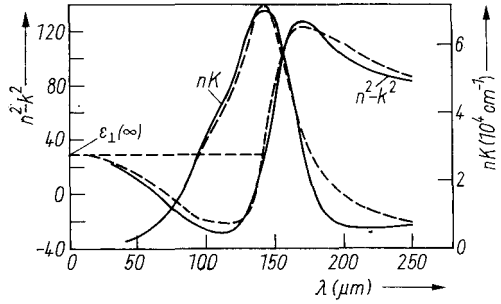


Fig. 1. Reflectivity of n- Bi_2Se_3 (single crystal with a carrier density of $5 \times 10^{17} \text{ cm}^{-3}$) versus frequency at nearly normal incidence of the radiation, where $\mathbf{E} \perp \mathbf{c}$. The optical surface of the sample is a cleavage plane

Fig. 2. Kramers-Kronig analysis of the reflectivity data in Fig. 1. The real part of the dielectric constant $n^2 - k^2$ (solid line) and the absorption $nK = 4\pi nk/\lambda$ (solid line) is plotted versus the wavelength. The theoretical results from (1) and (2) using the parameter values given in (3) are drawn as broken lines (----)



$E \perp c$ at 300 K with a Polytec FIR 30 Fourier spectrometer. The results for one sample with a free carrier concentration of $5 \times 10^{17} \text{ cm}^{-3}$ are shown in Fig. 1 for frequencies between 10 and 280 cm^{-1} . The experimental resolution is given. There is a steep rise in the reflectivity R from 170 to 145 cm^{-1} , which is followed by a more gradual increase of R down to 75 cm^{-1} . The drop of R from 70 to 50 cm^{-1} indicates the position of one optical mode eigenfrequency. The increase in the reflectivity below 40 cm^{-1} for decreasing frequency is caused by free carriers. The steep part of the curve near 160 cm^{-1} is shifted to higher frequencies for crystals with larger free carrier concentrations but is not influenced by crystals with lower free carrier concentrations. Thus the contribution of free carriers is almost negligible in the results shown in Fig. 1.

3. Analysis and Discussion

In order to evaluate the measurements a Kramers-Kronig analysis was performed, taking into account known reflectivity data for higher wave numbers and approximating the $R(\tilde{\nu})$ dependence by free carrier influence below 20 cm^{-1} .

The results of this calculation are given in Fig. 2, where the real part of the dielectric constant $n^2 - k^2$ and the absorption nK ($K = 4\pi k/\lambda$ absorption constant) are plotted versus the wavelength (unbroken curves). A maximum in the absorption is found at $\lambda = 144 \mu\text{m}$, where one of the E_u eigenfrequencies occurs ($\tilde{\nu}_{\perp 1} = 69.5 \text{ cm}^{-1}$). The unsymmetric shape of the absorption curve suggests the presence of a second lattice vibration, which is also expected from group theory.

We tried to fit theoretical calculations (broken curves in Fig. 2) to the Kramers-Kronig results, assuming a model with two independent classical oscillators for the lattice vibrations and using Drude's theory for the free carrier contributions ($E \perp c$):

$$n^2 - k^2 = \epsilon_{\perp}(\infty) + \sum_{i=1,2} \frac{\Delta\epsilon_{\perp i}(\omega_{\perp i}^2 - \omega^2) \omega_{\perp i}^2}{(\omega_{\perp i}^2 - \omega^2)^2 + \omega^2 \gamma_{\perp i}^2} - \frac{N_e^2}{\epsilon_0 m^*} \frac{\tau^2}{(1 + \omega^2 \tau^2)}, \quad (1)$$

$$nK = \sum_{i=1,2} \frac{\Delta\epsilon_{\perp i} \omega^2 \omega_{\perp i}^2 \gamma_{\perp i} / c}{(\omega_{\perp i}^2 - \omega^2)^2 + \omega^2 \gamma_{\perp i}^2} + \frac{N_e^2}{\epsilon_0 m^* c} \frac{\tau}{(1 + \omega^2 \tau^2)}. \quad (2)$$

Here $\omega_{\perp i} = 2\pi c \tilde{\nu}_{\perp i}$ are the E_u frequencies, $\Delta\epsilon_{\perp i}$ are the contributions of the classical oscillators to the dielectric constant, and $\gamma_{\perp i}$ describe the damping of the lattice vibrations. N is the free carrier concentration, m^* their susceptibility mass, and τ their relaxation time. The frequency ω of the radiation is related to the wave number $\tilde{\nu}$ and wavelength λ by $\omega = 2\pi c \tilde{\nu} = 2\pi c/\lambda$. m^* is known from

Shubnikov-de Haas investigations [9], N was determined from the Hall constant, and τ could be estimated from transport coefficients.

The best fit (broken lines in Fig. 2) was achieved with the following parameters. We should mention here the failure of one classical oscillator to describe the experimental data.

$$\left. \begin{aligned} \tilde{\nu}_{\perp 1} &= 69.5 \text{ cm}^{-1}, & \Delta\varepsilon_{\perp 1} &= 43, & 2\Delta\tilde{\nu}_{\perp 1} &= 22 \text{ cm}^{-1}, \\ \tilde{\nu}_{\perp 2} &= 92 \text{ cm}^{-1}, & \Delta\varepsilon_{\perp 2} &= 24, & 2\Delta\tilde{\nu}_{\perp 2} &= 55 \text{ cm}^{-1}, \\ N &= 5 \times 10^{17} \text{ cm}^{-3}, & m^* &= 0.124 m_0, & \tau &= 7 \times 10^{-13} \text{ s}, & \varepsilon_{\perp}(\infty) &= 29, \end{aligned} \right\} \quad (3)$$

where $\gamma = 2\Delta\omega = 2\pi c(2\Delta\tilde{\nu})$, $(2\Delta\tilde{\nu})$ being the width at half-maximum. Indeed, the free carrier contribution is not important. The static dielectric constant $\varepsilon_{\perp}(0) = \varepsilon_{\perp}(\infty) + \Delta\varepsilon_{\perp 1} + \Delta\varepsilon_{\perp 2}$ was found to be 96. Taking into account experimental uncertainties, the quality of the crystal surface and errors introduced by the assumed classical model, the value $\varepsilon_{\perp}(0) = 100 \pm 10$ is reasonable. Even, though the polarizability of Bi_2Se_3 is considerable, it is still much less than that of Bi_2Te_3 , where $\varepsilon_{\perp}(0) = 360 \pm 50$ was found [1]. This explains why acoustical phonon scattering plays such an important role in transport phenomena in Bi_2Te_3 down to 10 K, and thus an influence of charged impurities or defects is partially screened out by the polarizability of the host lattice. Thus the differences in transport phenomena in Bi_2Se_3 [12] and Bi_2Te_3 [13] can be explained by a much lower static dielectric constant with less screening of the charged centres.

The damping constants, especially $\gamma_{\perp 2}$, are considerable. This indicates in the same way as for Bi_2Te_3 that the Bi_2Se_3 lattice has to contain a high concentration of lattice defects.

The results confirm that the lattice force constants of Bi_2Te_3 and Bi_2Se_3 are approximately equal, but that the polarizability of the tellurium atom has to be much higher than that of the selenium atom in the corresponding compound.

Neglecting the contribution by free carriers, $n^2 - k^2 = 0$ occurs at about 149 cm^{-1} . This may be compared to the value $k\theta_{\infty}/(hc) = 139 \text{ cm}^{-1}$ which was calculated from the Debye temperature $\theta_{\infty} = 200 \text{ K}$, and which is therefore sort of an average frequency, showing that also for $\mathbf{E} \parallel \mathbf{c}$ $n^2 - k^2 = 0$ should occur at about 149 cm^{-1} .

Neglecting the free carrier contribution in (1), $n^2 - k^2 = 0$ yields ($\tilde{\nu} = \tilde{\nu}_0$)

$$\begin{aligned} (\varepsilon_{\perp}(\infty) + \Delta\varepsilon_{\perp 1}) \frac{\tilde{\nu}_{\perp 1}^2}{\tilde{\nu}_0^2} + (\varepsilon_{\perp}(\infty) + \Delta\varepsilon_{\perp 2}) \frac{\tilde{\nu}_{\perp 2}^2}{\tilde{\nu}_0^2} &= \\ = \varepsilon_{\perp}(0) \frac{\tilde{\nu}_{\perp 1}^2}{\tilde{\nu}_0^2} \frac{\tilde{\nu}_{\perp 2}^2}{\tilde{\nu}_0^2} + \varepsilon_{\perp}(\infty), \end{aligned} \quad (4)$$

when the influence of damping is omitted. Upon inserting the above values in (4) quite a good agreement between the sides of the equation is found. This encourages one to use the same relation for the case $\mathbf{E} \parallel \mathbf{c}$, where $\tilde{\nu}_0$ should be equal or somewhat less than 149 cm^{-1} . Taking into account that eigenfrequencies for $\mathbf{E} \parallel \mathbf{c}$ were calculated from the lattice model of Jenkins et al. [10] to be greater than for $\mathbf{E} \perp \mathbf{c}$ and in addition $\varepsilon_{\perp}(\infty) \approx \varepsilon_{\parallel}(\infty)$ [14], a smaller static dielectric constant may be expected for $\mathbf{E} \parallel \mathbf{c}$ in comparison with $\mathbf{E} \perp \mathbf{c}$.

For the same reasons ($n^2 - k^2 = 0$ occurs at $\tilde{\nu}_0 = 125 \text{ cm}^{-1}$ for $\mathbf{E} \perp \mathbf{c}$ and $k\theta_{\infty}/(hc) = 107 \text{ cm}^{-1}$) and upon taking into consideration the values of $\varepsilon_{\perp}(\infty) \approx$

≈ 80 and $\epsilon_{||}(\infty) \approx 50$ of Bi_2Te_3 [15] a strongly anisotropic static dielectric constant has to be assumed for Bi_2Te_3 , which recently was proved experimentally [16].

Acknowledgement

The financial support of the Deutsche Forschungsgemeinschaft is appreciated.

References

- [1] K. H. UNKELBACH, CH. BECKER, H. KÖHLER, and A. VON MIDDENDORF, *phys. stat. sol. (b)* **60**, K41 (1973).
- [2] J. R. DRABBLE, *Progr. Semicond.* **7**, 45 (1963).
- [3] H. J. GOLDSMID, *Materials Used in Semiconductor Devices*, Ed. C. A. HOGARTH, Interscience Publishers, New York 1965 (p. 165).
- [4] J. R. DRABBLE, R. D. GROVES, and R. WOLFE, *Proc. Phys. Soc. (London)* **71**, 430 (1958).
- [5] I. G. AUSTIN, *Proc. Phys. Soc. (London)* **76**, 169 (1960).
- [6] R. B. MALLINSON, J. A. RAYNE, and R. W. URE, *Phys. Rev.* **175**, 1049 (1968).
- [7] A. VON MIDDENDORF and G. LANDWEHR, *Solid State Commun.* **11**, 203 (1972).
- [8] H. KÖHLER and G. LANDWEHR, *phys. stat. sol. (b)* **45**, K109 (1971).
- [9] H. KÖHLER, *phys. stat. sol. (b)* **58**, 91 (1973).
- [10] J. O. JENKINS, J. A. RAYNE, and R. W. URE, *Phys. Rev. B* **5**, 3171 (1972).
- [11] G. E. SHOEMAKE, J. A. RAYNE, and R. W. URE, *Phys. Rev.* **185**, 1046 (1969).
- [12] A. VON MIDDENDORFF, H. KÖHLER, and G. LANDWEHR, *phys. stat. sol. (b)* **57**, 203 (1973).
- [13] P. A. WALKER, *Proc. Phys. Soc.* **76**, 113 (1960).
- [14] H. GOBRECHT and S. SEECK, *Z. Phys.* **222**, 93 (1969).
- [15] R. GROTH and P. SCHNABEL, *J. Phys. Chem. Solids* **25**, 1261 (1964).
- [16] K. H. UNKELBACH, private communication.

(Received August 23, 1973)