

Short Notes

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Centro de Estudios de Semiconductores, Facultad de Ciencias,
Universidad de Los Andes, Mérida¹⁾

On the Thermal Conductivity of $\text{CuInSe}_{2x}\text{S}_{2(1-x)}$

By

S. M. WASIM and R. TOVAR B.

The electrical and optical properties of the ternary compound semiconductors CuInS_2 and CuInSe_2 , which crystallize in the chalcopyrite structure, have been studied extensively by several authors /1 to 4/. This is because they are promising candidates for applications in electro-optical devices. From X-ray and DTA studies, the existence of their solid solutions $\text{CuInSe}_{2x}\text{S}_{2(1-x)}$, for the whole range of x between 0 and 1, has been established and their lattice parameters have been reported /5/. Recently, the lattice thermal conductivity (K) of p-type polycrystalline $\text{CuInSe}_{2x}\text{S}_{2(1-x)}$ samples, which gives valuable information about the interatomic forces and lattice anharmonicity, has been published /6/. It is suggested that K decreases for the mixed ternary compounds because of the decrease in lattice periodicity.

In the present note, after examining briefly the different models that have been proposed to explain the thermal conductivity of ternary compounds at room temperature, the mechanism responsible for variation of K with x in $\text{CuInSe}_{2x}\text{S}_{2(1-x)}$ has been suggested. The empirical relation found for K satisfactorily explains this behavior.

The thermal conductivity of $\text{CuInSe}_{2x}\text{S}_{2(1-x)}$ at 300 K for different values of x , taken from /6/, is plotted in Fig. 1. As compared to the initial CuInS_2 and CuInSe_2 compounds, the lattice thermal conductivity of the solid solutions decreases and has a minimum at about $x = 0.5$. It can perhaps be argued that this reduction in K for x different from 0 and 1 could be due to additional scattering of phonons at the grain boundaries of the polycrystalline samples. However, this effect, if present, should be small since the K value of CuInS , and CuInSe_2 , also polycrystalline samples, are in good agreement with that calculated by Wasim /7/ and Makovetskaya et al. /8/.

1) Mérida 5101, Venezuela.

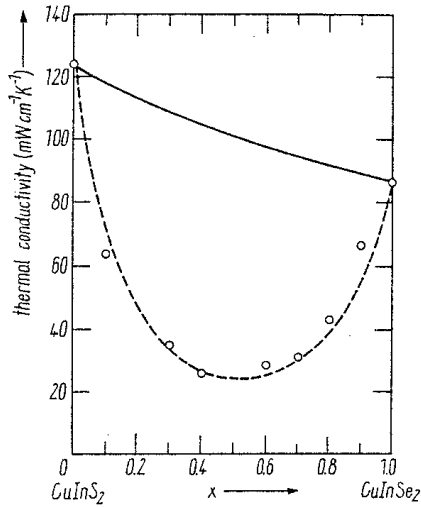


Fig.1

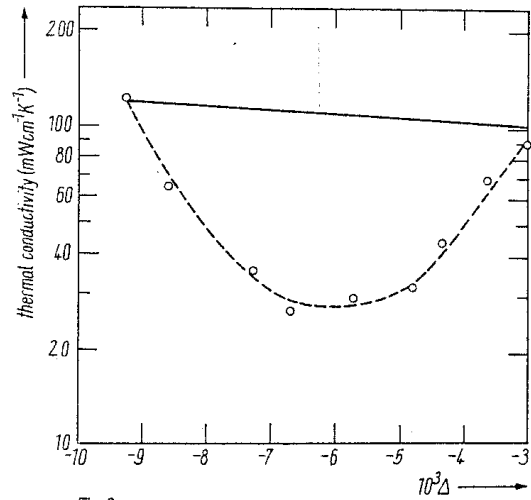


Fig.2

Fig. 1. The thermal conductivity of $\text{CuInSe}_{2x}\text{S}_2(1-x)$ as a function of x taken from /6/. The continuous and dashed lines represent the calculated thermal conductivity with (1) and its modified form explained in the text, respectively

Fig. 2. The thermal conductivity of $\text{CuInSe}_{2x}\text{S}_2(1-x)$ taken from /6/ as a function of the corresponding parameter Δ calculated from /6/. The continuous and dashed lines represent the calculated thermal conductivity with (3) and its modified form discussed in the text, respectively

To explain the thermal conductivity of the ternary compounds at room temperature, three different approaches have been made. Wasim /7/ has calculated the K value of all the I-III-VI₂ and II-IV-V₂ chalcopyrite compounds by extending the expression of Leibfried and Schlöman as modified by Steigmeier. This is given by

$$K = \frac{12}{5} 4^{1/3} \left(\frac{k_B}{h} \right)^3 \frac{\bar{M} \sigma^3}{(\gamma + \frac{1}{2})^2 T}, \quad (1)$$

where \bar{M} is the average atomic mass in grams, σ^3 is the average volume occupied by one atom of the crystal, Θ is the Debye temperature, and γ is the Grüneisen constant. The predicted values of K for I-III-VI₂ compounds at 300 K, with $\gamma = 1.7$ as an adjustable parameter, are in fairly good agreement /7/ with the reported values.

Garabato and Rucci /9, 10/, using the Philips ionicity scale defined by the dielectric model, propose an expression for the thermal conductivity of II-VI,

III-V, I-III-VI₂, and III-IV-V₂ tetrahedrally bonded semiconductors which is given by

$$K^* = K_{\text{cov}}^* \left(\frac{n_0}{n} \right)^2 \left(1 - \frac{f_i}{F_i} \right).$$

Here $K^* = kT/T^*$, where T^* is the melting point and K the lattice component of the thermal conductivity. K_{cov}^* refers to the K^* value of the purely covalent semiconductors, and $F_i = 0.78$ is the critical ionicity which separates the tetrahedral and octahedral structures. n_0 and n correspond to the number of atoms in the unit cell of zincblende and chalcopyrite structures which are 8 and 16, respectively. The thermal conductivity at 300 K of the II-IV-V₂ compounds calculated by this formula seems to agree with the measured values. However, in the case of CuInS₂ and CuInSe₂ of the I-III-VI₂ family, which are less ionic than the II-VI-V₂ compounds, recent experimental data of K /7/ are higher by at least a factor of 3 as compared to their corresponding calculated value. For this reason, in the present analysis, this model has not been considered.

Makovetskaya et al. /8/ have suggested an empirical relation of the form

$$K = Ae^{-B\Delta}, \quad (3)$$

where $\Delta = (2 - c/a)/(c/a)$ gives a measure of the tetragonal distortion of the crystal lattice. A logarithmic plot of the experimental values of K of some of the I-III-VI₂ compounds against their corresponding Δ , as expected, seems to give a straight line.

Using (1) with the corresponding \bar{M} and δ for CuInSe_{2x}S_{2(1-x)} and Θ calculated from the melting point as given in /6/, the thermal conductivity at 300 K of the solid solutions is calculated with $\gamma = 1.87$. This is also shown in Fig. 1.

To check the possible validity of the empirical relation proposed in /8/ for the I-III-VI₂ compounds also for their solutions, Δ is calculated for different values of x from the smoothed out curve /5/ of the ratio of the lattice constant c/a versus x . With $A = 8.87$ mW/cm K and $B = 30.84$, as in the case of I-III-VI₂ compounds, the thermal conductivity of CuInSe_{2x}S_{2(1-x)} is calculated from (3). This is plotted in Fig. 2. In the same figure, the thermal conductivity measured for these values of Δ is also shown.

It can be observed from Fig. 1 and 2 that the two models which satisfactorily explain the thermal conductivity behavior of the I-III-VI₂ compounds at room temperature cannot be used to account for the low magnitude of K of their mixed

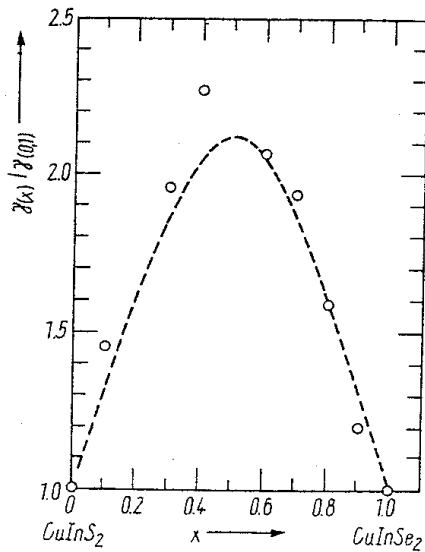


Fig. 3. The variation of the calculated $\gamma(x)/\gamma(0,1)$ from the measured thermal conductivity of $\text{CuInSe}_{2x}\text{S}_{2(1-x)}$ in /6/ as a function of x . The dashed curve represents a theoretical fit with an expression of the form $\exp(\beta x(1-x))$, where $\beta = 3$

alloys. Several empirical relations were tried to explain the K data between 0 and 1. A reasonable fit, as shown in Fig. 1 and 2, can be obtained by multiplying the thermal conductivity expressions given in both (1) and (3) by an additional term of the form $\exp(-\sqrt{2\alpha x(1-x)})$ where $\alpha = 4$. Physically, this term can be related to the fact that the substitution of one type of anion with another of the same group, for example S with Se, in the chalcopyrite structure increases the lattice anharmonicity. Since the Grüneisen parameter γ is a measure of this anharmonicity, it is reasonable to expect that it should be higher for the solid solutions as compared to the initial CuInS_2 and CuInSe_2 compounds. This would thus explain the decrease of the thermal conductivity of $\text{CuInSe}_{2x}\text{Se}_{2(1-x)}$. An increase in γ has also been reported /11/ for the Si-Ge alloy. For this reason, with the measured value of K of $\text{CuInSe}_{2x}\text{S}_{2(1-x)}$ and (1), the corresponding $\gamma(x)$ is calculated. The ratio $\gamma(x)/\gamma(0,1)$ would thus give an estimate of the change in the lattice anharmonicity. This is plotted in Fig. 3 as a function of x and fitted again, as expected, to an empirical relation of the form $\exp(\beta x(1-x))$ with $\beta = 3$. The scattering of the data from the theoretical curve could perhaps have its origin in the contribution of the thermal resistivity from the additional scattering of phonons at the grain boundary of the polycrystalline samples /12/.

It would be interesting to find out if the relation of the form $\gamma(x) = \gamma(0) \times \exp(\beta x(1-x))$ also holds true for other mixed ternary systems of the I-III-VI₂ family such as $\text{CuGaSe}_{2x}\text{S}_{2(1-x)}$.

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References

- /1/ J.J.M. BINSMA, L.J. GILING, and J. BLOEM, *J. Lum.* 27, 35 (1982).
- /2/ D.C. LOOK and J.C. MANTHUMUTHIL, *J. Phys. Chem. Solids* 37, 173 (1976).
- /3/ C. RINCÓN, C. BELLABARBA, J. GONZÁLEZ, and G. SÁNCHEZ PÉREZ, *Solar Cells* 16, 335 (1986).
- /4/ S.M. WASIM, *Solar Cells* 16, 381 (1985).
- /5/ I.V. BODNAR, A.P. BOLOGA, and B.V. KORZUN, *Kristall und Technik* 15, 1285 (1980).
- /6/ L.A. MAKOVETSKAYA, I.V. BODNAR, B.V. KORZUN, and G.P. YAROSHEVICH, *phys. stat. sol. (a)* 74, K59 (1982).
- /7/ S.M. WASIM, *phys. stat. sol. (a)* 51, K35 (1979).
- /8/ L.A. MAKOVETSKAYA, N.N. BELIEVICH, I.V. BODNAR, S.A. GRUSTO, and G.P. YAROSHEVICH, *Izv. Akad. Nauk SSSR, Ser. neorg. Mater.* 20, 382 (1984).
- /9/ L. GARABATO and A. RUCCI, *Chem. Phys. Letters* 61, 542 (1979).
- /10/ L. GARABATO and A. RUCCI, *Chem. Phys. Letters* 64, 350 (1979).
- /11/ R. NAVA, M.P. VEECHI, J. ROMERO, and B. FERNÁNDEZ, *Phys. Rev. B* 14, 800 (1976).
- /12/ H. NEUMANN, *Solar Cells* 16, 399 (1986).

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