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Temperature Dependence of Lattice Thermal Conductivity for Some of I-III-VI_2 Group Compound Semiconductors

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Abstract

Callaway formula is used to investigate the lattice thermal conductivity for nine compounds from the ternary group I-III-VI_2 semiconductors at the temperature range from 5 to 300K. The maximum conductivities are found to be in the temperature range 5-15K.The effects of the Debye temperature on lattice thermal conductivity as well as maximum conductivity are investigated in some details. Many imperical formula are found to relate these compounds with their lattice thermal conductivities. The effects of carrier impurities (N) on this type of conductivity for the compound $CuInSe_2$ are investigated and the N^x dependence is found.

Keywords:- Lattice thermal conductivity, ternary compounds , semiconductors , impurity effects.

Introduction

Thermal properties of semiconductors have recently attracted a lot of attention of researchers[1,2,3]. That, first, because of the continuous scaling down of the feature sizes in microelectronic devices and circuits, which leads to an increase in the power dissipation per unit area of the semiconductor chip. So the size effect influence on the thermal conduction becomes extremely important for the design and reliability of the device[4]. A second factor is a rebirth of the field of thermoelectric materials, which has been brought about by the emergence of the large number of new artificially synthesized materials, including those structured on an atomic scale[5].

Ternary I-III-VI_2 group semiconducting compounds are regarded as a valence analogs to the II-VI compounds[6]. They crystallize in the chalcopyrite structure which is closely related to that of the zinc-blende[7].The space lattice for chalcopyrite structure is a body-central tetragonal and the reciprocal lattice is a face-central tetragonal[8].

In this work, an application of the current understanding of the theoretical frame work of the lattice thermal conductivity of some compounds of the ternary group I-III-VI_2 semiconductors will be investigated.

Methods of calculation

The Callaway model is used to calculate the lattice thermal conductivity

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*Cited from his M.Sc.Thesis.

for several ternary chalcopyrite semiconducting compounds from the group I-III-VI_2. This model was used successfully to calculate this phenomenon for lementary and multinary compound semiconductors at temperatures ranging from low up to near their Debye temperatures (θ_D). The mathematical model which has been proved by Callaway is[9];

$$K = \frac{k_B}{2\pi^2 v}\left(\frac{k_B}{\hbar}\right)^3 . T^3 \int_0^{\theta_D/T} \tau_c \frac{x^4 e^x}{(e^x-1)^2} dx \qquad \ldots\ldots\ldots(1)$$

Where $x = \dfrac{\hbar w}{k_B\ T}$ is the reduced phonon energy parameter, $\hbar$ is the Dirac constant, w is the phonon frequency, k_B is the Boltzmann constant and T is the interested absolute temperature. The speed of sound v can be calculated from the relation[10];

$$v = \frac{k_B\,\theta_D}{\hbar}\left(\frac{V}{6\pi^2}\right)^{1/3} \qquad \ldots\ldots\ldots\ldots(2)$$

where V is the atomic unite volume. τ_c is the combined relaxation time which is the additive combinations due to impurities τ_D, phonon-phonon τ_{ph}, and the boundary scattering processes τ_B, as follows [9]:

$$\tau_c^{-1} = \tau_D^{-1} + \tau_{ph}^{-1} + \tau_B^{-1} \qquad \ldots\ldots\ldots(3)$$

These scattering processes can be verified as follows :The relaxation time due to imp-urity scattering τ_D is given by the form [11];

$$\tau^{-1}{}_D = Aw^4 \qquad \ldots\ldots\ldots\ldots(4)$$

Where A is the impurity strength parameter, W is the angular frequency. A is a sum of at least two terms ($A_{iso} + A_{imp}$), where the former is due to the scattering by distributions of isotopes of the elements in the compound and that can be given by the form [12] :

$$A_{iso} = \frac{V}{4\pi\ v^3}\ \Gamma \qquad \ldots\ldots\ldots(5)$$

Where Γ is a parameter given by :

$$\Gamma = \sum_i f_i\ (1 - \frac{M_i}{\overline{M}})^2$$

$$\overline{M} = \sum_i f_i\ M_i$$

$$\overline{M} = x\overline{M}_{(I)} + y\overline{M}_{(III)} + z\overline{M}_{(VI)}$$

Where:

$\overline{M}$ is the average atomic mass, f_i and M_i are the fraction and atomic weight of the i^{th} isotope respectively. While A_{imp} is regarded as the scattering caused by impurities, which is given by[11]:

$$A_{imp} = \frac{3 V S_i^2}{\hbar v^3} N_{imp}$$

.........(6)

Where S_i is the scattering factor which usually has a value of nearly to unity [13], and N_{imp} is the concentration of impurities.

The phonon-phonon scattering relaxation time is assumed to be due to the Umklapp processes which is given by[14] :

$$\tau_u^{-1} = B_u w^2 T e^{-\frac{\theta_D}{bT}} \quad ....(7)$$

Where B_u is the Umklapp parameter strength and is given by:

$$B_u = \frac{\hbar \gamma^2}{M v^2 \theta_D}$$

Here, γ is the anharmonicity parameter called Gruneisen constant , for these ternary compounds it is assumed to be equal to(1.7) [7] , b is a fitting parameter which can be deduced experimentally, and it is related to the type and structure of materials and the value 2 was used in this work. However, it has been reported that the value of b is in the range of 1-5 [11,15,16].

Finally, the relaxation time τ_B^{-1} for the boundary scattering process is given by [17]:

$$\tau_B^{-1} = \frac{v}{FL_c} \quad ....(8)$$

Where F is the experimental fitting factor and usually suggested to be equal to unity for the diffusely conduction's , L_c is the Casimir length which is equal to [17,18]:

$$L_c = 1.12 \sqrt{L_1 L_2}$$

where L_1, L_2 are the dimensions of the cubic samples. By substituting eqs.(4), (7) and (8) into eq.(3), a new equation can be obtained in the form as :

$$\tau_C^{-1} = A w^4 + B_u w^2 T e^{\frac{\theta_D}{2T}} + \frac{v}{L_c} \quad ....(9)$$

Using $x = \frac{\hbar w}{k_B T}$ one gets:

$$\tau_C^{-1} = \frac{v}{L_c}[Dx^4 + Ex^2 + 1] \quad ....(10)$$

where

$$D = \frac{L_c}{v} A .(\frac{k_B T}{\hbar})^4$$

$$E = \frac{L_c}{v} B_u (\frac{k_B}{\hbar})^2 T^3 e^{-\frac{\theta_D}{2T}}$$

By inserting eq.(10) in to eq.(1), a complete formula will be obtained for the lattice thermal conductivity which is called the Callaway expression as :

$$K = \left(\frac{k_B L_c}{2\pi^2 v^2}\right)\left(\frac{k_B T}{\hbar}\right)^3 \int_o^{\theta_D/T} \frac{x^4 e^x}{[Dx^4 + Ex^2 + 1][e^x - 1]^2}\, dx$$

...........(11)

This is the relation which is used for the intermediate range of temperatures.

Results and analysis

Calculated lattice thermal conductivity for nine compound semiconductors from the group I-III-VI_2 are represents in Fig.(1).

The data used for this calculation are reported in Table(1). In these calculations isotops are used as they have the effects of impurities. That is because isotops are considered to be one of the major types in which have a scattering similar to that of the impurities. Their influences on the crystal will result from the difference in their masses as well as the interatomic force constant compared to that of the host atoms[15]. The more concentration is for the isotopic impurity, the less will be the conductivity maximum, as can be seen in Fig.(2).

where it is found to be changes according to the relation ;

$$K_{max}(A_{iso}) = 67.22(A_{iso})^{-0.4802}$$

This could be attributed from the fact that impurities are destroy the perfect periodicity of the lattices and consequently, scatters the phonons which lead to a thermal resistance[11]. It has been suggested that the state of the best purity of the specimens may be limited by scattering

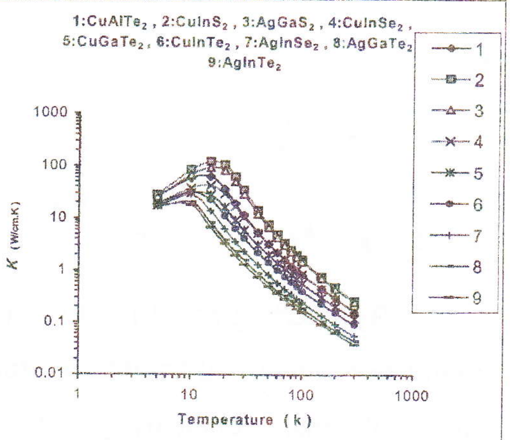

Fig.(1) Calculated lattice thermal conductivity as a function of temperature for nine compounds from group I-III-VI_2 semiconductore

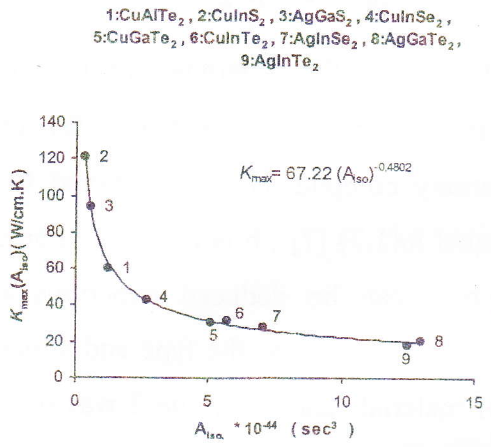

Fig.(2) Variation of the conductivity maximum as a function of A_{iso} for nine compounds from the group I-III-VI_2 semiconductore

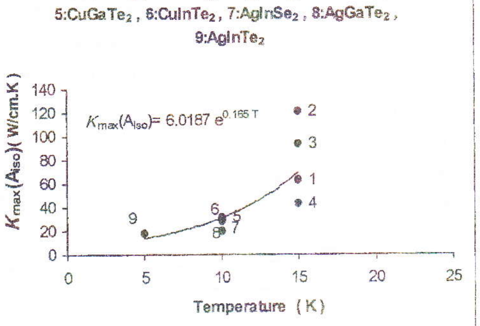

Fig.(3)Conductivity maximum resulted from A_{iso} versus temperature.

from isotops[19]. However, at low temperatures, the resistivity due to isotops will almost be the most pronounced effect which can be used as a guide to determine the high of the conductivity maximum as indicated in Fig.(3).

An imperical relation for the temperature dependence $K_{max}(A_{iso})$ for these ternary compounds will be obtained from this figure as :

$$K_{max}(A_{iso})=6.0187\ e^{0.165T}$$

The Debye temperature dependence of temperature for the $K_{max}(A_{iso})$ was also evaluated in this work as indicated in Fig.(4).

The increase in the Debye temperature will produce a corresponding increase in $T[K_{max}(A_{iso})]$ according to the relation ;

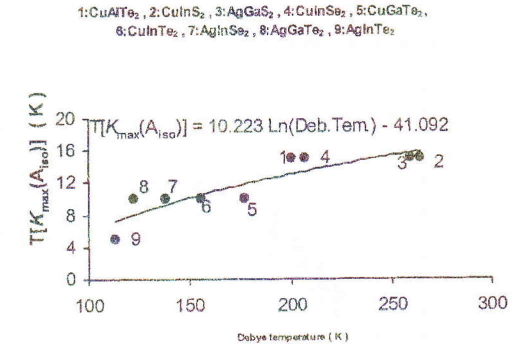

Fig.(4)Variation of temperature in which the conductivity maximum due to A_{iso} is occures versus the Debye temperature.

$$T[K_{max}(A_{iso})] = 10.223\ \mathrm{Ln}(\theta_D) - 41.092$$

Experimental results have been indicated that for temperature $T \geq 0.1\ \theta_D$, the lattice thermal conductivity will mainly be controlled by the U-process[20]. In this range of temperature, it has been found that, the conductivity was expressed by ($K \propto e^{-\frac{\theta_D}{bT}}$). Hence, a higher thermal conductivity should be resulted for materials which have higher θ_D as shown in Fig.(5).

However, a curve fiting for this figure will give equations for K for the three compounds $AgGaS_2$, $CuInSe_2$ and $CuInTe_2$ respectivily as followes:

$$\mathrm{Ln}K=0.5283\ \theta_D/T - 0.87$$

$$\mathrm{Ln}K=0.466\ \theta_D/T - 0.819$$

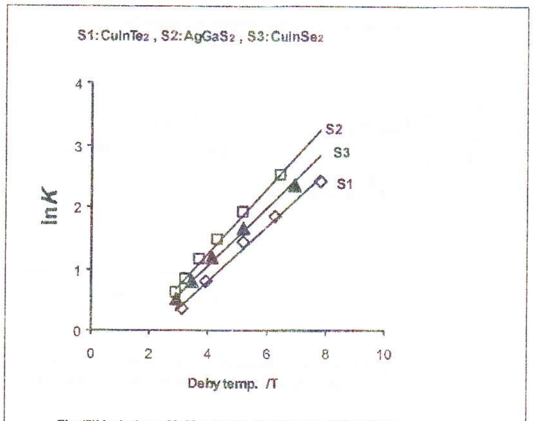

Fig.(5)Variation of lnK versus Debytemp. /T for three compounds, the Debye temperature of the compounds as follows: S1=156K , S2=259K , S3=207K.

$$\mathrm{Ln}K = 0.441\ \theta_D/\mathrm{T} - 0.95$$

The impurity effects on the lattice thermal conductivity is investigated in the ternary compound $\mathrm{CuInSe_2}$ (L_c=0.274 and N_{imp} from reference[22] the data used for this calculation are reported in Ttable(2), which the results are drawn in Fig.(6).

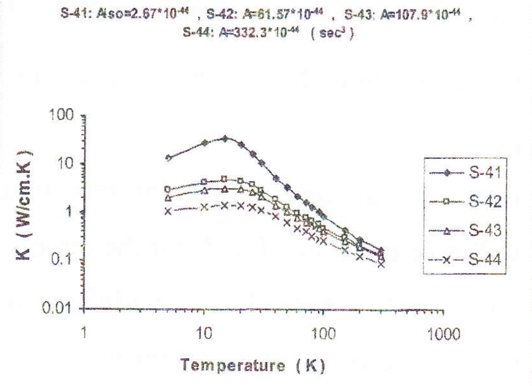

Fig.(6) Calculated lattice thermal conductivity versus temperature for four samples of the compound $\mathrm{CuInSe_2}$.

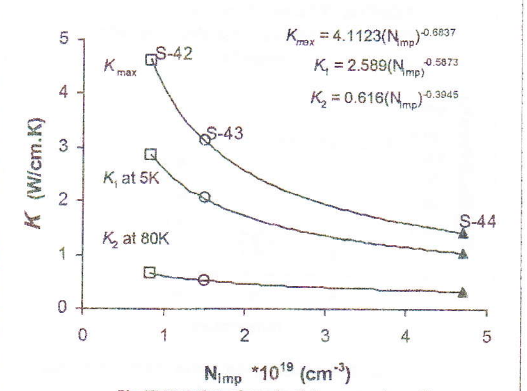

Fig.(7) Variation of conductivity versus impurity concentration, for three samples of the compound $\mathrm{CuInSe_2}$

The examination of the impurity dependence of lattice thermal conductivity at the conductivity maximum and for temperature below and above that, are shown in Fig.(7).

Then, the impurity dependence of conductivity can be obtained and found to change according to $N_{imp}{}^{x}$ [13],where x is found to be equal (-0.6837),(-0.587) and (-0.3945)for conductivity maximum, below and above that respectively.

However, for a strong scattering process and for a wide range of impurity concentration, x is found to be in the range (-0.75) to (-0.55) [21].

Conclusion

Thermal conductivities are calculated theoretically for nine compounds from I-III-VI_2 ternary semiconductors. Maximum values is found for $CuInS_2$ at 15 K while the minimum is for $AgInTe_2$ at 5 K. A mathematical relation is formulated for the Debye temperature dependence of $K_{max}(A_{iso})$. Thermal conductivity dependence on carrier impurities $N_{imp}{}^{x}$ indicates a strong scattering processof phonons. Then, the impurity dependence of conductivity can be obtained and found to change according to $N_{imp}{}^{x}$ [13],where x is found to be equal (-0.6837),(-0.587)and(-0.3945)for conductivity maximum, below and above that respectivily. However, for a strong sca-ttering process and for a wide range of imp-urity concentration, x is found to be in the range (-0.75) to (-0.55) [21].

Table(1): *parameters related to calculations of lattice thermal conductivity for nine compounds in the ternary group I-III-VI_2 semiconductors.All compounds suggested to have a cubic shape with dimensions of 5 mm.*

Compounds	**Classified. no**	θ_D (K)	V $*10^5$ (cm/sec)	$\overline{M}$ **(amu)**	**V*10^{-23} (cm^3)**	**A_{iso}*10^{-44} (sec^3)**	**Bu *10^{-18} (sec/K)**	**K_{max} (W/cm.K)**	**T_m (K)**
$CuAlTe_2$	1	200	2.0	86.5	2.62	1.23	2.65	62.9	15
$CuInS_2$	2	264	2.47	60.6	2.125	0.327	1.88	121.4	15
$AgGaS_2$	3	259	2.44	60.41	2.2	0.55	1.99	93.5	15
$CuInSe_2$	4	207	2.02	84.05	2.46	2.67	2.59	42.6	15
$CuGaTe_2$	5	177	1.8	97.18	2.75	5.09	3.29	30.6	10
$CuInTe_2$	6	156	1.63	108.4	3.01	5.7	4.09	31.55	10
$AgInSe_2$	7	138	1.5	95.13	3.37	7.04	6.22	28	10
$AgGaTe_2$	8	122	1.36	108.3	3.63	13	7.51	20.5	10
$AgInTe_2$	9	113	1.28	119.5	3.86	13.5	8.3	18.2	5

A_{iso} : isotop strength parameter calculated by using equ.(5).

K_{max} :maximum conductivity at a maximum temperature T_{max}.

Table(2):*Calculated parameters related to the lattice thermal conductivity and the conductivity maximum for four samples of the compound $CuInSe_2$.*

Samples	$N_{imp}*10^{19}$ (cm^{-3})	$A_{iso}*10^{-44}$ (sec^3)	$A_{imp}*10^{-44}$ (sec^3)	$A*10^{-44}$ (sec^3)	B_u*10^{-18} (sec/K)	K_{max} (W/cm.K)	T_{max} (K)
41		2.67		2.67	2.59	33.52	15
42	0.84	2.67	58.9	61.57	2.59	4.61	15
43	1.5	2.67	105.2	107.87	2.59	3.14	15
44	4.7	2.67	329.5	332.17	2.59	1.424	15

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گەرمی گەیاندنی تۆڕی پابەند بە پلەی گەرمی بۆ هەندێك ئاوێتەی نیمچە گەیەنەرەکانی گروپی $I\text{-}III\text{-}VI_2$

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پوختە

هاوکێشەی کالاوی (Callaway) لە پلەی گەرمی ٥-٣٠٠ پلەی پەتی بۆ ژمێریار کردنی گەرمی گەیاندنی تۆڕی بەکارهێنراوە بۆ (٩) نۆ ئاوێتەی سیانی لە کۆمەڵەی $I\text{-}III\text{-}VI_2$ نیمچە گەیەنەرەکان . بەرزترین گەیاندنی گەرمی تۆڕی دۆزراوەتەوە بە تیوری کە لە نێوان ٥ تا ١٥ پلەی پەتییە بۆ ئاوێتەکان . کاریگەری پلەی گەرمی دیبای لەسەر گەیاندنی گەرمی و بەرزترین گەیاندنی گەرمی دراسە کراوە بە فراوانی .

هاوکێشەی بیرکاری لەو پلە گەرمیانەدا بەدەست هێنراوە بۆ گەرمی گەیاندنی تۆڕی ئەو ئاوێتانە . کاریگەری بونی خلتە (N_{imp}) لەسەر گەیاندنی گەرمی تۆڕی بۆ ئاوێتەی $CuInSe_2$ دراسە کراوە ، پەیوەندێتی $(N_{imp})^{x}$ لەم ئاوێتەیەدا رون کراوەتەوە .

إعتماد التوصيل الحراري الشبيكي على درجة الحرارة لقسم من المركبات الثلاثية لشبه الموصل من نوع $I\text{-}III\text{-}VI_2$

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الخلاصة

تم استعمال معادله كالاواى (Callaway) لدراسة التوصل الحراري الشبيكي لتسعة من المركبات الثلاثية للشبه الموصل من نوع $I\text{-}III\text{-}VI_2$ لمدى الدرجات الحرارية ٥-٣٠٠ درجة مطلقة ، وجدت التوصيلية الحرارية العظمى .

من مدى ٥ الى ١٥ درجة مطلقة ، وتم دراسة تاثير درجة حرارة ديباى على التوصيل الحراري الشبيكي والتوصيلية العظمى حصلت على علاقات الرياضية نظريا للتوصيل الحراري الشبيكي . تم دراسة تاثير الشوائب (N_{imp}) على التوصيلية الحرارية الشبيكية للمركب $CuInSe_2$ ، وتم دراسة اعتماد $(N_{imp})^{x}$ من هذا المركب ايضا .

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