# INFRARED TRANSMISSION LIMITS OF CHALCOPYRITE CRYSTALS

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ABSTRACT

It is shown that three simple force constant models which satisfactorily represent interatomic distances for binary crystal groups, are also applicable to the ternary crystals: II–IV–$V_2$ and I–III–$VI_2$. The infrared transmission cut-offs are arrived at from a study of the force-constant ($\nu^2\mu$) models by knowing the equilibrium interatomic distance. The problem of finding the interatomic distances is also discussed. The relations are therefore useful for the analysis of force constants of chalcopyrite crystals, like the sphalerite crystals.

IN a recent paper[1] we have considered several relations for sphalerite crystals with a view to finding their infrared transmission limits. The chalcopyrite semiconductors ($ABC_2$) have been of recent interest because of their applications in lasers and nonlinear optics[2]. For application in nonlinear optical devices the infrared transmission limit is an important design parameter. It is determined by two-phonon summation absorption processes[3] like the sphalerite crystals. The applicability of the relations to the chalcopyrite crystals is considered for the first time and the infrared transmission limits are predicted for some of these crystals, which remained unstudied due to difficulties in crystal growth.

The fundamental lattice vibration frequency $\nu$ is used to calculate the force constant $\nu^2\mu$ ($\mu$ being the reduced mass of the vibrating atoms) whose dominant dependence on the equilibrium interatomic distance $r$ has led to the following simple relations within a given crystal group (whereby ionicity is kept as constant):

$$\text{Varshni model} \quad : \quad \nu^2\mu = A/(r + B)^3 \qquad (1)$$

$$\text{Anderson model} \quad : \quad \nu^2\mu = C \cdot e^{-sr} \qquad (2)$$

$$\text{Exponential model} \quad : \quad \nu^2\mu = K \cdot r^{-x} \qquad (3)$$

where A and B, C and $s$ and $k$ and $x$ are constants of the three models, and they remain constant for a group of crystals.

Unlike the sphalerite crystals, $ABC_2$ crystals, exhibit more than one lattice vibration mode. Of these, we consider the sphalerite-like mode[4] which is strong, dominant and of highest frequency, and so, essentially determines the infrared transmission cut-off. The excitation of this mode corresponds to the antiphase vibration of the atoms, forming IV–V bond in the case of II–IV–$V_2$ chalcopyrites, while for I–III–$VI_2$ chalcopyrites, it corresponds to the III–VI bond. And the evaluation of bond length is beset with special problems, not encountered in case of sphalerite crystals.

The two ways of calculating equilibrium interatomic distance have been discussed[1]; these are, (1) sum of covalent radii and (2) utilisation of structural constants. Both the methods require modification in the case of chalcopyrite crystals. Unlike diamond and sphalerite crystals, the degree of covalency in chalcopyrite crystals deviates considerably as is evident from the significant departure of bond angle[5,6] from perfect tetrahedron, *viz.*, 109·47°. And consequently bond-length calculation from the tabulated covalent radii[7] of the elements would show considerable deviation from the value determined from x-ray structure analysis (Table I). Large differences in the size and the electronegativity between the two types of cations introduce distortions of the chalcopyrite lattice. The distortion of interest is the departure of anions from the so-called 'sphalerite like' position, and this should be taken into consideration while calculating bond-length from structural parameters. For II–IV–$V_2$ crystals it has been found by Abrahams and Bernstein[5] that a regular IV–$V_4$ tetrahedron is formed and the positional x-coordinate, then no longer remains as an independent parameter but becomes a function of lattice constants $c$ and $a$ as

$$x = 0{\cdot}5 - \left(\frac{c^2}{32a^2} - \frac{1}{16}\right)^{1/2}.$$

For such crystals the IV–V bond length is then calculable from lattice constants $c$, $a$ and $x$, as

$$r = [a^2(\tfrac{1}{2} - x)^2 + (4a^2 + c^2)/64]^{1/2} \qquad (4)$$

Such calculated values are found to be in close agreement (within the limits of experimental error) with the experimental findings as shown in Table I. Similar is the result for II–V bond.

For I–III–$VI_2$ crystals, as no regular $BC_4$ tetrahedron is formed, the values of bond-length so calculated are found to deviate considerably from experimental values. However by introducing some correction, the values are made nearer to the experimental finding but this agreement is poor when compared to that with II–IV–$V_2$ crystals and greatly exceed experimental error (Table I). Again as the bonds in I–III–$VI_2$ group are very much ionic in nature, the bond-length calculated from covalent radii of the constituent elements

differ considerably from that of experimental findings (Table I).

TABLE I

*Comparison of BC bond-length (in Å) calculation for $ABC_2$ crystals*

| Crystal | Calculated from lattice const.[a] | Expt. value[b] | Sum of covalent radii[c] |
|---|---|---|---|
| *II–IV–$V_2$* | | | |
| $ZnSiP_2$ | 2·256 | 2·254 | 2·301 |
| $CdSiP_2$ | 2·256 | 2·247 | 2·301 |
| $ZnGeP_2$ | 2·321 | 2·324 | 2·353 |
| $CdGeP_2$ | 2·330 | 2·330 | 2·353 |
| $ZnSiAs_2$ | 2·355 | 2·352 | 2·398 |
| $CdGeAs_2$ | 2·429 | 2·430 | 2·450 |
| *I–III–$VI_2$* | | | |
| $AgGaS_2$ | 2·267 | 2·276 | 2·352 |
| $CuGaS_2$ | 2·303 | 2·288 | 2·352 |
| $CuGaSe_2$ | 2·416 | 2·435 | 2·450 |
| $CuInS_2$ | 2·460 | 2·464 | 2·532 |

*Notes* : (*a*) These are calculated from eqn. (4) in the text using the lattice constants[2]. (*b*) The experimental values are from refs. 5, 6. (*c*) Values of covalent radii are from reference 7.

TABLE II

*Least-squares straight line fitted constants for Varshni, Anderson and Exponential models in II-IV-$V_2$ and I-III-$VI_2$ chalcopyrite crystals*

| Mode / Group | | II–IV–$V_2$ | I–III–$VI_2$ |
|---|---|---|---|
| Av. force const. (cm$^{-2}$. amu) | $10^{-4} \times \nu^2 \mu$ | 314·5 | 268·5 |
| Varshni model | $10^{-9}$ A | ·032 | 10·1 |
| | B | −·193 | 13·2 |
| | $10^{-4}\bar{R}$ | 11·8 | 20·1 |
| | M | 3·9 | 8·2 |
| Anderson model | $10^{-4}$ C | 8197 | 422·7 |
| | *s* | −1·38 | −1·92 |
| | $10^{-4}\bar{R}$ | 12·1 | 20·2 |
| | M | 4·0 | 8·3 |
| Exponential model | ln(K) | 17·8 | 15·2 |
| | *x* | −3·3 | −·48 |
| | $10^{-4}\bar{R}$ | 11·9 | 20·1 |
| | M | 3·9 | 8·3 |

Thus in view of the foregoing discussions the BC bond-lengths are calculated from structural parameters[2]. Sphalerite-like mode frequencies are available for eight II–IV–$V_2$ crystals[4]. The values of force constant are calculated and plotted in accordance with Varshni, Anderson and exponential models and are shown in Figs. 1–3. It is seen that they can be approximated to straight lines and least-square analyses of the data yield the model constants. They are shown in Table II along with the average absolute residuals

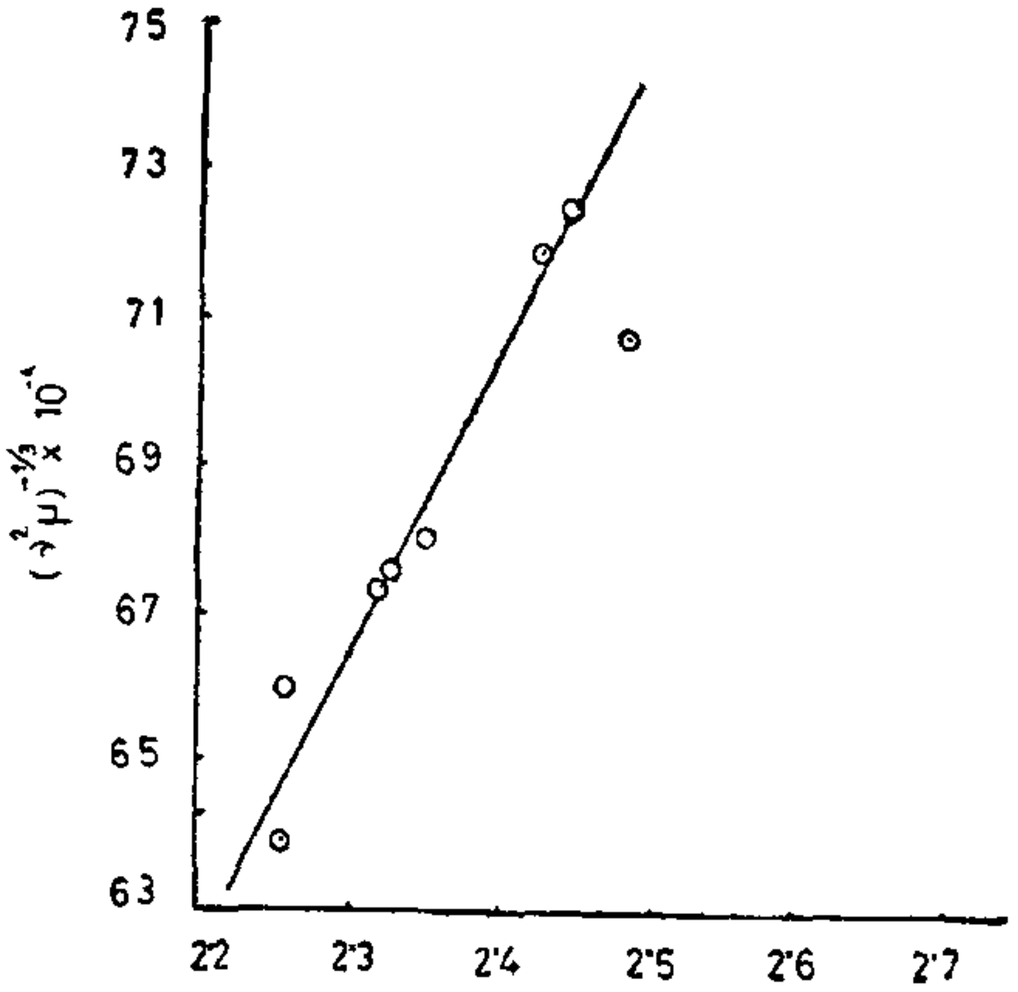


FIG. 1. Vershni model : $(\nu^2 \mu)^{-1/3}$ *vs.* *r* plot for II–IV–$V_2$ crystals.

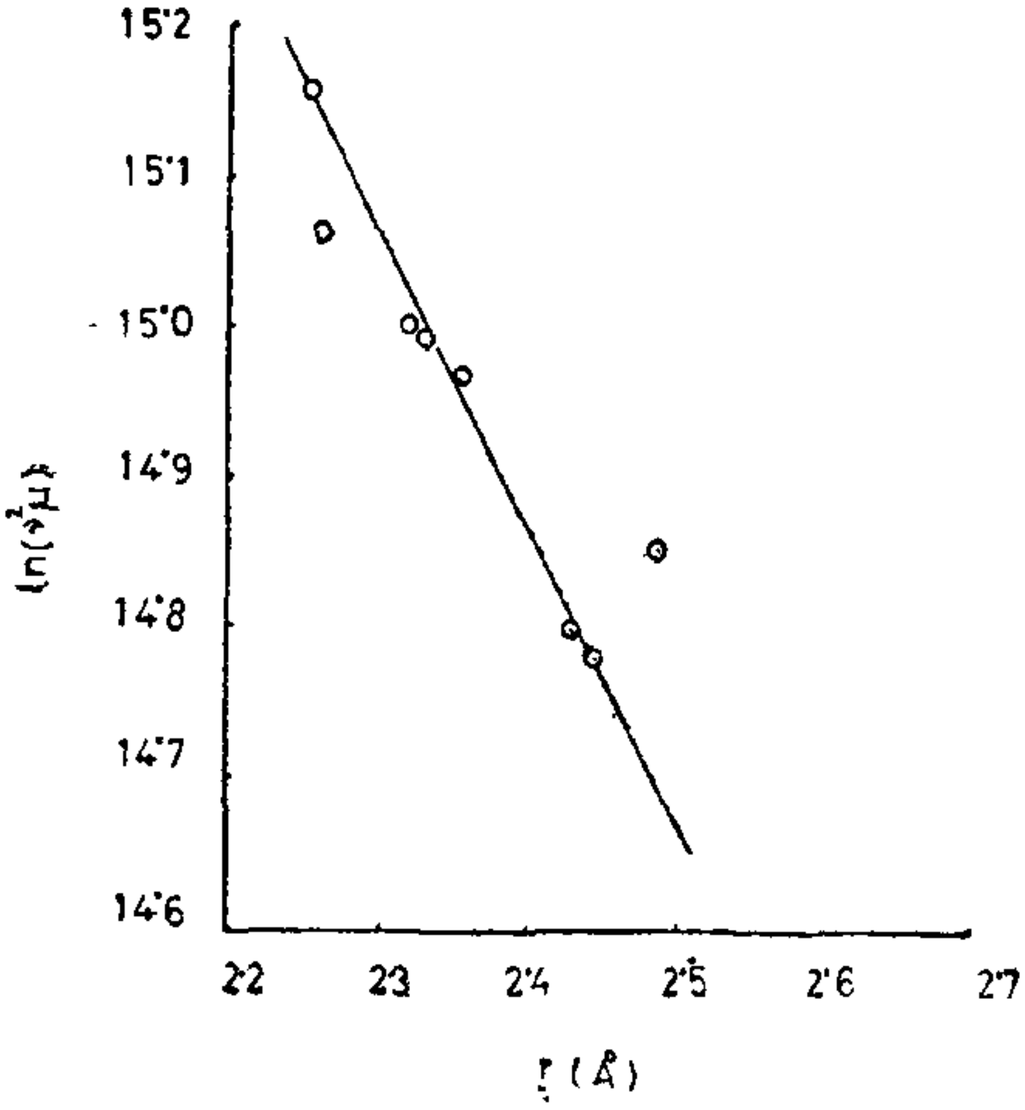


FIG. 2. Anderson model : in $(\nu^2 \mu)$ *vs.* *r* plot for II-IV-$V_2$ crystals.

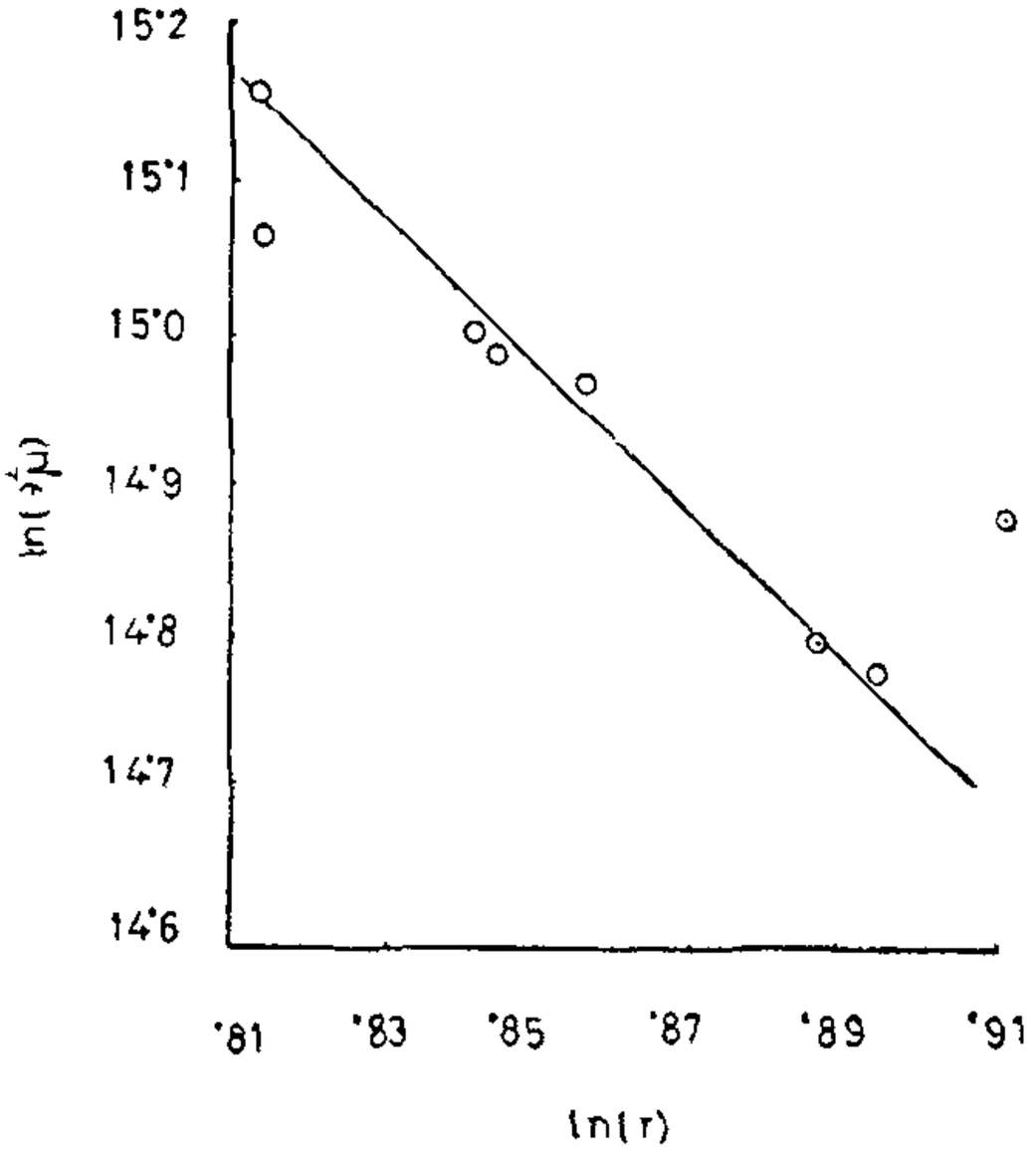


FIG. 3. Exponential model: in $(\nu^2 \mu)$ *vs.* Inr plot for II–IV–$V_2$ crystals.

$\bar{R}$ in force constants and the maximum percentage deviation in the lattice vibration frequency M from the experimental points. The latter quantity is within 4% which is of the same order as that in sphalerite crystals. For I–III–$VI_2$ chalcopyrite crystals, the lack of accurate values of interatomic distances does not show good plots. However, least-square analyses of the data, for all these models, show a value of M as high as 8%. The model constants are presented. Using such constants the sphalerite-like mode frequency and hence the infrared transmission cut-offs can be calculated. The approximate infrared transmisxion cut-offs are available for $CdSiAs_2$[8] and $AgInSe_2$[9]. These values (13 $\mu$m and 20 $\mu$m) can be compared with the predicted values using the model constants 12·8 $\mu$m and 21·3 $\mu$m. In this way the predicted values of infrared transmission cut-offs of $CdSnAs_2$, $ZnGeAs_2$ and $ZnSnAs_2$ are 22·2, 17·8 and 21·6 $\mu$m and for $AgAlS_2$, $AgAlSe_2$ are 11·5 and 13·7 $\mu$m respectively.

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## VARIATION IN THE MAJOR LIPID COMPONENTS, TOTAL, FREE AND ESTERIFIED STEROLS, GLYCEROL, GLYCOGEN AND LIPASE ACTIVITY IN THE FAT BODY OF THE DIAPAUSING PUPA OF *ANTHERAEA MYLITTA* (LEPIDOPTERA)

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ABSTRACT

Lipase, total lipids and their associated components, free fatty acids (FFA), phospholipids (PL), neutral lipids (NL), total cholesterol (TC), free and esterified cholesterol (FC and EC), glycerol and glycogen have been studied in the fat body of the diapausing pupa of *A. mylitta* and their role have been discussed.

### INTRODUCTION

*A. MYLITTA* is an insect of economic importance in tasar silk Industry. It has a feeding larval phase and a quiescent pupal period during which adult formation takes place. The energy required for the differentiation is supplied by oxidation of carbohydrates and lipids which are stored in the fat body which is analogous to the mammalian liver.

Fat body is a major site for lipid metabolism. Lipids are stored in the fat body mostly in the form of triglycerides[1]. Glycerol has been considered to bring about a marked depression in the freezing point of