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S R Yang, K N R Taylor and F Y Zhang

Advanced Electronic Materials Group, School of Physics, University of New South Wales, PO Box 1, Kensington, NSW 2033, Australia

Abstract. Observations of the polarisation-sensitive optical absorption in single-crystal proustite have been made over the temperature range from 82 to 460 K. By combining the data obtained from a number of samples of varying thickness the complete absorption spectrum has been found for absorption coefficients of up to $\simeq 2 \times 10^4\,\mathrm{cm}^{-1}$. The experimental results show that the optical inter-band transitions are dominated by indirect processes up to photon energies of about 3 eV. The phonons involved in these transitions have been tentatively identified.

Deviations from the simple indirect transition scheme at high absorption coefficients are attributed to additional indirect transitions to higher branch conduction band minima. A possible schematic band structure is suggested close to the Γ point.

1. Introduction

Despite the extensive studies which have been made during the past two decades of the well known non-linear optical material, proustite, [1–5] very little is known about its band structure. Some estimates have been made of both the direct and indirect energy gaps from optical studies [6, 7]; however, the results are largely incomplete and controversial. It has long been recognised that in the absence of phonon structure in the absorption edge it is difficult to determine the details of the energy gap for materials whose optical response involves indirect electronic transitions. While Dovgii and co-workers [6] reported both an indirect energy gap and two associated phonon energies there was no detailed analysis of the structure of the absorption edge itself. On the other hand, Golovach and co-workers [7] interpreted their room-temperature data in terms of four phonon branches. For maximum values of the absorption coefficient 4×10^2 and $2 \times 10^3\,\mathrm{cm}^{-1}$, respectively, both these groups claimed evidence for features that could be interpreted in terms of direct transitions, and values for a direct energy gap were derived (see table 1).

In order to establish the nature of the optical processes that may involve direct electronic transitions, it is vital to obtain information in the range of absorption coefficients near to $10^4\,\mathrm{cm}^{-1}$ by the use of extremely thin samples. As part of our exhaustive studies of the optical and electrical properties of this interesting material [8–10] we have recently carried out a series of optical absorption measurements on oriented single-crystal proustite samples with thicknesses varying from 4.6 mm to 4 μm, at various

Table 1. Previous studies of the absorption edge at room temperature in proustite.

Reference	Phonon energies (meV)	Indirect energy gap, E_g^* (eV)		Direct energy gap, E_g (eV)		Average temperature coefficient (eV deg^{-1})
		$E\|c$	$E \perp c$	$E\|c$	$E \perp c$	
[6]	$E_{PTO} = 45$ $E_{PLA} = 24$	2.012	2.004	2.156	2.125	-3.48×10^{-4}
[7]	$E_{PTA} = 7, 10$ $E_{PLA} = 21, 24$ $E_{PTO} = 41, 56$ $E_{PTO} = 33, 36$	2.100	2.067	2.235	2.177	Experiments were done at $T = 295$ K only

temperatures between 82 and 460 K. As a result of the high sample quality, and the wide range of thicknesses (more than three orders of magnitude), we have been able to resolve the detailed structure of the phonon-assisted indirect transitions. As a result we have determined both the magnitude of the indirect energy gap and the associated phonon energies.

By combining the data obtained from the range of samples, the complete absorption spectrum has been determined between ≈ 400 and ≈ 650 nm, covering a range of absorption coefficients from ≈ 1 cm^{-1} to $\approx 2 \times 10^4$ cm^{-1}. These experimental results show that up to photon energies of 3 eV the optical inter-band transitions are dominated by two groups of indirect transitions. There is no evidence for direct transitions in this range, in contrast to the observations reported earlier [6, 7]. The details of these measurements are described in the following.

2. Experimental

The observations described in this work were carried out on a series of specimens prepared from a synthetic single crystal. The optical absorption measurements were made in polarised light, with the electric vector parallel or perpendicular to the optical c axis. The initial sample used for the low-absorption region of the spectrum was in the form of a parallelepiped with dimensions $4.6 \times 4.3 \times 4.6$ mm^3 parallel to the x, y and z (i.e. c) axes respectively. For the subsequent, higher-absorption levels, specimens were cut from this larger crystal and polished with Imperial Lapping Film obtained from the 3M company, with a limiting grit size of 0.3 μm.

The polished sample faces were maintained perpendicular to the y axis so that all measurements could be related to the same crystallographic direction. For the samples with thicknesses less than 50 μm, special care was taken to ensure uniform thickness and searches were made for the presence of pinholes using optical microscopy. The thinnest samples were prepared by polishing one face and then attaching the sample to an optical flat by a layer of acetone-soluble resin before polishing the second face. Using this technique it was possible to prepare samples of high uniform thickness in the range 3 to 10 μm.

The final sample thicknesses were obtained by direct micrometer measurement for samples greater than 10 μm and by optical interference for thicknesses less than this.
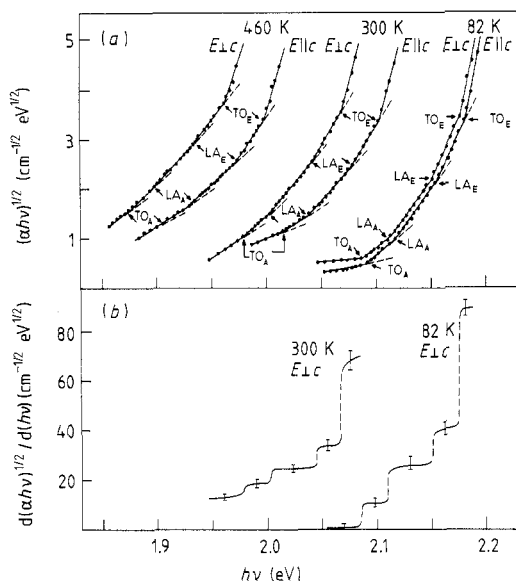
Figure 1. (*a*) Low-level absorption spectrum for 4.6 mm thick Ag_3AsS_3 sample at several temperatures in polarised light with $E\|c$ and $E \perp c$. Arrows indicate the thresholds of different absorption components resulting from different phonon energies. The labelling of the phonons is discussed in the text. (*b*) A plot of the derivative of $(\alpha h\nu)^{1/2}$ with $h\nu$ against $h\nu$ for $E \perp c$ light at 82 and 300 K.

For the thinnest samples, the colour viewed by transmitted light was observed to change from the characteristic deep red of bulk proustite, to yellow green.

Specimens prepared in this way, were mounted in an optical cryostat whose temperature could be controlled to an accuracy of 0.1 K. Optical measurements were made at several temperatures in the range from 82 to 460 K with a rapid scanning ROFIN 6080 'spectralyser' for the low-level absorption region and with a VARIAN DMS100 uv–visible double-beam spectrometer for the higher-absorption values using the thinner samples.

The values of the absorption coefficient were calculated using the well known formula for the transmittance normal to a parallel plate, neglecting interference effects [11]

$$T = I_t/I_0 = (1 - R)^2 \exp(-\alpha t)/[1 - R^2 \exp(-2\alpha t)] \tag{1}$$

where t is the sample thickness and R the surface reflectivity. In the present study, R was calculated from the refractive index data [12] using the relation [13]

$$R = (n - 1)^2/(n + 1)^2. \tag{2}$$

We have assumed that the variation of the refractive index across the wavelength region studied is small and its values may be given by $n_o = 2.96$ and $n_e = 2.69$ [12]. This assumption is similar to that made in studies of other materials [14, 15].

3. Results and discussion

3.1. Low-absorption region

The experimentally determined absorption spectrum, obtained using the technique described above for the 4.6 mm sample is shown in figure 1(*a*) in the form of a plot of

Table 2. Average temperature coefficient.

Temperature range (K)	Polarisation (eV deg^{-1})	
	$E\|c$	$E \perp c$
82–300	-3.578×10^{-4}	-4.908×10^{-4}
300–460	-6.688×10^{-4}	-6.563×10^{-4}

$(\alpha h\nu)^{1/2}$ against $h\nu$. The data recorded relate to temperatures of 82, 300 and 460 K for two orientations of the polarised light.

Examination of the low-temperature variation clearly shows a series of linear regions whose gradients increase with increasing photon energy, and is strongly suggestive of phonon participation in an indirect optical transition [16]. This segmented structure is shown more obviously in figure 1(b), where the derivative $d(\alpha h\nu)^{1/2}/dE$ is plotted as a function of energy. As the temperature increases, the details of this structure become blurred due to thermal effects of the phonon spectrum, as might be anticipated [17], and the entire spectrum moves to lower energies. The temperature coefficients for both $E\|c$ and $E \perp c$ were determined from these shifts and the values obtained for the two temperature intervals are given in table 2. As may be seen, these values are in reasonable agreement with those of [6] shown in table 1.

Tentative identification of the phonons involved in the various absorption regions has been made on figure 1 at the thresholds of the onset of each process. The 82 K absorption appears to show evidence for four components in the form of the absorption and emission of both TO and LA phonons, in contrast to four independent phonons as proposed in [7]. The threshold energies of these processes are shown in table 3 along with other values derived in the discussion below.

Close to the onset of indirect optical transitions in a semi-conductor, the energy dependence of the absorption obeys an approximate quadratic dependence given by [16, 18, 19]

$$\alpha h\nu = \sum_{i=1}^{n} a_i \left(\frac{(h\nu - E_g^* + E_{pi})^2}{(\exp(E_{pi}/kT) - 1)} + \rho_i \frac{(h\nu - E_g^* - E_{pi})^2}{(1 - \exp(-E_{pi}/kT))} \right). \tag{3}$$

The sum over i involves the phonons of energy E_{pi} having the necessary momentum for the indirect process, a_i is a weakly temperature dependent constant, E_g^* is the indirect energy gap and the value of ρ_i is given by

$$\rho_i = (\delta E + E_{pi})^2 / (\delta E - E_{pi})^2 \tag{4}$$

where δE is the energy separation between the principal intermediate states in the virtual transition and the final state.

Equation (3) predicts that the threshold energies of the various phonon absorption and emission processes should be spaced uniformly about E_g^* with separation of $2E_{pi}$. Inspection of figure 1 and table 3 shows that this is the case for the present data, and the derived values of the phonon energies are given in that table also. As may be seen, there appears to be no temperature dependence of the values of E_{pi}, in agreement with the behaviour to be expected for indirect optical transitions [20]. The two phonon energies involved are close to those reported previously [6].

Table 3. Analysis of the absorption-component threshold energies.

Temperature, T (K)	Polarisation	Threshold energy (eV)	Assignment	Phonon energy (meV)	Indirect energy gap, E_{g1}^* (eV)	Second indirect energy gap, E_{g2}^* (eV)
82	$E \parallel c$	2.182	$E_{g1}^* + E_{PTO}$	$E_{PTO} = 44.5$	2.138	2.44
		2.093	$E_{g1}^* - E_{PTO}$			
		2.157	$E_{g1}^* + E_{PLA}$	$E_{PLA} = 19$	2.138	
		2.119	$E_{g1}^* - E_{PLA}$			
	$E \perp c$	2.178	$E_{g1}^* + E_{PTO}$	$E_{PTO} = 45$	2.133	2.264
		2.088	$E_{g1}^* - E_{PTO}$			
		2.152	$E_{g1}^* + E_{PLA}$	$E_{PLA} = 20$	2.132	
		2.112	$E_{g1}^* - E_{PLA}$			
300	$E \parallel c$	2.104	$E_{g1}^* + E_{PTO}$	$E_{PTO} = 45$	2.059	2.337
		2.014	$E_{g1}^* - E_{PTO}$			
		2.080	$E_{g1}^* + E_{PLA}$	$E_{PLA} = 20$	2.060	
		2.040	$E_{g1}^* - E_{PLA}$			
	$E \perp c$	2.070	$E_{g1}^* + E_{PTO}$	$E_{PTO} = 45$	2.025	2.20
		1.980	$E_{g1}^* - E_{PTO}$			
		2.045	$E_{g1}^* + E_{PLA}$	$E_{PLA} = 20$	2.025	
		2.005	$E_{g1}^* - E_{PLA}$			
460	$E \parallel c$	1.998	$E_{g1}^* + E_{PTO}$	$E_{PTO} = 45$	1.953	2.242
		1.908	$E_{g1}^* - E_{PTO}$			
		1.973	$E_{g1}^* + E_{PLA}$	$E_{PLA} = 20$	1.953	
		1.933	$E_{g1}^* - E_{PLA}$			
	$E \perp c$	1.966	$E_{g1}^* + E_{PTO}$	$E_{PTO} = 45$	1.921	2.146
		1.875	$E_{g1}^* - E_{PTO}$			
		1.939	$E_{g1}^* + E_{PLA}$	$E_{PLA} = 20$	1.920	
		1.899	$E_{g1}^* - E_{PLA}$			

Turning now to the problem of phonon assignment, proustite has 14 atoms per unit cell, providing 42 vibrational modes, 39 of which are optical and 3 acoustic, all of which can be described in terms of the irreducible representations of the symmetry group $\Gamma = 7A_1 + 7A_2 + 14E$ where the A_1 and E modes are both Raman and infrared active and the A_2 modes silent [21]. With the exception of the three acoustic modes, all the active phonon modes have been experimentally determined [21, 22].

According to the theory of indirect transitions [18], only a small number of the available phonon modes will make a dominant contribution to the details of the absorption edge because of the differences in the matrix elements describing the electron–phonon coupling. In the case of proustite, as we have observed, there appear to be only two phonons involved. One of these has been identified as a TO mode and the other an LA mode by [6] with energies close to our own as has been shown above.

Support for these assignments can be obtained from a consideration of the selection rules describing the indirect transitions and a comparison of the Raman and infrared phonon studies [21, 22]. Again, within indirect transition theory, the most important intermediate state is the conduction band minimum at $k = 0$ if the transition is optically allowed. For proustite, the conduction band minimum at $k = 0$ has symmetry Γ_1 (or Γ_6 if the spin is included). Group theory shows that transitions occurring through such a state are allowed only for scattering by an LA phonon and indirect transitions via the higher conduction band minimum are for LO, TA and TO phonons [19].

The phonon energy of 0.045 eV determined in this study is close to that of one of the TO phonons (0.048 eV) observed in the Raman and infrared observations referred to earlier. This phonon belongs to the E modes, with a frequency of 360 cm^{-1} and is similar to that observed in both amorphous [23] and crystalline [24] As$_2$S$_3$, being associated with the As–S stretching vibrations. Consequently we have attributed the present 0.045 eV phonon in this way as a TO phonon with symmetry of E-type. There is no Raman or infrared evidence for optical phonons at 0.020 eV and we have been forced to assign this second phonon to an acoustic branch. The association with an LA branch specifically has been done on the basis of the matrix element for the indirect transition. As we have seen, this is proportional to $(\delta E)^{-1}$, which is known to be larger for LA phonons than for TA phonons.

The data of figure 1 show a very strong polarisation dependence of the absorption edges as is also observed in many other ternary semi-conductors [25, 26]. This shift is attributed to the spin–orbit splitting of the valence band and to the influence of the symmetric components of the crystal field. The magnitude of this polarisation shift is strongly temperature dependent, as may be seen, increasing from 6 meV at 82 K to about 35 meV at 300 K and above.

It is known that the structure of proustite belongs to the trigonal system having a C_{3v}^6 space group with two formula units per unit cell [27]. The symmetry of the conduction and valence bands at the Γ point are described by the Γ_1 and Γ_3 representations with no spin–orbit interaction. With spin–orbit splitting the degeneracy of the Γ_3 band is removed and becomes $\Gamma_3 \times D^{(1/2)} = \Gamma_6[\Gamma_4 + \Gamma_5]$ and the Γ_1 band changes to a Γ_6 band [28]. In addition the lowest valley of the conduction band is located at the Σ_3' point. Consequently, the indirect transitions occur from $[\Gamma_4 + \Gamma_5, \Gamma_6]_v$ to $[\Sigma_3']_c$ and the polarisation shift thus corresponds to the splitting of the Γ_6 and $[\Gamma_4 + \Gamma_5]$ sub-bands. This situation is shown in figure 2 on which is also presented energy gap details derived in the next section.

It would be extremely interesting to explore the temperature dependence of the gap splitting in detail, as it is likely to be associated with one of the phase changes reported
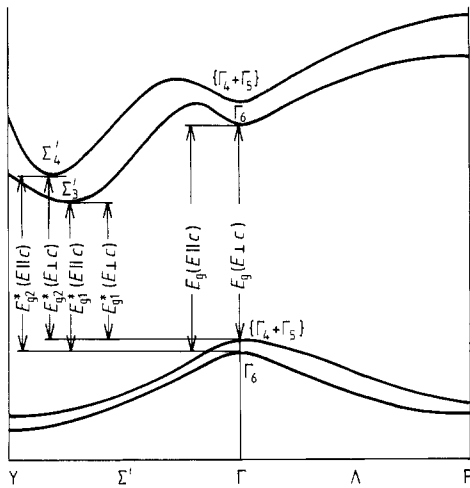
Figure 2. A modified schematic energy band structure of Ag_3AsS_3. $E_{g_1}^*$ and $E_{g_1}^*$ represent the first and second lowest indirect energy gaps and E_g is the direct energy gap.
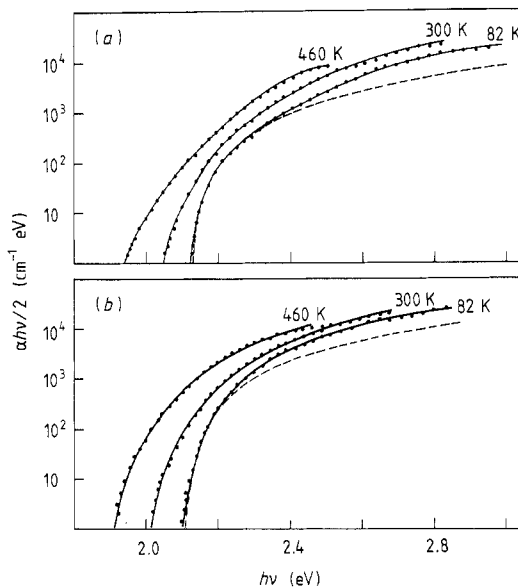

Figure 3. Plots of $(\alpha h\nu)$ against $h\nu$ for Ag_3AsS_3 at various temperatures for two orientations of the polarisation vector $((a), E\|c; (b), E \perp c)$. The broken curve is the theoretical fitting $\alpha h\nu = A(h\nu - E_g)^2$ with $A = 3 \times 10^4$, $E_g = 2.124$ eV and $A = 6 \times 10^4$, $E_g = 2.106$ eV for $E\|c$ and $E \perp c$ respectively.

by other workers in this temperature range [29, 30] and observed by ourselves in the previous photo-electric studies of this material [8, 10]. Such a study is now in progress.

3.2. High-absorption region

The complete variation of the absorption coefficient over the absorption range from $1\,\mathrm{cm^{-1}}$ to $1.9 \times 10^4\,\mathrm{cm^{-1}}$ for both orientations of the polarisation are shown in figure $3(a), (b)$ in the form of plots of $(\alpha h\nu)$ against $h\nu$. A theoretical curve $\alpha h\nu = A(h\nu - E_g)^2$ is also shown for comparison. The experimental data were obtained from the entire
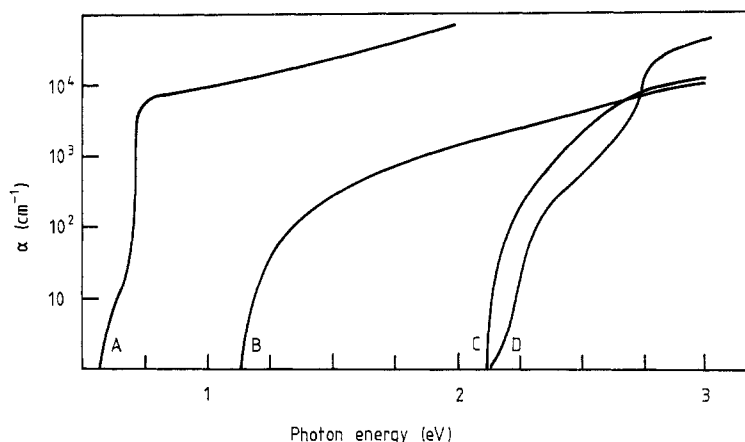
Figure 4. Comparison of the absorption edge in Ag_3AsS_3 (curve C) ($E\|c$, $T = 82$ K) with various indirect semiconductors: A, Ge(77 K), B, Si(77 K), and D, GaP(290 K).

series of samples with extremely good agreement in the overlap regions. In figure 4, the spectral variation for $E\|c$ at $T = 82$ K is compared with similar data for various known indirect semiconductors [20, 31].

The close agreement between the experiment and theoretical variations at the lower-absorption regions ($0 < \alpha < 850$ cm^{-1}, $E\|c$) and ($0 < \alpha < 550$ cm^{-1}, $E\|c$) provide strong support for the existence of indirect transitions in this range. Although the absorption coefficients rise more rapidly than the theoretical predictions at higher values, there is no sign of an abrupt increase characteristic of the onset of a direct transition such as is observed in germanium and GaP (see figure 4).

It is interesting to note the strong similarity between the absorption spectra of proustite and silicon shown in figure 4. While the latter material, which is a well known indirect band gap semiconductor, has been studied to energies almost three times that of the indirect band gap, no sign of a direct transition has been reported [16]. The close comparison of the two sets of data suggest intuitively that we are not seeing a direct transition in proustite in the 2–3 eV range.

Replotting the data of figure 3 in the form of $(\alpha h\nu)^{1/2}$ versus $h\nu$ in figure 5(a), (b) shows that the experimental values for both polarisations, and at the three temperatures, can be fitted to two linear variations. The first of these clearly corresponds to the indirect transition discussed in the previous section. The second may be associated with an additional indirect transition to a minimum in a higher branch conduction band, Such effects have been reported in GaP [18, 31] and AlAs [18]. If we assume that the 0.045 eV TO phonon is also involved in this transition, then the band gap corresponding to this higher-energy indirect transition lies in the range 2.15–2.44 eV as shown for various temperatures in table 3. The splitting between the two conduction band branches derived from these values is comparable to those reported in GaP and AlAs.

These results, which suggest that only indirect transitions occur in the wavelength range studied, are in contradiction to those of Golovach and co-workers [7] who report a linear α^2–$h\nu$ variation at high ($\alpha > 600$ cm^{-1}) absorptions as evidence for a direct transition. Despite repeated measurements on many different samples we have found no evidence for such a variation in the absorption range $1 < \alpha < 1.9 \times 10^4$ cm^{-1}.
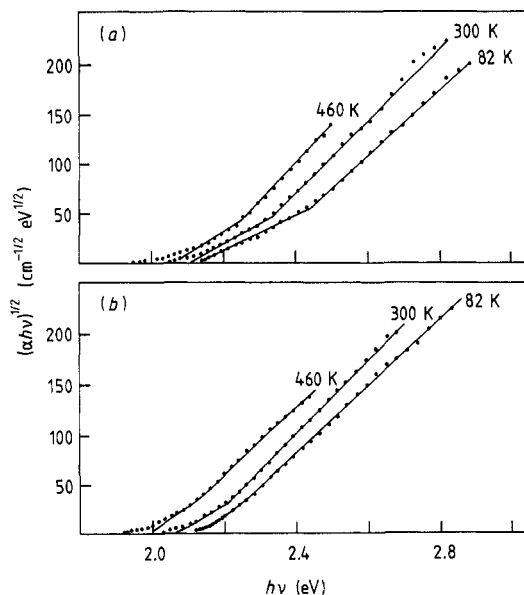
Figure 5. The absorption coefficient of figure 3 in the form of $(\alpha h\nu)^{1/2}$ against $h\nu$. (a), $E\|c$; (b) $E \perp c$.

4. Conclusion

In the course of this study of the optical absorption edge in proustite the values of two indirect energy gaps have been established, along with the associated phonon structure. The temperature dependence of both the energy gap and the polarisation shift have been determined. Contrary to previous reports [6, 7] we have found no evidence for direct optical transitions in the range of photon energies 2–3 eV at 82 K and propose that the direct band gap is >3 eV.

Below 3 eV, the optical absorption is dominated by two sets of indirect transitions, which are proposed to be associated with a split conduction band comparable to that in other compound semiconductors. The phonons involved in these transitions have been identified as TO and LA modes with energies of 0.045 to 0.020 eV respectively.

A combination of these derived values has allowed us to propose modifications to the schematic band structure of [28], which is shown in its amended form in figure 2.

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