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X-ray studies on the thermal expansion of $ZnSiAs_{2-x}P_x$ (x=0.5, 1.5) alloys

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The tetragonal unit cell dimensions a and c of $ZnSiAs_{1.5}P_{0.5}$ and $ZnSiAs_{0.5}P_{1.5}$ have been accurately determined over the temperature range 28 to 671° C by X-ray powder diffraction. In both compounds, a increased nonlinearly and c linearly with temperature, the linear coefficient of expansion in the a-direction ($\alpha_\perp$) being greater than that in the c-direction ($\alpha_\parallel$). This indicates an "increase" in the tetragonal distortion, (2-c/a), with temperature. An attempt is made to explain the anisotropic thermal expansion and the increase in the tetragonal distortion with temperature of these crystals in terms of the thermal expansion of the II–V and IV–V bonds.

1. Introduction

The present investigation is a part of a programme dealing with studies on the lattice thermal behaviour of ternary semiconductors of the type II–IV–V_2 and their solid solutions. The II–IV–V_2 compounds crystallize in the tetragonal chalcopyrite structure (space group $I\bar{4}2d$) and can be regarded as valence analogues of the III–V compound semiconductors [1]. Recently, these compounds have drawn great attention because of their possible applications in electro-optical devices [2, 3]. Among these compounds, zinc silicon arsenide ($ZnSiAs_2$) and zinc silicon phosphide ($ZnSiP_2$) have attracted much interest for nonlinear optical applications and solar cells [4]. The two compounds show mutual solubility in the solid state. The tetragonal structure is maintained throughout the range of solid solutions [5] with the lattice parameters deviating only slightly from those predicted by Vegard's law [6]. The electrical and optical properties of $ZnSiAs_{2-x}P_x$ alloys have been studied in detail [5, 7, 8]. However, very little work has been reported on the thermal properties of these alloys. Practically no information is available in the literature on their thermal expansion. Therefore, it was thought worthwhile to include these alloys in a programme of high temperature X-ray studies on some ternary semiconducting compounds undertaken in our laboratory [9].

The present paper deals with the accurate determination of the lattice parameters of $ZnSiAs_{1.5}P_{0.5}$ and $ZnSiAs_{0.5}P_{1.5}$ and the evaluation of the tetragonal distortion and the coefficients of thermal expansion at elevated temperatures.

2. Experimental procedure

The polycrystalline samples of $ZnSiAs_{2-x}P_x$ alloys used in the present study were kindly supplied by Professor W. C. Clark of the University of Bath, UK. Details of the growth and purity analysis of these crystals have been described earlier by Stroud and Clark [5].

The specimens for the diffraction study were prepared by filling fine thin-walled quartz capillaries with the powders. In each case, the powder photographs were taken at seven different temperatures in the range 28 to 671° C using a Unicam 19-cm high-temperature powder camera and Cu$K\alpha$ radiation. Temperature control was facilitated by the use of a voltage stabilizer and variac; the temperature could be held constant to within about 2° C. The experimental apparatus and the construction of the camera have been described elsewhere [10].

Eight reflections, $(6\,2\,0)\alpha_1$, $(6\,2\,0)\alpha_2$, $(2\,0\,12)\alpha_1$, $(2\,0\,12)\alpha_2$, $(4\,4\,8)\alpha_1$, $(4\,4\,8)\alpha_2$, $(5\,5\,2)\alpha_1$ and $(5\,5\,2)\alpha_2$, recorded in the Bragg angle region 61° to 82° and ten reflections, $(6\,2\,0)\alpha_1$, $(6\,2\,0)\alpha_2$, $(2\,0\,12)\alpha_1$, $(2\,0\,12)\alpha_2$, $(5\,3\,6)\alpha_1$, $(5\,3\,6)\alpha_2$,

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TABLE I Lattice parameters of $ZnSiAs_{2-x}P_x$ ($x = 0.5, 1.5$) alloys at room temperature

Source	Lattice parameter (Å)			
	$ZnSiAs_{1.5}P_{0.5}$		$ZnSiAs_{0.5}P_{1.5}$	
	a	c	a	c
Gallay *et al.* [8]	5.559 ± 0.001	10.778 ± 0.002	5.450 ± 0.001	10.542 ± 0.003
Present study	5.5554 ± 0.0001	10.7646 ± 0.0003	5.4460 ± 0.0001	10.5356 ± 0.0003

$(3\,3\,10)\alpha_1$, $(3\,3\,10)\alpha_2$, $(4\,4\,8)\alpha_1$ and $(4\,4\,8)\alpha_2$, recorded in the Bragg angle region 63° to 82°, were used in determining the accurate lattice parameters of $ZnSiAs_{1.5}P_{0.5}$ and $ZnSiAs_{0.5}P_{1.5}$, respectively. In evaluating the lattice parameters, Cohen's [11] least-squares method was used. That is, for each reflection $(h\,k\,l)$ an equation of condition, applicable to crystals of tetragonal system to which the $ZnSiAs_{2-x}P_x$ alloys belong, can be written:

$$\frac{4}{\lambda^2}\sin^2\theta = \frac{1}{a^2}(h^2+k^2)+\frac{1}{c^2}l^2+Df(\theta), \quad (1)$$

where $Df(\theta)$ is the so-called drift function, which makes allowance for the various systematic errors due to absorption, sample excentricity, etc., which affect the measured values of θ. The form of the drift function in the range $\theta > 60°$ was taken to be that of Nelson and Riley [12]:

$$f(\theta) = \frac{1}{2}\left(\frac{\cos^2\theta}{\theta}+\frac{\cos^2\theta}{\sin\theta}\right). \quad (2)$$

The values of $1/a^2$ and $1/c^2$ and D were then calculated for each film by the method of least squares. The mean standard error of the lattice parameter, obtained at different temperatures, was found to be about 0.0001 Å in the a parameter and about 0.0003 Å in the c parameter for both crystals. The details of the extrapolation function used for determining accurate values of a and c and the procedure followed in evaluating the standard errors in the lattice parameters have been given elsewhere [13, 14].

3. Results

In Table I, the lattice parameters of $ZnSiAs_{1.5}P_{0.5}$ and $ZnSiAs_{0.5}P_{1.5}$, obtained at room temperature in the present study, are compared with the earlier data available in the literature. The values obtained in the present investigation are in good agreement with those reported by earlier workers.

The lattice parameters obtained at different temperatures are given in Table II and shown graphically in Figs 1 and 2. In both cases, the a parameter increases nonlinearly while the c parameter increases linearly with increasing temperature. The temperature dependence of a and c can be represented by the following expressions, obtained by a least-squares fitting of the lattice parameter data.

$ZnSiAs_{1.5}P_{0.5}$:

$$a(\text{Å}) = 5.554\,19 + 4.200\,46\times10^{-5}\,T - 1.677\,92\times10^{-9}\,T^2 \quad (3)$$

TABLE II Lattice parameters of $ZnSiAs_{2-x}P_x$ ($x = 0.5, 1.5$) alloys at different temperatures

Temperature (° C)	Lattice parameter (Å)							
	$ZnSiAs_{1.5}P_{0.5}$				$ZnSiAs_{0.5}P_{1.5}$			
	a		c		a		c	
	Obs.	Calc. (Eq. 1)	Obs.	Calc. (Eq. 2)	Obs.	Calc. (Eq. 3)	Obs.	Calc. (Eq. 4)
28	5.5554	5.5554	10.7646	10.7657	5.4460	5.4462	10.5356	10.5365
106	5.5584	5.5586	10.7697	10.7687	5.4490	5.4491	10.5399	10.5391
209	5.5631	5.5629	10.7725	10.7727	5.4534	5.4530	10.5422	10.5425
326	5.5679	5.5677	10.7786	10.7773	5.4578	5.4575	10.5475	10.5463
451	5.5725	5.5728	10.7813	10.7821	5.4619	5.4624	10.5503	10.5503
561	5.5772	5.5772	10.7860	10.7864	5.4665	5.4668	10.5530	10.5539
671	5.5817	5.5816	10.7908	10.7906	5.4717	5.4714	10.5577	10.5575

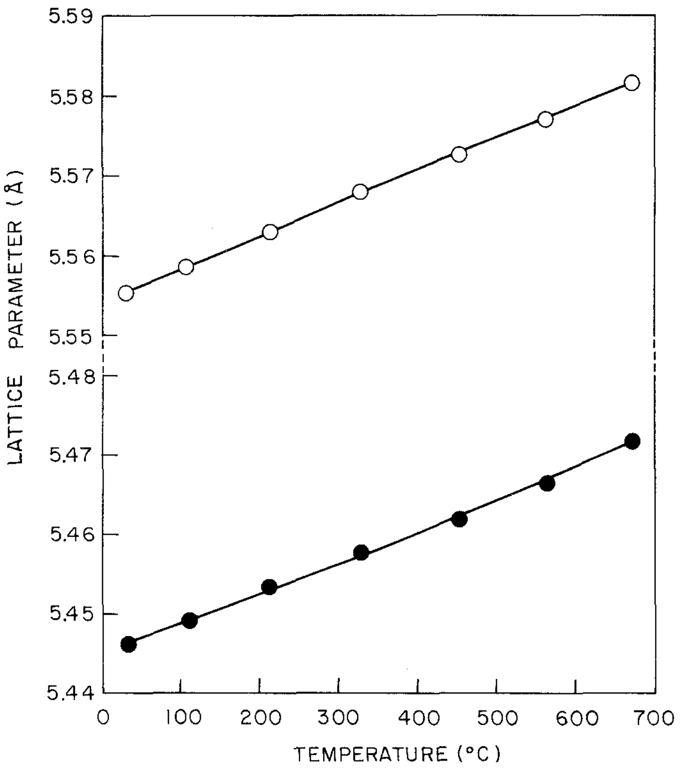

Figure 1 Temperature dependence of *a* parameter. ○, $ZnSiAs_{1.5}P_{0.5}$; ●, $ZnSiAs_{0.5}P_{1.5}$.

$$c(\text{Å}) = 10.76460 + 3.88046 \times 10^{-5}\,T \quad (4)$$

$ZnSiAs_{0.5}P_{1.5}$:

$$a(\text{Å}) = 5.44516 + 3.65680 \times 10^{-5}\,T + 3.68038 \times 10^{-9}\,T^2 \quad (5)$$

$$c(\text{Å}) = 10.53567 + 3.25311 \times 10^{-5}\,T, \quad (6)$$

where T is the temperature in ° C. In both cases, the expressions reproduce the data in Table II with an average deviation of 0.0001 Å in the *a* parameter and 0.0003 Å in the *c* parameter.

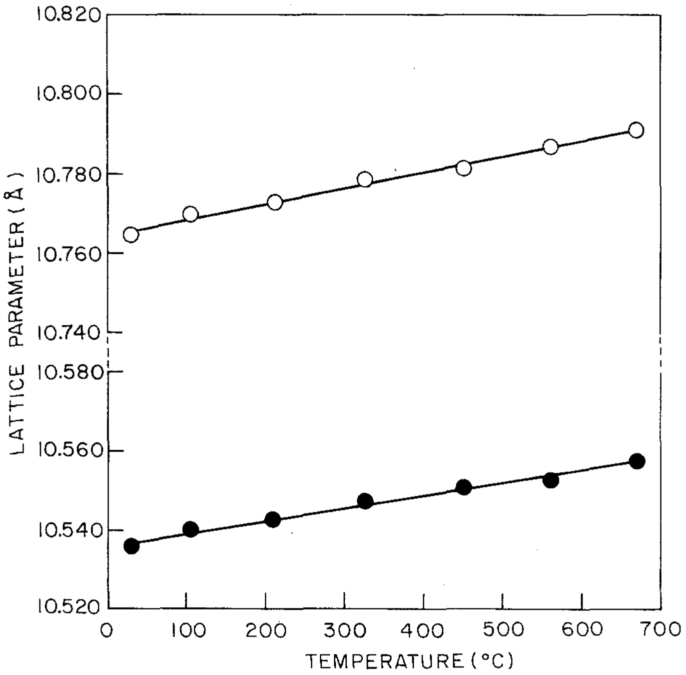

Figure 2 Temperature dependence of *c* parameter. ○, $ZnSiAs_{1.5}P_{0.5}$; ●, $ZnSiAs_{0.5}P_{1.5}$.

TABLE III Constants for Equations 7 and 8

Constant	$ZnSiAs_{1.5}P_{0.5}$		$ZnSiAs_{0.5}P_{1.5}$	
	$\ln a$	$\ln c$	$\ln a$	$\ln c$
A	1.714 55	2.376 26	1.694 73	2.354 77
B	7.562×10^{-6}	3.600×10^{-6}	6.718×10^{-6}	3.085×10^{-6}
C	-3.287×10^{-10}	–	6.467×10^{-10}	–

Thermal expansion coefficients, $\alpha(T)$, may be derived from these expressions. As

$$\alpha_\perp(T) = \frac{1}{a}\left(\frac{\mathrm{d}a}{\mathrm{d}T}\right) = \frac{\mathrm{d}\ln a}{\mathrm{d}T}$$

and

$$\alpha_\parallel(T) = \frac{1}{c}\left(\frac{\mathrm{d}c}{\mathrm{d}T}\right) = \frac{\mathrm{d}\ln c}{\mathrm{d}T},$$

it is more convenient to fit $\ln a$ to a parabolic curve of the type;

$$\ln a = A + BT + CT^2, \quad (7)$$

and $\ln c$ to a linear curve of the type;

$$\ln c = A + BT, \quad (8)$$

where T is the temperature in ° C. Table III gives the results obtained for both the crystals.

By definition, $\alpha_\perp(T)$ is obtained as $\mathrm{d}\ln a/\mathrm{d}T = B + 2CT$ and $\alpha_\parallel(T)$ as $\mathrm{d}\ln c/\mathrm{d}T = B$. Thus $\alpha_\perp$ varies linearly with temperature whereas $\alpha_\parallel$ remains constant throughout the temperature range covered in the present study. Fig. 3 shows the variation of $\alpha_\perp$ with temperature. For the composition $ZnSiAs_{1.5}P_{0.5}$, $\alpha_\perp$ increases with temperature, whereas it decreases with temperature for $ZnSiAs_{0.5}P_{1.5}$. However, the decrease in $\alpha_\perp$ with temperature for $ZnSiAs_{0.5}P_{1.5}$ is very small and it is almost constant within experimental error (about 3% in both $\alpha_\perp$ and $\alpha_\parallel$). The mean values of $\alpha_\perp$ and $\alpha_\parallel$, obtained in the present study, for the temperature range 28 to 671° C, are found to be,

$ZnSiAs_{1.5}P_{0.5}$:

$$\bar{\alpha}_\perp = 7.33 \times 10^{-6}\,{}^\circ\mathrm{C}^{-1}$$

$$\bar{\alpha}_\parallel = 3.60 \times 10^{-6}\,{}^\circ\mathrm{C}^{-1}$$

$ZnSiAs_{0.5}P_{1.5}$:

$$\bar{\alpha}_\perp = 7.17 \times 10^{-6}\,{}^\circ\mathrm{C}^{-1}$$

$$\bar{\alpha}_\parallel = 3.08 \times 10^{-6}\,{}^\circ\mathrm{C}^{-1}.$$

4. Discussion

The thermal expansion behaviour of $ZnSiAs_{1.5}P_{0.5}$ and $ZnSiAs_{0.5}P_{1.5}$ is similar to the other compounds of the chalcopyrite type in having a relatively small coefficient of expansion along the c-axis ($\alpha_\parallel$) and a large coefficient of expansion in the perpendicular direction ($\alpha_\perp$) [15]. The chalcopyrite structure of II–IV–V_2 compounds (see Fig. 4), symmetry $\bar{4}2m$, is an ordered superstructure of the zincblende type with corresponding group III elements of a III–V binary compound being replaced alternately by group II and group IV elements in a regular fashion so that each site retains the same number of valence electrons. Owing to the difference in radius of the two cations, the lattice is typically distorted with the unit cell height being slightly less than twice the

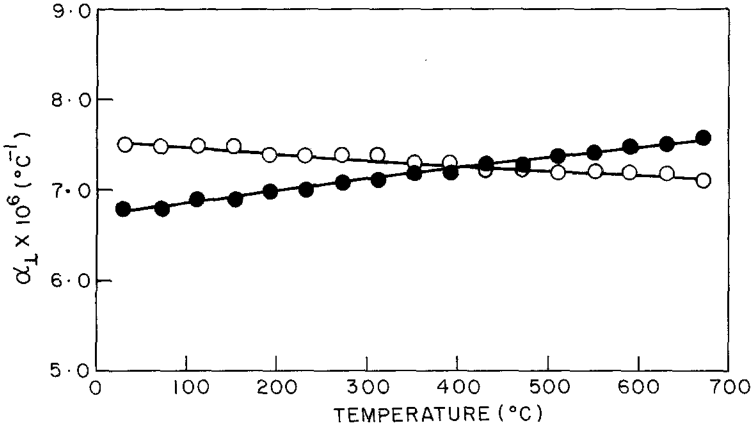

Figure 3 Temperature dependence of $\alpha_\perp$. ○, $ZnSiAs_{1.5}P_{0.5}$; ●, $ZnSiAs_{0.5}P_{1.5}$.

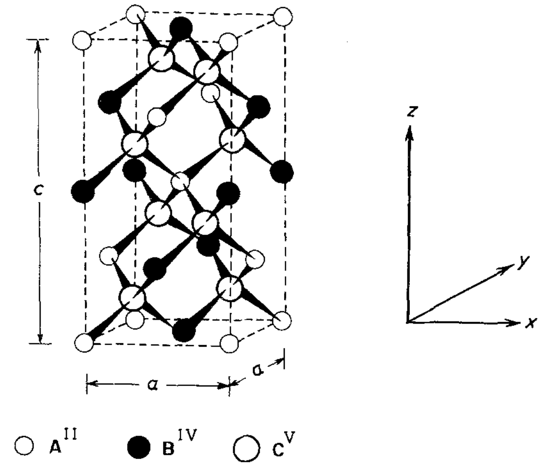

Figure 4 Unit cell of chalcopyrite-type structure.

base dimension. This distortion along the optic or c-axis is known as "tetragonal distortion" and is given by the expression $\delta = 2 - c/a$; c and a being the lattice parameters. As shown in Fig. 5, the most notable point is the temperature dependence of the axial ratio, c/a. Because of the very large difference between the expansion coefficients along a and c axial directions, the ratio c/a decreases with temperature away from the "ideal" value of 2, so that the tetragonal distortion, δ, increases with temperature. It is also evident from these two crystals that the rate of change of distortion increases with tetragonal distortion as pointed out by Weaire and Noolandi [16].

We have attempted to interpret the anisotropic thermal expansion and the increase in the tetragonal distortion with temperature of $ZnSiAs_{1.5}P_{0.5}$ and $ZnSiAs_{0.5}P_{1.5}$ in terms of the thermal expansion of the individual II–V and IV–V bonds. As described by Miller *et al.* [17] on II–IV–V_2 compounds, we can estimate the bond distances and bond expansion coefficients for the Zn–As and/or P (II–V) and Si–As and/or P (IV–V) bonds using the following relations given by Abrahams and Bernstein [18, 19].

$$x = 0.5 - \left[\frac{a^2}{32a^2} - \frac{1}{16}\right]^{1/2} \tag{9}$$

$$\overline{(A-C)} = \left[a^2x^2 + \frac{4a^2 + c^2}{64}\right]^{1/2} \tag{10}$$

$$\overline{(B-C)} = \left[a^2(0.5 - x)^2 + \frac{4a^2 + c^2}{64}\right]^{1/2} \tag{11}$$

$$c = \frac{8}{3^{1/2}}\overline{(B-C)} \tag{12}$$

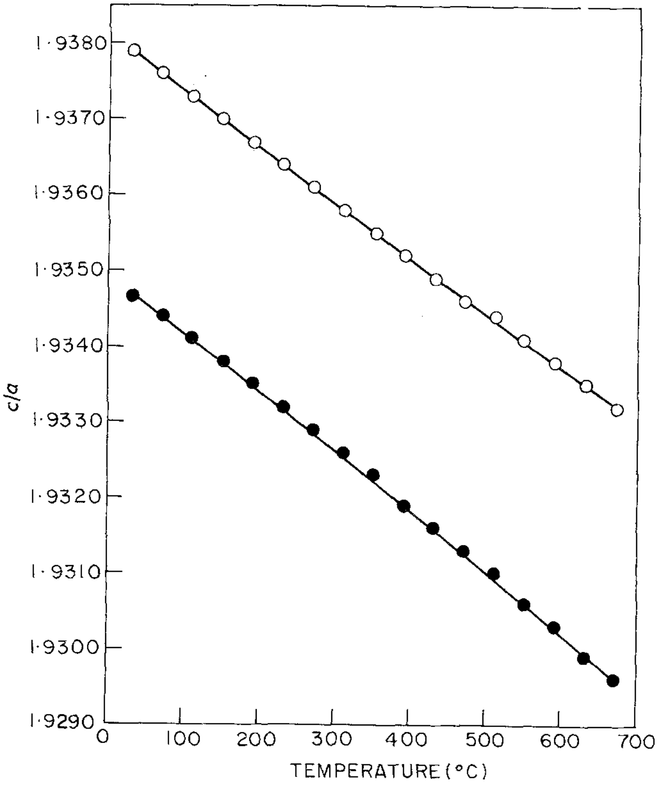

Figure 5 Variation of c/a with temperature. ○, $ZnSiAs_{1.5}P_{0.5}$; ●, $ZnSiAs_{0.5}P_{1.5}$.

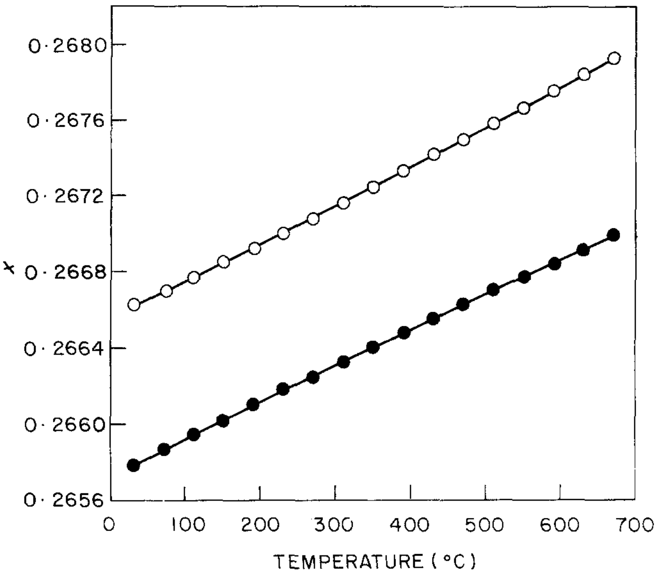

Figure 6 Variation of calculated x parameter with temperature. ○, $ZnSiAs_{1.5}P_{0.5}$; ●, $ZnSiAs_{0.5}P_{1.5}$.

Here $(\overline{A-C})$ and $(\overline{B-C})$ are the bond distances of the II–V and IV–V bonds, respectively, and the parameter x denotes the location of the C-atom relative to the A and B atoms by the following atomic arrangements in the ABC_2 chalcopyrite unit cell,

$$A\text{: }(0\,0\,0),\quad (0\,\tfrac{1}{2}\,\tfrac{1}{4});\quad \mathrm{b\,c}$$

$$B\text{: }(0\,0\,\tfrac{1}{2}),\quad (0\,\tfrac{1}{2}\,\tfrac{3}{4});\quad \mathrm{b\,c}$$

$$C\text{: }(x\,\tfrac{1}{4}\,\tfrac{1}{8}),\quad (\bar{x}\,\tfrac{3}{4}\,\tfrac{1}{8}),\quad (\tfrac{3}{4}\,x\,\tfrac{7}{8}),\quad (\tfrac{1}{4}\,\bar{x}\,\tfrac{7}{8});\quad \mathrm{b\,c},$$

with $x \simeq 0.25$ and where b c implies addition of the preceding co-ordinates to the $(\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2})$, body centred position [20].

Fig. 6 shows the calculated x parameters for the present results. The x parameters all increase with temperature as expected for increasing distortion from the cubic value of 0.25, so the group V atoms move relatively much closer to the group IV atoms. The thermal expansion of the bonds given by Equations 10 and 11 are shown in Fig. 7, and indicate the reason for the increase in the tetragonal distortion with temperature. The more ionic II–V bonds have higher thermal expansion coefficients than the covalent IV–V bonds, so that the group V anions move relatively nearer the group IV cations on heating, thus increasing the distortion. The calculated thermal expansion coefficients are listed in Table IV along with known values for other materials [21–24]. Covalent silicon has a small expansion coefficient. The values for the slightly ionic gallium phosphide are larger. These may be compared with the Si–P and/or As coefficients. The Zn–P and/or As coefficients resemble the more ionic ZnSe values.

The anisotropy of the linear coefficients of thermal expansion ($\alpha_\perp > \alpha_\parallel$) of $ZnSiAs_{1.5}P_{0.5}$ and $ZnSiAs_{0.5}P_{1.5}$ can be correlated with their structure. As shown in Fig. 4, in the chalcopyrite ABC_2

TABLE IV Average linear thermal expansion coefficients and the calculated bond expansion coefficients

Parameter	$ZnSiAs_2$*	$ZnSiAs_{1.5}P_{0.5}$†	$ZnSiAs_{0.5}P_{1.5}$†	$ZnSiP_2$‡	ZnSe§	GaP§	Si**
$\alpha_\perp$ $(10^{-6}\,°C^{-1})$	–	7.33	7.17	7.9	8.01	4.65	2.95
$\alpha_\parallel$ $(10^{-6}\,°C^{-1})$	–	3.60	3.08	3.2	–	–	–
α_L $(10^{-6}\,°C^{-1})$	5.8	6.10	5.80	6.3	8.01	4.65	2.95
$\frac{1}{(c/a)_0}\frac{d(c/a)}{dT}$ $(10^{-6}\,°C^{-1})$	–	−3.79	−4.04	−4.8	–	–	–
$\frac{1}{(x)_0}\frac{dx}{dT}$ $(10^{-6}\,°C^{-1})$	–	7.11	7.62	9.2	–	–	–
α_{A-C} $(10^{-6}\,°C^{-1})$	–	8.84	8.78	9.8	8.01	4.65	2.95
α_{B-C} $(10^{-6}\,°C^{-1})$	–	3.60	3.10	2.8	–	–	–

*[21]; †Present study; ‡[17]; §[22, 23]; **[24].

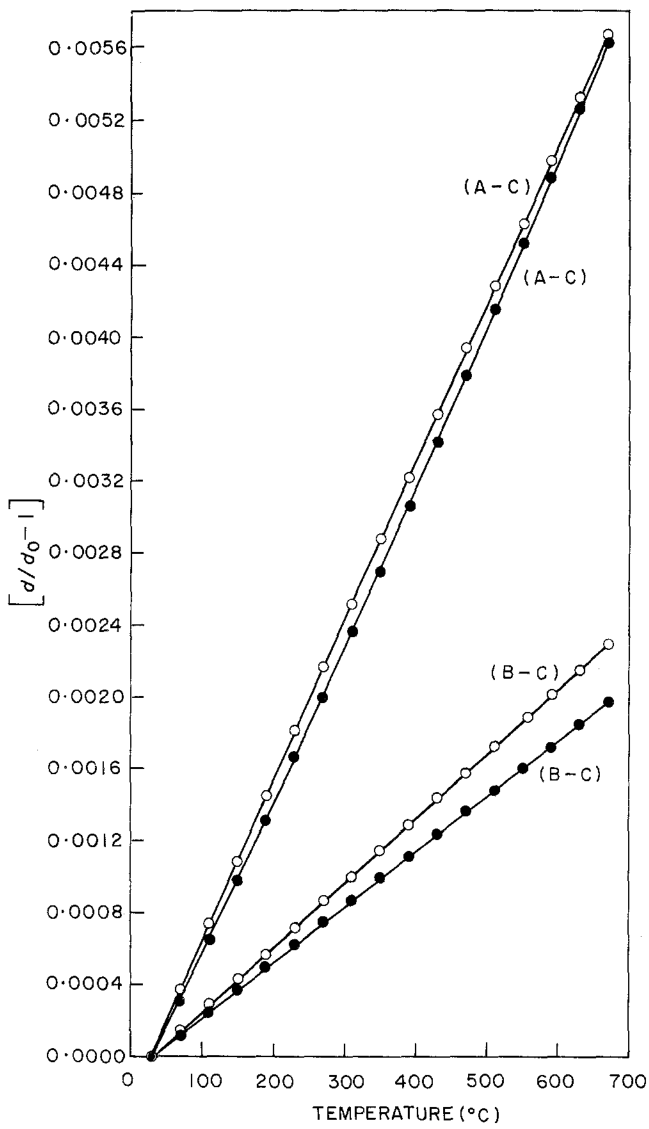

Figure 7 Variation of thermal expansion of *A–C* and *B–C* bonds with temperature. ○, $ZnSiAs_{1.5}P_{0.5}$; ●, $ZnSiAs_{0.5}P_{1.5}$.

each *A* atom has two *A* and two *B* atoms as nearest cation neighbours in the planes including the *c*-axis but in the planes normal to the *c*-axis, each *A* atom is surrounded by four *B* atoms and *vice versa*. Thus, there is a difference in interactions parallel and normal to the *c*-axis. As demonstrated by Abrahams and Bernstein [25], this difference in interactions can be approximated by the difference between *B–C* and *A–C* interactions, respectively. Therefore, the linear coefficient of expansion along the *c*-axis ($\alpha_{\parallel}$) will depend largely on the strength of the *B–C* bonds while the coefficient of expansion in a perpendicular direction ($\alpha_{\perp}$) will depend on the *A–C* bonds. From Fig. 7, it is evident that the *B–C* bonds are stiffer than the *A–C* bonds in both cases, and therefore the coefficients of thermal expansion along the *c*-direction are smaller than those along the perpendicular direction ($\alpha_{\parallel} < \alpha_{\perp}$).

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