Thermal Expansion of Zinc Sulfide: 300–1300 K

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Abstract

The thermal expansion of hot-pressed cubic polycrystalline zinc sulfide (Eastman Kodak: Irtran 2) was measured in a silica pushrod dilatometer. The coefficient of linear thermal expansion varies almost linearly from $6 \cdot 9 \times 10^{-6} \, \mathrm{K}^{-1}$ at 300 K to $10 \cdot 3 \times 10^{-6} \, \mathrm{K}^{-1}$ at 1200 K. The temperature variation of the Debye–Waller factor is calculated and compared with the experimental values found by Moss *et al.* (1980).

1. Introduction

The elements with the diamond structure, such as silicon and germanium, and the compounds of zincblende or sphalerite structure have attracted much attention for their band structure and lattice dynamics. Most display a negative thermal expansion coefficient at low temperatures due to the influence of a low-lying transverse acoustic (TA) mode, corresponding to the elastic constant $C' = \frac{1}{2}(C_{11} - C_{12})$, which softens under pressure. This is particularly so for the more ionically bonded members such as CuCl (a I–VII compound), HgTe and CdTe (II–VI) (see e.g. the review by Barron *et al.* 1980).

At higher temperatures the influence of longitudinal acoustic (LA) and transverse optic (TO) modes gives rise to a more normal positive expansion coefficient. A measure of this behaviour is given by the Grüneisen anharmonicity parameter $\gamma = \beta B_\mathrm{s} V / C_\mathrm{p}$, where B_s is the adiabatic bulk modulus, C_p/V is the heat capacity at constant pressure per unit volume, and β is the volume coefficient of expansion (which equals three times the linear expansion coefficient α for these cubic materials). Comparison of high temperature data on α for Ge and Si (see e.g. Slack and Bartram 1975) shows that α (and hence γ) increases quite rapidly for Ge above 500 K while it is much more constant for Si, despite the fact that Si has the higher Debye characteristic temperature Θ_D. This presumably reflects the different role of optic modes for which γ_i is larger (say 2) than it is for the acoustic modes.

For ZnS of sphalerite structure there are extensive data from 2 to 80 K (Smith and White 1975) and from 60 to 310 K (Browder and Ballard 1969, 1977) which show that $\gamma(T)$ follows the same pattern as other crystals which have this structure: near $T = 0$, γ has a limiting value of about $-0 \cdot 1$, then falls to $\gamma_\mathrm{min} \approx -0 \cdot 4$ at 25 K (cf. $\Theta_\mathrm{D} = 339$ K) and rises to $\approx 0 \cdot 7$ at room temperature (see also Yates *et al.* 1971).

Above room temperature there have been no published data other than recent measurements of lattice parameters at 200 K intervals by Moss *et al.* (1980). They

determined the intensities of neutron diffraction Bragg peaks up to ≈ 1200 K and interpreted them in terms of different models for the anharmonicity. Their model gave values for γ which are clearly at variance with those expected from thermal data at normal temperatures and the neutron dispersion curves of Vagelatos *et al.* (1974). These indicate that the optic modes have frequencies of 8–10 THz (corresponding to $\Theta_D \sim 400$–500 K) with mode γ_i values lying near $+2 \cdot 0$ (see Soma 1980).

We have, therefore, measured the linear expansion of cubic ZnS to ≈ 1300 K and calculated approximate values for the thermal averages $\gamma(T)$. Further, by relating the neutron intensities of Moss *et al.* (1980) to a *different* set of temperatures (by comparing our measured length changes and their measured lattice parameter changes), we are able to show that their observed temperature variation of the Debye–Waller factor is consistent with our value of $\gamma(T) \sim 1$.
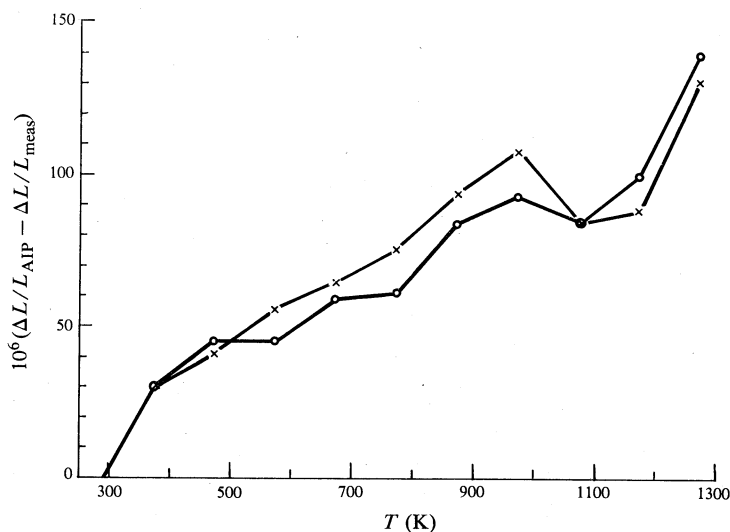

Fig. 1. Calibration curves, showing the difference between the AIP handbook (Gray 1972) and measured values of $\Delta L/L$ for tantalum for two separate runs.

2. Experiment

Measurements of thermal expansion were made by means of a conventional silica tube/single pushrod dilatometer. The relative length changes were determined with errors of less than $0 \cdot 2 \%$ by a linear variable differential transformer attached by a water-cooled clamp to the end of the tube. Temperatures were measured with a maximum inaccuracy of ± 2 K with a calibrated chromel–alumel thermocouple ($1 \cdot 5$ mm diameter sheath) and electronic gauge. The expansion of the active part of the silica tube was calculated from values given in the AIP handbook (Gray 1972) and amounted to $\approx 10 \%$ correction for the samples reported here.

To verify the accuracy and repeatability of the instrument, two measurement runs were made on a sample of tantalum (Johnson Matthey, $99 \cdot 9 \%$ pure) about the same size as the ZnS sample. Tantalum has an expansivity rather similar to that of ZnS so that deviations from reference data for tantalum can be applied directly to correct the ZnS results. Deviations from the AIP values for the relative length

changes of tantalum are shown for the two runs in Fig. 1 and amount to 2% of $\Delta L/L$ at 1300 K. The anomalies in the curves near 1100 K probably reflect inhomogeneities in the temperature distribution of the rod and tube. (The measuring instruments were proven to be unaffected by the furnace power supply.) The measurements were repeatable within 0·2% in $\Delta L/L$.

The ZnS sample was a cylinder (5 mm long × 13 mm diameter) diamond drilled from a slab of hot-pressed polycrystalline (cubic) Irtran 2 (Eastman Kodak) of density 4073 kg m^{-3} at 20°C. It was measured twice under the same conditions as the tantalum, namely shielded by nitrogen gas, following the same heating program. Measurements were made at intervals of 100 K up to 1300 K after the sample heating rate had slowed to less than 0·1 K min^{-1}. The ZnS was not attacked by the silica supports, contrary to the observations of Moss et al. (1980).
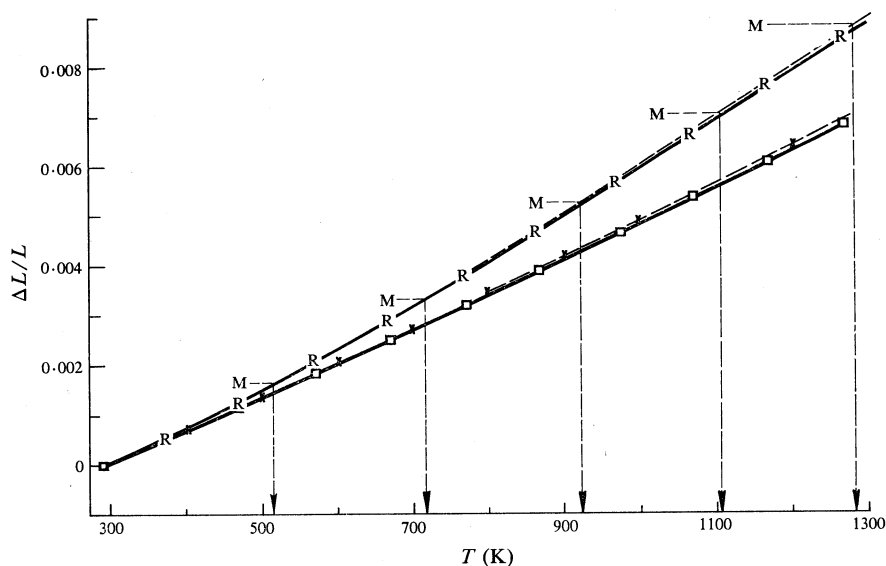

Fig. 2. Relative length change as a function of temperature: squares, the raw data for tantalum; crosses, the AIP values (Gray 1972) for tantalum; R, the raw data for ZnS; M, the ZnS neutron experiment of Moss et al. (1980). The dashed curve gives the corrected values from Fig. 1.

The results are shown in Fig. 2. The AIP values (Gray 1972) for tantalum (dashed curve) lie slightly above the present raw data. The dashed curve for ZnS was obtained by correcting the raw data for the deviations found in Fig. 1, so they should be as accurate as the AIP tantalum measurements, $\approx \pm 2\%$. The lattice parameter measurements of Moss et al. fall well outside this limit, suggesting a systematic error in their temperature determinations.

The linear thermal expansion coefficient α was calculated from the individual differences of successive (corrected) data points and is shown in Fig. 3 to vary almost linearly from $6·9 \times 10^{-6}$ K^{-1} at 300 K to $10·3 \times 10^{-6}$ K^{-1} at 1200 K. The smoothed values are given in Table 1. At the low end there is good agreement with the available data. (The measurement from Smith and White (1975) has been corrected for the presently accepted value for copper, their reference material.)
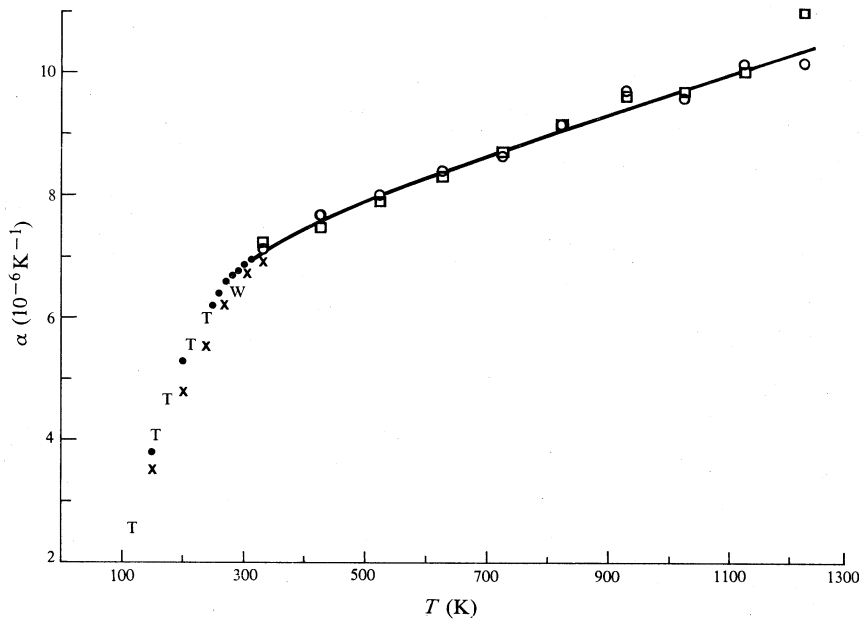
Fig. 3. Linear thermal expansion coefficient α for ZnS as a function of temperature: T, the TPRC (1977) recommended value; W, Smith and White (1975); crosses, Browder and Ballard (1977); solid circles, Browder and Ballard (1969); open circles and squares, present experiment.

Table 1.   Some thermal properties of ZnS

T (K)	$\Delta L/L$ (10^{-3})	α $(10^{-6}\ K^{-1})$	B_s (GPa)	C_p $(J\ mol^{-1}\ K^{-1})$	γ
100		1·6	73·3		$\approx 0\cdot4$
200		4·8	72·5		$\approx 0\cdot6$
293	0·00	6·8	71·9		$\approx 0\cdot7$
300		6·9	71·9		0·71
400	0·76	7·5	71·1	49·8	0·77
500	1·53	7·9	70·4	50·0	0·80
600	2·36	8·3	69·7	50·1	0·83
700	3·20	8·6	68·9	50·3	0·85
800	4·09	9·0	68·2	50·5	0·88
900	5·00	9·3	67·5	50·6	0·90
1000	5·98	9·6	66·7	50·8	0·92
1100	6·94	10·0	66·0	51·1	0·94
1200	7·97	10·3	65·3	51·3	0·96

3. Discussion

Having measured the linear expansion coefficient we can now calculate the thermal average $\gamma(T)$ if we calculate C_v using $\Theta_D(\infty) = 380$ K (see Yates *et al.* 1971), and extrapolate B_s from Einspruch and Manning (1963) and Nikanorov *et al.* (1978) (quoted in Moss *et al.* 1980). For example, at 1200 K, we have

$$\alpha = 10\cdot3 \times 10^{-6}\ K^{-1}\ \text{(measured)},$$

$$\beta = 3\alpha = 30\cdot9 \times 10^{-6}\ K^{-1},$$

$$V = V_0(1 + 3\Delta L/L) = 24 \cdot 4 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \text{ (Yates } et~al.\text{)},$$

$$B_s = \tfrac{1}{3}(C_{11} + 2C_{12}) = 6 \cdot 5 \times 10^{10} \text{ Pa (Moss } et~al.\text{, Table 2)},$$

$$C_v = (3\,R \text{ atom}^{-1}) \times (2 \text{ atom mol}^{-1}) = 49 \cdot 5 \text{ J mol}^{-1} \text{ K}^{-1} \text{ (since } T \gg \Theta_D),$$

$$C_p = C_v + \beta^2 B_s TV = 49 \cdot 5 + 1 \cdot 8 = 51 \cdot 3 \text{ J mol}^{-1} \text{ K}^{-1},$$

$$\gamma = \beta B_s V/C_p = 0 \cdot 96.$$

We see from Table 1 that the Grüneisen parameter γ behaves normally, increasing steadily to a value of about $1 \cdot 0$ at 1200 K, contrary to the conclusions of Moss $et~al.$ If we assume that the values of $\Delta a/a_0$ calculated from their measurements correspond to the present $\Delta L/L$ (Fig. 2), we find a new set of temperatures to which we can relate the intensity measurements (see arrows in Fig. 2, which generate the values in Table 2). The variation of the Debye–Waller factor with temperature can be calculated from our results.

Table 2. Recalculation of B using expansion measurements to identify temperature

T (K)		B (Å^2)	
Moss $et~al.$	Expansion	Moss $et~al.$	Calculated
285	285	$0 \cdot 759 \pm 0 \cdot 004$	$0 \cdot 73$
473	520	$1 \cdot 250 \pm 0 \cdot 004$	$1 \cdot 35$
676	720	$1 \cdot 86 \pm 0 \cdot 02$	$1 \cdot 89$
871	930	$2 \cdot 43 \pm 0 \cdot 02$	$2 \cdot 47$
1070	1120	$3 \cdot 07 \pm 0 \cdot 04$	$3 \cdot 03$
1173	1280	$3 \cdot 54 \pm 0 \cdot 04$	$3 \cdot 51$

In the quasiharmonic approximation, Willis and Pryor (1975) give (in the notation of this paper)

$$B = B^h(1 + 6\alpha\gamma T),$$

where B^h is the harmonic temperature factor which can be evaluated from our data at room temperature. We take $B_{285} = 0 \cdot 73$ Å^2, being the average of $B_{Zn} = 0 \cdot 74$ and $B_S = 0 \cdot 72$ Å^2 obtained by Hewat (1972) from shell model calculations and quoted by Moss $et~al.$ Then we solve for B^h at 285 K and allow B^h to vary as T for temperatures above Θ_D. We have the temperature dependence of the B factor explicitly as

$$B(T) = 0 \cdot 724\,T(1 + 6\alpha\gamma T)/285.$$

Using the temperatures given above from the thermal expansion measurements and appropriate values of α and γ interpolated from Table 1 we find the results given in Table 2.

4. Conclusions

We present data on the thermal expansion of ZnS which enable us to determine the temperature of a neutron diffraction sample from its lattice parameter. The temperature variation of the Debye–Waller factor is then found to be in good agreement with the quasiharmonic approximation, contrary to the conclusions of Moss $et~al.$ (1980).

References

Barron, T. H. K., Collins, J. G., and White, G. K. (1980). *Adv. Phys.* **29**, 609.

Browder, J. S., and Ballard, S. S. (1969). *Appl. Opt.* **8**, 793.

Browder, J. S., and Ballard, S. S. (1977). *Appl. Opt.* **16**, 3214.

Einspruch, N. G., and Manning, R. J. (1963). *J. Acoust. Soc. Am.* **35**, 215.

Gray, D. E. (Ed.) (1972). 'AIP Handbook' (3rd edn), Tables 4f–3 (McGraw–Hill: New York).

Hewat, A. W. (1972). *J. Phys.* C **5**, 1309.

Moss, B., McMullan, R. K., and Koetzle, T. F. (1980). *J. Chem. Phys.* **73**, 495.

Nikanorov, S. P., Burenkov, Yu. A., and Kardashev, B. K. (1978). *Acta Crystallogr.* A **34**, S285.

Slack, G. A., and Bartram, S. F. (1975). *J. Appl. Phys.* **46**, 87.

Smith, T. F., and White, G. K. (1975). *J. Phys.* C **8**, 2031.

Soma, T. (1980). *Solid State Commun.* **34**, 927.

Thermophysical Properties Research Centre (1977). 'Thermophysical Properties of Matter', Vol. 13 (Eds Y. S. Touloukian and C. Y. Ho) (Plenum: New York).

Vagelatos, N., Wene, D., and King, J. S. (1974). *J. Chem. Phys.* **60**, 3613.

Willis, B. T. M., and Pryor, A. W. (1975). 'Thermal Vibrations in Crystallography', p. 143 (Cambridge Univ. Press).

Yates, B., Cooper, R. F., and Kreitman, M. M. (1971). *Phys. Rev.* B **4**, 1314.