

## Thermal Expansion of Willemite, $\text{Zn}_2\text{SiO}_4$

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### Abstract

The linear thermal expansion of a natural crystal of willemite ( $\text{Zn}_2\text{SiO}_4$ ) has been measured parallel and normal to the hexagonal axis from 2 to 1200 K. The linear coefficient  $\alpha_{\parallel}$  is negative below 150 K and  $\alpha_{\perp}$  is negative below room temperature. The Grüneisen parameter  $\gamma$  is about 0.5 at 1000 K and falls to less than  $-1$  below 60 K.

### 1. Introduction

For nearly thirty years it has been known that tetrahedrally-bonded crystals of diamond or zincblende structure display a negative thermal expansion coefficient  $\alpha$  at low temperatures (see the review by Barron *et al.* 1980). It is also apparent in crystals with the wurtzite structure such as ZnO. Barron (1957) and Blackman (1958) have each shown that it is possible to understand the negative coefficient in terms of low-lying transverse acoustic (TA) modes of vibration which soften under pressure. Such modes are favoured by the open structure of the zincblende and wurtzite lattice. In the former it is the TA modes associated with the elastic stiffness  $C' = \frac{1}{2}(C_{11} - C_{12})$ , propagating in a (110) direction, that are chiefly responsible for the negative coefficient.

Slack and Huseby (1982) have pointed out that compounds of the phenacite structure also can be thought of as composed of tetrahedral groups with 'open channels running parallel to the  $c$ -axis'. The limited experimental data indicate that  $\alpha$  is relatively small at high temperature for such phenacite-type compounds as  $\text{Zn}_2\text{SiO}_4$ ,  $\text{Zn}_2\text{GeO}_4$ ,  $\text{Si}_3\text{N}_3$ ,  $\text{CdAl}_2\text{O}_4$  etc., i.e. small relative to silicates of olivine structure such as  $\text{Mg}_2\text{SiO}_4$  and many ceramic oxides. Slack (personal communication 1981) suggested that  $\text{Zn}_2\text{SiO}_4$  would probably show negative values of  $\alpha$  below 150 K or thereabouts. We have obtained and measured a natural crystal of  $\text{Zn}_2\text{SiO}_4$  (willemite) kindly given to us by the Smithsonian Institute of Washington. Complementary data on the heat capacity at constant pressure  $C_p$  are largely limited to the range 50-300 K, and the adiabatic bulk modulus  $B_s$  is an estimate by Slack and Huseby, so that derived values of the Grüneisen parameter  $\gamma = \beta V B_s / C_p$  (where  $\beta$  is the volume coefficient of expansion) are rather uncertain. However,  $\gamma(T)$  does show much the same form for willemite as observed before for zincblende and wurtzite structure crystals (see Barron *et al.* 1980).

## 2. Measurements

The crystal donated to us by the Smithsonian Institute (number C2834-1) was a parallelepiped, approximately  $16\text{ mm} \times 10\text{ mm} \times 5\text{ mm}$  in volume and was whitish to very pale brown in colour. We determined by X-ray back reflection that the  $c$ -axis was parallel within  $1^\circ$  to the longest dimension. Faces were ground and lapped so that it could be mounted in our three-terminal capacitance dilatometer (White and Collins 1972) for measurements below 150 K and 273–93 K, and in a push-rod dilatometer (Adamel-Lhomargy) for measurements above room temperature. Because of the small size of the sample, particularly normal to the  $c$ -axis, errors in  $\alpha$  values could be  $0.2 \times 10^{-8}\text{ K}^{-1}$  at liquid helium temperatures, and reach  $10 \times 10^{-8}\text{ K}^{-1}$  above 50 K.

A small chip of willemite from the same source was examined in a scanning electron microscope and found to contain a significant amount ( $>2\%$ ) of magnetic impurities, namely Fe and Mn.

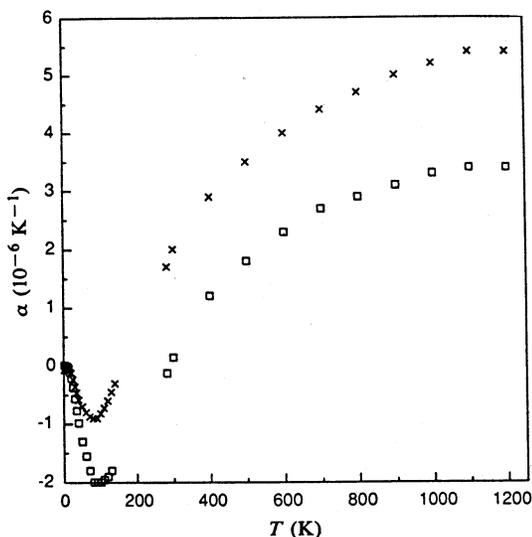


Fig. 1. Linear coefficients of thermal expansion for willemite, parallel (crosses) and perpendicular (squares) to the  $c$ -axis.

## 3. Results

The experimentally determined values of  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  in Fig. 1 are smoothed by differentiating the length curves  $l(T)$  at the given temperatures or by interpolating between individual measurements of  $\alpha$ . Included in Table 1 are values of the volume expansivity  $\beta = \alpha_{\parallel} + 2\alpha_{\perp}$ . The only previous data which we have for comparison are isolated X-ray lattice measurements of Wen *et al.* (1964) from which we have

$$\alpha_{\parallel} \text{ (average 293–555 K)} = 4.5 \times 10^{-6}\text{ K}^{-1},$$

$$\alpha_{\parallel} \text{ (average 555–936 K)} = 4.5 \times 10^{-6}\text{ K}^{-1},$$

$$\alpha_{\perp} \text{ (average 293–555 K)} = 3.8 \times 10^{-6}\text{ K}^{-1},$$

$$\alpha_{\perp} \text{ (average 555–936 K)} = 3.0 \times 10^{-6}\text{ K}^{-1}.$$

**Table 1.** Thermal expansivity of willemite and values of  $\gamma = \beta V B_s / C_p$  assuming  $B_s = 155$  GPa

Values of  $C_p$  in parentheses are extrapolated

$T$ (K)	$\alpha_{  }$ ( $10^{-8} \text{ K}^{-1}$ )	$\alpha_1$ ( $10^{-8} \text{ K}^{-1}$ )	$\beta$ ( $10^{-8} \text{ K}^{-1}$ )	$C_p$ (Jmol K $^{-1}$ )	$\gamma$
2	-6.7	1.4	-3.9	—	—
4	-3.8	1.0	-1.8	—	—
6	-1.5	-0.2	-1.9	—	—
8	-0.3	-1.4	-3.1	—	—
10	-0.1	-3.0	-6.2	—	—
12	-0.9	-5.1	-11.1	—	—
15	-3.8	-10.0	-23.8	—	—
20	-11.4	-21.0	-53.4	—	—
25	-23	-37	-97	—	—
30	-35.5	-56	-148	—	—
35	-46	-77	-200	(7.4)	-2.1
40	-58	-98	-254	(10.8)	-1.8
50	-70	-130	-330	19.4	-1.4
60	-80	-155	-390	27.2	-1.15
70	-87	-180	-447	34.1	-1.0
80	-90	-200	-490	41.0	-0.95
90	-90	-200	-490	46.7	-0.85
100	-82	-200	-480	52	-0.75
110	-72	-195	-460	58	-0.65
120	-60	-190	-440	63	-0.55
130	-45	-180	-405	-68	-0.48
140	-30	—	—	—	—
283	170	-12	145	120	0.10
300	200	15	230	124	0.16
400	290	120	530	(144)	0.30
500	350	180	710	(154)	0.37
600	400	230	860	(160)	0.43
700	440	270	980	(164)	0.48
800	470	290	1050	(166)	0.51
900	500	310	1120	(168)	0.54
1000	520	330	1180	(169)	0.56
1100	540	340	1220	(169)	0.57
1200	540	340	1220	(170)	0.58

Shelby (1981) also reported a room temperature value for the expansion of a polycrystalline sample to be  $2.8 \times 10^{-6} \text{ K}^{-1}$  which is comparable with present values for  $\beta$ . Finally Geller and Insley (1932) measured the length change in a devitrified polycrystalline specimen above  $25^\circ\text{C}$  which gives  $\alpha \approx 0.8 \times 10^{-6} \text{ K}^{-1}$  up to  $100^\circ\text{C}$  and  $1.2 \times 10^{-6} \text{ K}^{-1}$  to  $200^\circ\text{C}$ . Clearly there are discrepancies among these data but within their limits of error they do not conflict with present results.

The behaviour of the expansivity below 10 K is not revealed clearly by Fig. 1 which indicates that  $\alpha$  values approach zero as we expect in a pure material. In fact the variations of  $\alpha(T)$  appear to be more complicated probably due to the presence of impurities. Experimental errors in  $\alpha$  are relatively large ( $\sim 0.3 \times 10^{-8} \text{ K}^{-1}$ ), but data do indicate that  $\alpha_{||}$  becomes increasingly negative as  $T$  falls below 8 K, while  $\alpha_1$  becomes positive below 5 K, and the volume coefficient  $\beta$  is not approaching zero in the normal fashion.

Previous experience with natural zincblende crystals containing iron impurities (Sheard *et al.* 1977) shows the likelihood of Schottky contributions from magnetic impurities which can dominate the thermal properties at liquid helium temperatures, at concentrations of less than 1%. The iron or manganese impurities are likely to be responsible for the behaviour of  $\alpha(T)$  at these low temperatures, where the normal contribution from lattice vibrations is very small.

#### 4. Grüneisen $\gamma(T)$

For calculating  $\gamma$ , we use the values of  $C_p$  determined by Todd (1951) from 53 to 298 K. From his data we also calculated effective Debye temperatures  $\theta_D(T)$  which vary smoothly from 435 K at 53 K up to 815 K at 298 K. The values of  $C_p$  in parentheses in Table 1 were obtained by assuming  $\theta_D \approx 430$  K from 30 to 50 K and  $\theta_D \approx 800$  K above room temperature. We cannot extrapolate  $\theta_D(T)$  and  $C_p$  below 30 or 40 K as  $\theta_D$  presumably changes rapidly in this range. Values reported by Egorov and Smirnova (1965) for  $C_p$  in the range above 600 K agree within a few per cent with these extrapolated values. For the adiabatic bulk modulus  $B_s$ , we are on more shaky ground as there do not appear to be experimental values for compressibility or elastic moduli. Therefore we use  $B_s = 155$  GPa deduced by Slack and Huseby (1982) from a model of the  $\text{ZnO}_4/\text{SiO}_4$  arrangement. The uncertainty in  $B_s$  is so large that we have not attempted to correct either  $B_s$  or  $V = 52.5 \text{ cm}^3$  for changes in temperature.

Note that the variation of  $\gamma$  with temperature above 50 K is very similar to that shown by many of the zincblende structure materials. The magnitude of  $\gamma = 0.5$  in the vicinity of  $\theta_D$  is a little smaller than the value of  $\sim 0.7$  for Ge, ZnS, GaAs and ZnO (hexagonal), but comparable with that of CdTe, HgTe and CuCl.

We cannot estimate  $\gamma$  below 30 or 40 K without knowledge of the heat capacity. It appears that  $\beta$  varies roughly as  $T^3$  from 30 down to 10 K, i.e.  $\beta \sim -6 \times 10^{-11} T^3$ . If we assumed that the limiting value of the Debye temperature is  $\theta_0 \approx 700$  K, as estimated by Slack and Huseby (1982), it would lead to  $\gamma$  decreasing to a value of  $\sim -10$ . Below 10 K, we consider the influence of impurities is likely to affect the expansivity.

#### 5. Discussion and Conclusions

The present measurements of linear expansivity in the principal crystal directions confirm that the coefficients  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  are both negative at low temperature and follow a pattern not unlike that of other simpler tetrahedrally bonded crystals of zincblende and wurtzite structure. The absolute values for the thermal Grüneisen parameter  $\gamma$  are in some doubt as we lack an experimental value of the bulk modulus, but  $\gamma(T)$  changes with temperature in much the same way as for the zincblende compounds. This is in contrast with a silicate of olivine structure, namely forsterite ( $\text{Mg}_2\text{SiO}_4$ ), for which expansivity is always positive and  $\gamma$  lies in the range 1.1 to 1.3 from low temperatures up to over 1200 K (White *et al.* 1985).

It would be interesting to have data on heat capacity and expansivity of a high purity sample of  $\text{Zn}_2\text{SiO}_4$  at low temperatures and of elastic moduli over the whole temperature range.

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