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Thermal Expansion of InBi at Low Temperatures

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Abstract

Linear thermal expansions from 2 to 80 K are reported for a single crystal of tetragonal InBi. In the more compressible direction, parallel to the tetrad axis, $\alpha_{||}$ is negative except between 6 and 10 K. In the harder basal plane, α_{\perp} is positive. This unusual behaviour confirms earlier observations between 100 and 250 K. The volume coefficient is positive at all temperatures and leads to values of $\gamma \sim 1$ for the Grüneisen parameter above 4 K.

1. Introduction

InBi is a semi-metal crystallising in a tetragonal B10 structure with layers of In and Bi atoms arranged in planes normal to the *c* (tetragonal) axis. Indium layers are separated by corrugated double layers of Bi atoms between which the bonding is presumed to be weak and therefore responsible for easy cleavage (Jorgensen and Clark 1980). The elastic moduli measured at room temperature by Akgöz *et al.* (1973) show a high degree of anisotropy, the linear compressibility in the *c*-direction ($\chi_{||}$) being ten times larger than that in the basal plane (χ_{\perp}). Of the principal elastic stiffness constants, c_{ij} , the weakest is $c' = (c_{11} - c_{12})/2 = 7$ GPa (0.070 Mbar) for a shear wave propagating in a [110] direction with [110] polarisation. Fritz (1976) measured the pressure dependence of the moduli up to 2.4 GPa and found anomalous behaviour. Modulus *c'* softens under pressure with dc'/dP = -0.36. Another shear modulus, c_{66} , stiffens under pressures up to about 1.2 GPa and then softens slightly, and the quasi-shear mode at 45° to the [100] and [001] directions softens up to about 1.6 GPa and then hardens.

The present interest was aroused by the expansion measurements of Takano and Sato (1973; also T. J. White *et al.* 1975) at and below room temperature which showed that α_{\perp} was relatively large and positive in the *hard* direction and α_{\parallel} was large and negative in the *soft* direction. This is very different to the usual behaviour of highly anisotropic crystals, whether layer-like such as graphite, chain-like such as tellurium, or metallic such as zinc and cadmium. For these the linear expansion is positive in the soft direction and small or negative in the hard direction (see the review by Barron *et al.* 1980).

We have determined α_{\parallel} and α_{\perp} down to 2 K, and with data for the heat capacity at constant pressure C_p (Martin 1981), we have calculated values for

the principal Grüneisen functions

$$\gamma_{\perp} = [(c_{11} + c_{12})\alpha_{\perp} + c_{13} \alpha_{\parallel}]V/C_{p}, \qquad (1)$$

$$\gamma_{||} = [c_{33} \alpha_{||} + 2c_{13} \alpha_{\perp}] V/C_p, \qquad (2)$$

where V is the molar volume. The reciprocal relations are

$$\alpha_{\perp} = [(s_{11} + s_{12})\gamma_{\perp} + s_{13}\gamma_{\parallel}]C/V, \qquad (3)$$

$$\alpha_{||} = [(s_{33} \gamma_{||} + 2s_{13} \gamma_{\perp}]C/V, \qquad (4)$$

where the s_{ij} are elastic compliances. The γ_{\perp} and γ_{\parallel} are positive. The negative values of α_{\parallel} arise from a cross contraction controlled by the compliance s_{13} , which is large and negative. Below 10 K both γ_{\perp} and γ_{\parallel} show strong temperature dependence and the variations observed in the expansion coefficients are the result of a delicate balance between the relative magnitude of the γ values coupled by the cross compliance s_{13} .



Fig. 1. Experimental values of α_{\perp} (open circles) and α_{\parallel} (solid circles) for InBi (note the scale differences).

2. Experiment

Thermal expansions were measured on a single crystal 'cube' about $6 \times 6 \times 7 \text{ mm}^3$ in a three-terminal capacitance dilatometer (White and Collins 1972) from $1 \cdot 7$ to 90 K and at room temperature. The sample was spark cut at Sandia Laboratories, New Mexico, from the same material used by Fritz (1976) and by Schirber and Van Dyke (1977). It was ground and lapped to have flat parallel faces and mounted in a copper cell between cylindrical copper end-pieces (spring-loaded) to make up our usual 50 mm sample length.

At low temperatures the resolution of length change was ~1 pm (0.01 Å), but overall inaccuracy in determining the linear coefficients α was much larger due to the small length of the sample. Systematic errors were checked by doing a calibration run with a 6 mm cube of silicon. We believe that errors in α at helium temperatures do not exceed $0.2 \times 10^{-8} \text{ K}^{-1}$ and at higher temperatures are less than 0.5%.

The 'bump' in the plot of $\alpha_{\parallel}(T)$ (Fig. 1) raised doubts as to whether there could be significant amounts of a superconducting phase present, i.e. In_2Bi or In_5Bi_3 (see Schirber and Van Dyke 1977). Therefore susceptibility measurements on the sample were made in the CSIRO laboratory by Drs J. B. Dunlop and R. K. Day in an ac balance from 2 to 10 K. A small change in signal of ~2%

| Values in parentheses from 100 to 250 K are graphical data of White et al. (1975) | | | | | | | |
|---|---|---|--|------------------------------|--------------|--------------|--------------|
| Т (К) | α_{\perp} (10 ⁻⁸ K ⁻¹) | $\alpha_{ }$ (10 ⁻⁸ K ⁻¹) | β (10 ⁻⁸ K ⁻¹) | C _p (mJ/mol K) | У | γ⊥ | Y |
| 2 | 2 · 1±0 · 2 | $-4 \cdot 7 \pm 0 \cdot 2$ | -0.5 ± 0.6 | 14.5 | | | |
| 3 | 4 • 5 | -7.3 | 1.7 | 55 | 0.38 | $1 \cdot 07$ | 0.23 |
| 4 | 8.7 | $-8 \cdot 0$ | $9 \cdot 4$ | 162 | 0.72 | 1.13 | 0.62 |
| 5 | 17.8 | -5.7 | 29.9 | 397 | 0.93 | 1.25 | 0.85 |
| 6 | 34 • 2 | $-1 \cdot 6$ | 66.8 | 770 | 1.07 | 1.38 | $1 \cdot 00$ |
| 8 | 95 | 6.0 | 184 | 1990 | $1 \cdot 15$ | 1.55 | $1 \cdot 14$ |
| 10 | 190 | $-4 \cdot 3$ | 376 | 3780 | 1.23 | 1.58 | $1 \cdot 14$ |
| 12 | 306 | -41 | 571 | 5750 | 1.23 | 1.61 | $1 \cdot 14$ |
| 14 | 438 | -98 | 778 | 7802 | 1.23 | $1 \cdot 64$ | $1 \cdot 14$ |
| 15 | 501 | -133 | 869 | 8820 | 1.22 | 1.63 | 1.12 |
| 16 | 570 | -176 | 964 | 9920 | 1.20 | 1.62 | 1.10 |
| 18 | 708 | -278 | 1138 | 12100 | $1 \cdot 16$ | 1.59 | 1.06 |
| 20 | 840 | -384 | 1296 | 14150 | 1.13 | 1.58 | 1.03 |
| 25 | 1170 | -648 | 1692 | 19120 | $1 \cdot 10$ | 1.55 | 0.99 |
| 30 | 1473 | -931 | 2015 | 23350 | 1.06 | $1 \cdot 54$ | 0.96 |
| 35 | 1740 | -1195 | 2285 | 27290 | $1 \cdot 04$ | 1.52 | 0.92 |
| 55 | 2530 | -2030 | 3030 | 36800 | 1.02 | $1 \cdot 54$ | 0.90 |
| 65 | 2790 | -2395 | 3185 | 40200 | 0.98 | 1.51 | 0.86 |
| 75 | 3010 | -2680 | 3340 | 42400 | 0.97 | 1.52 | 0.85 |
| (100 | 3800 | -3400 | 4200) | | | | |
| (150 | 4400 | -4800 | 4000) | | | | |
| (200 | 4800 | -5800 | 3800) | | | | |
| (250 | 5400 | -6800 | 4000) | | | | |
| | | | | s 51000 | 0.88 | 1.86 | 0.67 |
| 283 | 6080 | -8520 | 3640 | l 59000 | 0.76 | 1.60 | 0.57 |

Table 1. Smoothed values of the principal expansion coefficients and Grüneisen parameters for InBi

occurred between $4 \cdot 0$ and $7 \cdot 3$ K with the 'cube' of InBi. This is equivalent to the change produced by 2 mg of lead and is probably caused by solder on the attached thermocouple. Thus, there is no evidence of a significant proportion of other In–Bi phases.

3. Results

Experimental values below 20 K are shown in Fig. 1 and values at rounded temperatures are given in Table 1 together with the Grüneisen parameters γ_{\perp} , γ_{\parallel} and $\gamma = \beta B_{\rm s} V/C_p$. Elastic moduli and density used in calculating γ are room temperature data of Akgöz *et al.* (1973), namely

$$c_{11} = 51 \cdot 1 \text{ GPa}$$
 (0.511 Mbar), $c_{12} = 37 \cdot 0 \text{ GPa}$, $c_{13} = 32 \cdot 0 \text{ GPa}$,
 $c_{33} = 34 \cdot 6 \text{ GPa}$, $B_s = 34 \cdot 4 \text{ GPa}$, $\rho = 8 \cdot 979 \text{ g cm}^{-3}$.

The heat capacity C_p is from Martin (1981) for T < 30 K. At 35 and 55–75 K we extrapolated his $\Theta_D(T)$ curve and estimate that resulting errors in C_p and hence γ should not exceed ±2%.

At room temperature White *et al.* (1975) gave an experimental value of $C_p = 0.044 \pm 0.004$ cal/g which converts to 59.7 ± 5.7 J/molK compared with a calculated Debye value of ~51 J/molK (using 1 mole of formula units) assuming $T/\Theta_D \sim 2$ and $C_p - C_v = 0.5$ J/molK. Both values are given in Table 1.

From these room-temperature values for c_{ij} we have calculated a lowtemperature limiting elastic value for the Debye temperature of $\Theta_0^{\text{el}} = 119 \text{ K}$ compared with $\Theta_0^{\text{c}} = 139 \cdot 8 \pm 0 \cdot 4 \text{ K}$ from Martin's measurements. We have estimated the possible changes in c_{ij} on cooling to 4 K, assuming that they scale with volume change to the same extent as the c_{ij} for indium ($\Delta V/V = 2 \cdot 1\%$) and bismuth ($\Delta V/V = 0 \cdot 9\%$). This leads to values of c_{11} which are 9% larger at 4 K than at 293 K, while c_{33} is 7% larger, and *B* is 4% larger. From these we have calculated $\Theta_0^{\text{el}} \approx 130 \text{ K}$ in reasonable agreement with the experimental value obtained from the heat-capacity value Θ_0^{c} . Note that the extrapolation of c' is very uncertain and may be critical.

We have calculated values for γ at 20, 10, 4, 3 K using these extrapolated values of $c_{11} + c_{12}$, c_{13} and c_{33} and they do not differ by more than $0 \cdot 1$ above 4 K. Below this the change is significant, particularly for $\gamma_{||}$ which is small and very sensitive to the relative magnitudes of $c_{11} + c_{12}$ and c_{13} .

4. Discussion

The magnitude of the cubic expansion coefficient,

$$\beta = (\mathrm{dln}V/\mathrm{d}T)_{\nu} = -(\mathrm{dln}V/\mathrm{d}P)_T (\mathrm{d}P/\mathrm{d}T)_{\nu} = \chi_T (\mathrm{d}P/\mathrm{d}T)_{\nu},$$

clearly depends on two factors: the internal pressure *P* generated by temperature change and the change in volume generated by this pressure through the elastic compressibility χ .

For a crystal with axial symmetry, the principal linear coefficients are given by equations (3) and (4). The cross compliance s_{13} is negative, so that in each expression α depends on the difference between two terms. If values of γ_{\perp} and $\gamma_{||}$ are similar, then the relative magnitudes of elastic parameters control the sign of α .

For InBi, room temperature values of these important compliances are

 $s_{11} + s_{12} = 3 \cdot 46 \times 10^{-11}$, $s_{13} = -3 \cdot 21 \times 10^{-11}$, $s_{33} = 8 \cdot 83 \times 10^{-11} \text{ Pa}^{-1}$,

so that *if* the principal γ values were comparable, there would be a close balance between the positive and the negative terms.



Fig. 2. Grüneisen functions for InBi (lower) and indium (upper curves from Collins *et al.* 1967).

The bump in $\alpha_{||}$ arises from or is linked to this balance and to the change in γ (particularly $\gamma_{||}$) with T (see Fig. 2). The behaviour of $\gamma(T)$ for indium (see also Fig. 2) is qualitatively similar and produces associated bumps or oscillations in α_{\perp} and $\alpha_{||}$ as found by Collins *et al.* (1967). The question arises as to what causes $\gamma_{||}$ and γ_{\perp} to behave as they do.

In most close-packed metals (cubic or hexagonal), γ values are relatively insensitive to direction and temperature (see Barron *et al.* 1980). In lowcoordination crystals of zincblende or rocksalt structure, the high temperature (γ_{∞}) and low temperature (γ_0) averages may differ greatly through the influence of low-lying transverse acoustic TA lattice vibrational modes. This is most marked if the pressure dependence of such modes is small or negative. In chain-like crystals, such as selenium and tellurium there is strong covalent binding along the chains and weak interchain forces. As a result $\gamma_{||}$ becomes

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small or negative in the long-wave (T = 0) limit because the long-wave TA mode frequencies are increased ('hardened') by stretching. The weak interchain forces produce a larger positive value of γ_{\perp} (see the rhombohedral model of Barron and Gibbons 1974).

For layer-like graphite and boron nitride, the experimental data point to the reverse situation wherein γ_{\perp} becomes negative as T = 0 and γ_{\parallel} remains positive.

We have calculated γ_0 in the low temperature limit from the pressure derivatives of the elastic moduli using $\gamma_0^{\rm el} = -{\rm dln}\Theta_0/{\rm dln}V$, where Θ_0 is an average calculated from the directional dependence of the elastic wave velocities at various pressures (or volumes). The result, $\gamma_0^{\rm el} = 0.0$, is consistent with the extrapolation of our thermal data.

Hitherto we have not mentioned an electronic contribution as there is no experimental evidence that it is significant. Theoretically, we expect the magnitude of the electronic component to be given by

$$\beta_{\rm e} = \gamma_{\rm e} C_{\rm e} / VB$$
,

with $\gamma_e \sim 1$ (cf. a value of $\frac{2}{3}$ for free electrons and about 2–3 for In, Al) and $C_e \sim 0.8 \text{ T mJ/mol K}$ (Martin 1981). This leads to $\alpha_e \approx 0.02 \times 10^{-8} \text{ T K}^{-1}$ which is smaller than our present limits of error.

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