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On the thermal expansion of of indium.*

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The negative coefficient of thermal expansion parallel to the tetragonal axis of indium at room temperature is interpreted in terms of the elastic properties of the lattice. A suggestion that the negative thermal expansion implies a negative linear compressibility in the same direction is refuted.

The thermal expansion of the tetragonal metal indium between 300 and 379°K was recently reported by Deshpande & Pawar (1969), who used an X-ray method. The thermal expansion coefficient $\alpha_\perp$ perpendicular to the tetragonal axis is positive, but the coefficient $\alpha_\parallel$ parallel to the axis is negative and decreases with increasing temperature. Deshpande & Pawar discussed their results assuming that the negative value of $\alpha_\parallel$ should be accompanied by a negative value of $\kappa_\parallel$, the linear compressibility along the tetragonal axis. Although elastic data (Winder & Smith, 1958) gave a positive value of $\kappa_\parallel$, Deshpande & Pawar pointed out that errors of about 2·5% in the elastic constants could give a negative value of $\kappa_\parallel$, and suggested a redetermination of the elastic constants. Here it is shown that the unusual room-temperature thermal expansion of indium can be explained in terms of its elastic properties without invoking a negative value for $\kappa_\parallel$. Attention is also drawn to elastic constant data (Chandrasekhar & Rayne, 1961) and thermal expansion data (Collins, Cowan & White, 1967) overlooked by Deshpande & Pawar.

The thermal expansion coefficients of axial solids can be expressed in the form (Barron & Munn, 1967; Munn, 1968)

$$\alpha_\perp = (C_\eta/V)\,[c_{33}\gamma_\perp - c_{13}\gamma_\parallel]/[c_{33}(c_{11}+c_{12}) - 2c_{13}^2]\,, \quad (1)$$

$$\alpha_\parallel = (C_\eta/V)\,[(c_{11}+c_{12})\gamma_\parallel - 2c_{13}\gamma_\perp]/[c_{33}(c_{11}+c_{12}) - 2c_{13}^2]\,. \quad (2)$$

Here C_η is the heat capacity at constant strain, the $c_{\lambda\mu}$ are isothermal elastic stiffnesses, and $\gamma_\perp$ and $\gamma_\parallel$ are Grüneisen functions defined by

$$\gamma_\perp = (1/2C_\eta)\,(\partial S/\partial \ln a)_{T,c}\,, \quad (3)$$

$$\gamma_\parallel = (1/C_\eta)\,(\partial S/\partial \ln c)_{T,a}\,, \quad (4)$$

a and c being the dimensions of the crystallographic unit cell. The Grüneisen functions are a measure of the thermodynamic driving force producing thermal expansion, while the elastic constants characterize the response of the solid. The thermal expansion coefficients given by equations (1) and (2) describe the resultant behaviour of the solid.

The right-hand side of equation (2) is not proportional to $\kappa_\parallel$, and a negative value of $\kappa_\parallel$ is neither necessary nor sufficient to make $\alpha_\parallel$ negative. The conditions for mechanical stability require that $[c_{33}(c_{11}+c_{12})-2c_{13}^2]$ should be positive (Alers & Neighbours, 1957); then from equation (2) $\alpha_\parallel$ is negative if and only if $2c_{13}\gamma_\perp > (c_{11}+c_{12})\gamma_\parallel$. The condition for $\kappa_\parallel$ to be negative is $2c_{13} > c_{11}+c_{12}$.

The Grüneisen functions $\gamma_\perp$ and $\gamma_\parallel$ can be calculated from experimental thermal expansion coefficients, heat capacities, and elastic constants by inverting equations (1) and (2). The thermal expansion of indium has been measured between 2 and 284°K by Collins, Cowan & White (1967), by the use of the three-terminal capacitance method. These data are consistent with the results of Deshpande & Pawar (1969) at 300°K. The elastic constants of indium have been measured between 4·2 and 300°K by Chandrasekhar & Rayne (1961). These data are in agreement with those of Winder & Smith (1958) used by Deshpande & Pawar, and confirm that $\kappa_\parallel$ is positive. From the data of Collins, Cowan & White (1967) and of Chandrasekhar & Rayne (1961) the ratio of the Grüneisen functions at 284°K is calculated to be $\gamma_\perp/\gamma_\parallel = 1{\cdot}05$.

The highly anisotropic thermal expansion of indium therefore arises despite this nearly isotropic strain dependence of the entropy, that is, despite a nearly isotropic driving force for thermal expansion. [This situation contrasts with that found in zinc, where expansion coefficients of opposite sign occur because $\gamma_\perp$ and $\gamma_\parallel$ differ markedly (Barron & Munn, 1967).] The negative values of $\alpha_\parallel$ for indium occur although $\gamma_\perp/\gamma_\parallel$ is only 1·05, because this ratio still exceeds $(c_{11}+c_{12})/2c_{13}$, which is 1·04. Thus the strong anisotropy results from the nature of the elastic response of the lattice, rather than from that of the driving force. The ratio $(c_{11}+c_{12})/2c_{13}$ is unusually small (for zinc it is about 2) because $c_{11}-c_{12}$ is an order of magnitude smaller than c_{11} and c_{13}, which are nearly equal. The measured values of $c_{11}-c_{12}$ also decrease rapidly with increasing temperature (Chandrasekhar & Rayne, 1961). For elastic stability c_{11} must exceed c_{12} (Alers & Neighbours, 1957), and hence the negative values of $\alpha_\parallel$ arise from the incipient elastic instability of the lattice, which makes it very sensitive to even slight anisotropy in the Grüneisen functions.

These considerations show that negative thermal expansion coefficients can occur in non-cubic crystals without necessarily indicating negative linear compressibilities, negative Grüneisen functions, or even highly anisotropic Grüneisen functions. In particular, the negative values of $\alpha_\parallel$ for indium are entirely consistent with the positive values of $\kappa_\parallel$ and no redetermination of the elastic constants is necessary.

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