Generalized Grüneisen parameters and low temperature limit of lattice thermal expansion of cadmium and zirconium

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Abstract. The generalized Grüneisen parameters (γ'_j) and (γ''_j) for cadmium and zirconium were calculated from the second- and third-order elastic constants to determine the low temperature limit of the volume thermal expansion of these metals of hexagonal symmetry. The low temperature limit of cadmium and zirconium was calculated to be positive values indicating a positive volume expansion down to 0 K even though many Grüneisen gammas were found to be negative.

1. Introduction

A detailed understanding of the thermal expansion is necessary for a wide range of important applications. Very low thermal expansion is desirable for optical applications such as telescopes and laser devices, so that precise focusing or alignment is not lost with temperature fluctuations. The primary use for materials with negative thermal expansion is in composites to adjust the thermal expansion of the composite to a particular value such as zero. However, there are also applications for negative thermal expansion materials in the pure form as temperature compensators. Thermal expansion is a direct consequence of anharmonicity of the crystal lattice. Grüneisen parameter is an important property that characterize the anharmonic properties of solids. Recently many studies have been carried out to calculate the Grüneisen parameter γ [1,2]. The higher-order elastic constants were calculated using the finite strain elasticity theory of Murnaghan [3] considering the sublattice displacements up to second degree in strain. These expressions were used to calculate the second- and third-order elastic constants of cadmium and zirconium [4,5].

Here we have selected cadmium and zirconium for further calculations. Cadmium has only limited use as a pure metal but it forms many binary and more complex alloys which have useful properties for many commercial applications. The most important zirconium compound, the zircon, is used as refractory material for mould-casting, as an abrasive and as constituent of insulating materials, enamels and other temperature-resistance materials. The applications of cadmium and zirconium are important for further investigations of their properties. We have calculated the higher-order elastic constants and hence from these the two transverse acoustic mode Grüneisen gammas and the longitudinal mode gammas. From these modes, the low temperature limit of volume thermal expansion is calculated which would be useful for the applications of these materials.

2. Theory

In the harmonic approximation the atoms execute symmetric vibrations about its mean position. At higher temperature, the vibrations become more and more vigorous but the mean position remains unchanged irrespective of the temperature. Thus thermal expansion is a consequence of anharmonicity of the lattice i.e. deviation of the value of γ from zero. The anharmonicity of this lattice vibration is taken into account here using quasi-harmonic theory of thermal expansion.

In this quasi-harmonic approximation the vibrations are assumed to be harmonic even in a strained lattice, but the interatomic forces and hence the frequencies are assumed to be functions of the strain components of the lattice. The strained state of the lattice is completely specified by the six strain components η_{rs} ($r, s = 1, 2, 3, \eta_{sr} = \eta_{rs}$).

For hexagonal crystals there are two principal thermal expansion coefficients: $\alpha_{\parallel}$, the linear expansion coefficient parallel to the unique axis; $\alpha_{\perp}$, the linear expansion coefficient perpendicular to the unique axis. So it is convenient to use the following strains:

(i) a uniform longitudinal strain ε'' along the unique axis. Then η_{rs} will be zero except $\eta_{33} = \varepsilon'' = d \log c$, where c is the axial length.

(ii) A uniform areal strain ε' in the basal plane perpendicular to the unique axis. Then $\eta_{11} = \eta_{22} = 1/2 dA/A = \varepsilon'/2$, where A is the area of the basal plane. All other η_{rs} vanish.

The behavior of these expansion coefficients at low temperatures is governed by two generalized Grüneisen parameters $\gamma'_j(\theta, \phi)$ and $\gamma''_j(\theta, \phi)$ defined as

$$\gamma'_j(\theta, \phi) = [-1/v_j(\theta, \phi)][\partial v_j(\theta, \phi)/\partial \varepsilon'], \qquad (1)$$

$$\gamma''_j(\theta, \phi) = [-1/v_j(\theta, \phi)][\partial v_j(\theta, \phi)/\partial \varepsilon''], \qquad (2)$$

where $v_j(\theta, \phi)$ is the velocity of the elastic waves traveling in a direction (θ, ϕ), j is the polarization index of the wave, θ is the angle in which the direction of wave propagation makes with the hexagonal axis and ϕ is the azimuthal angle, ε' is a

uniform areal strain perpendicular to the unique axis and ε'' is a uniform longitudinal strain parallel to the unique axis. These generalized Grüneisen parameters can be calculated from the second- and third-order elastic constants as shown by Ramji Rao and Srinivasan [6]. The linear thermal expansion coefficients of a uniaxial crystal is given by

$$V\alpha_{\parallel} = [2S_{13}\gamma'(T) + S_{33}\gamma''(T)]C_{\mathrm{v}}(T), \tag{3}$$

$$V\alpha_{\perp} = [(S_{11} + S_{12})\gamma'(T) + S_{13}\gamma''(T)]C_{\mathrm{v}}(T). \tag{4}$$

Here V is the molar volume, S_{ij} are the elastic compliance coefficients and $C_{\mathrm{v}}(T)$ is the molar specific heat at temperature T. The temperature variation of the thermal expansion coefficients of a crystal can be conveniently studied by plotting the effective Grüneisen function as a function of temperature as was discussed by Barron [7] for cubic crystals. $\gamma'(T)$ and $\gamma''(T)$ are the effective Grüneisen functions, being the weighted averages of the Grüneisen functions of all the normal modes of the crystal. The effective Grüneisen functions are given as

$$\bar{\gamma}_{\perp}(T) = ((C_{11}^s + C_{12}^s)\alpha_{\perp} + C_{13}^s\alpha_{\parallel})V/C_p, \tag{5}$$

$$\bar{\gamma}_{\parallel}(T) = ((2C_{13}^s\alpha_{\perp} + C_{33}^s\alpha_{\parallel})V/C_p. \tag{6}$$

The C_{ij}'s are the adiabatic elastic constants, C_{p} is the specific heat at constant pressure and V is the volume of the crystal.

At very low temperatures, the effective Grüneisen parameters are determined by the mode gammas of the elastic waves and $\gamma'(T)$ and $\gamma''(T)$ attain limiting values γ_0' and γ_0''.

The lattice thermal expansion coefficients at various temperatures can be expressed in terms of the effective Grüneisen functions $\gamma_{\perp}(0)$ and $\gamma_{\parallel}(0)$ as follows:

$$V\alpha_{\perp} = [(S_{11} + S_{12})\gamma_{\perp}(0) + S_{13}\gamma_{\parallel}(0)]C_{\mathrm{v}} = \gamma_{\perp}^{\mathrm{Br}}C_{\mathrm{v}}\chi_{\mathrm{iso}}, \tag{7}$$

$$V\alpha_{\parallel} = [2S_{13}\gamma_{\perp}(0)S_{33}\gamma_{\parallel}(0)]C_{\mathrm{v}} = \gamma_{\parallel}^{\mathrm{Br}}C_{\mathrm{v}}\chi_{\mathrm{iso}}. \tag{8}$$

Here, S_{ij} are the elastic compliance coefficients, V is the molar volume, χ_{iso} is the isothermal compressibility and C_{v} is the specific heat at constant volume. The Brugger gammas $\gamma_{\perp}^{\mathrm{Br}}$ and $\gamma_{\parallel}^{\mathrm{Br}}$ are

$$\gamma_{\perp}^{\mathrm{Br}} = [(S_{11} + S_{12})\gamma_{\perp}(T) + S_{13}\gamma_{\parallel}(T)]\chi_{\mathrm{iso}}^{-1}, \tag{9}$$

$$\gamma_{\parallel}^{\mathrm{Br}} = [2S_{13}\gamma_{\perp}(T) + S_{33}\gamma_{\parallel}(T)]\chi_{\mathrm{iso}}^{-1}, \tag{10}$$

where T is the temperature. At low temperatures, the Brugger gammas are

$$\gamma_{\perp}^{\mathrm{Br}}(0) = [(S_{11} + S_{12})\gamma_{\perp}(0) + S_{13}\gamma_{\parallel}(0)]\chi_{\mathrm{iso}}^{-1}, \tag{11}$$

$$\gamma_{\parallel}^{\mathrm{Br}}(0) = [2S_{13}\gamma_{\perp}(0) + S_{33}\gamma_{\parallel}(0)]\chi_{\mathrm{iso}}^{-1}. \tag{12}$$

The low temperature limit of the volume Grüneisen function (γ_L) is then obtained by

$$\gamma_L = 2\gamma_\perp^{\mathrm{Br}}(0) + \gamma_\parallel^{\mathrm{Br}}(0). \tag{13}$$

The mode Grüneisen gammas and hence the low temperature limit of the hexagonal crystals cadmium and zirconium are calculated from the third-order elastic constants [4,5]. The second- and third-order elastic constants from refs [4] and [5] are used here to obtain the mode Grüneisen gammas $\gamma'(\theta, \phi)$ and $\gamma''(\theta, \phi)$ for the acoustic modes for different values of θ and ϕ at intervals of 5° ranging from 0° to 90°. The variation of the generalized functions $\gamma'(\theta, \phi)$ and $\gamma''(\theta, \phi)$ with the angle θ for two typical values of ϕ for cadmium and zirconium is shown in figures 1–4 respectively with azimuthal angle $\phi = 15°$. The low temperature limits $\gamma_\perp(0)$ and $\gamma_\parallel(0)$ are calculated using the data from the above graphs. From these values the Brugger gammas $\gamma_\perp^{\mathrm{Br}}(0)$ and $\gamma_\parallel^{\mathrm{Br}}(0)$ are calculated using eqs (11) and (12). The low temperature limits of volume Grüneisen function γ_L of cadmium is thus calculated using eq. (13) and these values are given in table 1. These calculated values are compared with the experimental values available [8–10]. Here the discrepancy in the value of γ_L may be because of the variation in the value of calculated C_{333}.

Figures 1 and 2 show the variation of Grüneisen functions γ' and γ'' for the three acoustic branches of the elastic waves as a function of the angle θ, which the direction of propagation makes with the hexagonal axis of cadmium. It is seen from figures 3 and 4 that the anisotropy in the two transverse acoustic branches γ_1' and γ_2' are quite large. This indicates a possible phase change which is confirmed by Pratesi *et al* [11]. They report a pressure-induced structural phase transition in cadmium.

Figures 3 and 4 give the plot of variation of the Grüneisen functions γ' and γ'' for the three acoustic branches as a function of θ for hexagonal zirconium. From the plot it is seen that the anisotropy is large for branches 1 and 2. The anisotropy in the γ_1' branch is more pronounced than in the γ_3' branch. The anisotropy in γ'' is considerable for zirconium. In the transverse acoustic branches the Grüneisen gammas are negative for a large number of directions. These negative gammas indicate that at high temperature a large number of Grüneisen gammas may become negative when the crystal is subjected to transverse thermal strains in the basal plane,
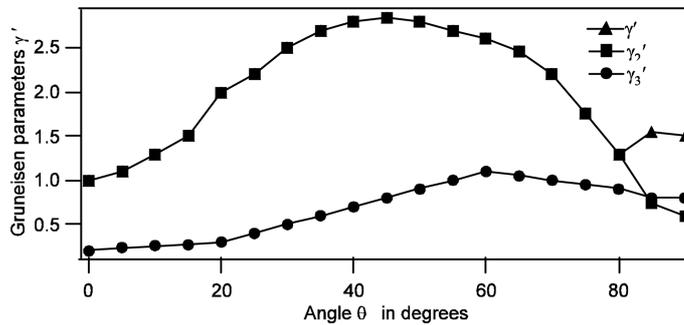

Figure 1. Variation of the generalized Grüneisen parameters γ' as a function of θ for the azimuthal angle $\phi = 15°$ in cadmium.
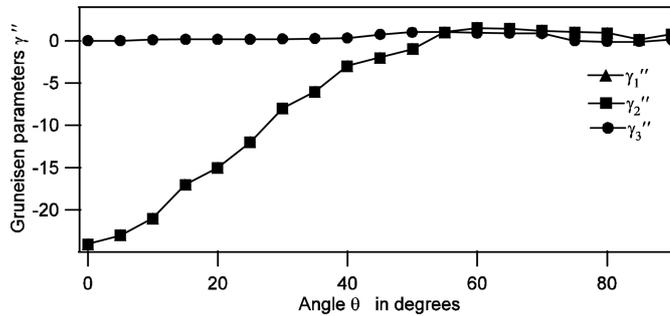
Figure 2. Variation of the generalized Grüneisen parameters γ'' as a function of θ for the azimuthal angle $\phi = 15°$ in cadmium.
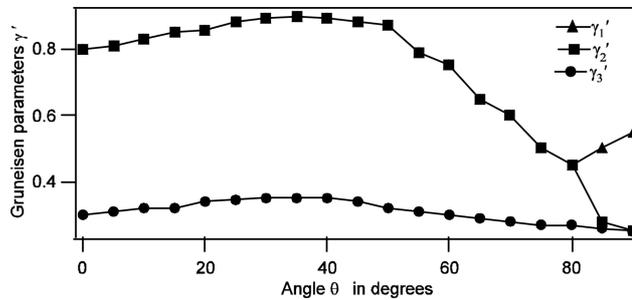

Figure 3. Variation of the generalized Grüneisen parameters γ' as a function of θ for the azimuthal angle $\phi = 15°$ in zirconium.
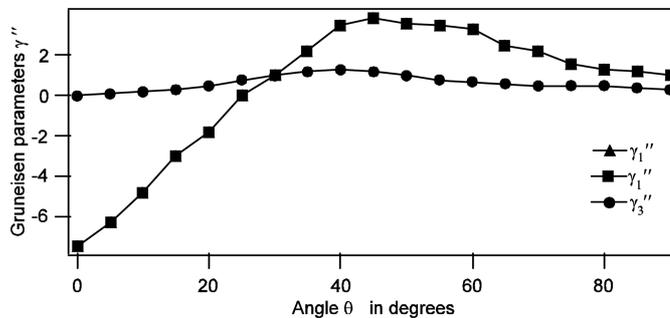

Figure 4. Variation of the generalized Grüneisen parameters γ'' as a function of θ for the azimuthal angle $\phi = 15°$ in zirconium.

which lead to lattice instability and hcp to bcc transformation in zirconium. Fisher and Renken [12] also predict from their study of the temperature variation of the shear modulus C_{66} of zirconium that transverse thermal strains could cause phase transformations in zirconium at high temperatures. The prediction of pressure- and temperature-induced phase changes of zirconium is confirmed from the works of Greff [13]. Table 2 gives the low temperature limit value of zirconium and is compared with the available values [14,15].

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Table 1. $\gamma_\perp(0)$, $\gamma'_\parallel(0)$, $\gamma''_\parallel(0)$, $\gamma^{\mathrm{Br}}_\parallel(0)$ and γ_L for cadmium.

$\gamma_\perp(0)$	$\gamma'_\parallel(0)$	$\gamma''_\parallel(0)$	$\gamma^{\mathrm{Br}}_\parallel(0)$	γ_L (present work)	γ_L (cadmium)
1.937	-2.20	0.970	-0.005	1.935	2.40 [8] 2.70 [9] 3.19 [10]

Table 2. $\gamma_\perp(0)$, $\gamma'_\parallel(0)$, $\gamma''_\parallel(0)$, $\gamma^{\mathrm{Br}}_\parallel(0)$ and γ_L for zirconium.

$\gamma_\perp(0)$	$\gamma'_\parallel(0)$	$\gamma''_\parallel(0)$	$\gamma^{\mathrm{Br}}_\parallel(0)$	γ_L (present work)	γ_L (zirconium)
0.515	0.287	0.141	1.38×10^{-3}	0.283	0.30 [11] 0.30 [12]

The low temperature limit of volume thermal expansion calculated here for cadmium and zirconium is found to be positive and so we expect a positive volume expansion down to 0 K even though the mode gammas are negative. The measurement of higher-order elastic constants and hence the calculation of the thermal expansion coefficients is important to explain the anharmonic properties of solids with accuracy.

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