First-principles study of the anisotropic thermal expansion of hcp metals Be and Y

Nie Yaozhuang[a,b,*], Xie Youqing[b], Li Xiaobo[b], Peng Hongjian[b]

[a]*School of Physics Science and Technology, Central South University, Changsha 410083, China*
[b]*School of Material Science and Engineering, Central South University, Changsha 410083, China*

Abstract

A first-principles study of the anisotropic thermal expansion of hcp metals Be and Y is reported. According to quasiharmonic approximation, the phonon spectra were computed at a set of lattice parameters using the pseudopotential plane wave method with the local density approximation in the framework of the density functional perturbation theory. The free energies were obtained according to the calculated phonon spectra and thermal properties such as specific heat at constant volume (pressure) were calculated. The electronic contribution to specific heat was found important to metal Y not only at very low temperature but also over room temperature. The calculated results are in good agreement with available experimental data in a wide range of temperature.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: A. Metals; C. Ab initio calculations; D. Thermal expansion; D. Specific heat

1. Introduction

In the past, the theoretical calculations of thermal expansion were mostly based on Debye–Grüneisen model [1] and restricted to cubic materials. Thermal expansion calculations for metals [2,3], compounds [4] had been carried out based on this model. The first-principles calculations of thermal expansion without any adjustable parameters were not possible until recent years. Thanks to density functional perturbation theory (DFPT) [5,6], which allowed exact calculations of vibrational frequencies in every point of the Brillouin zone, the vibrational free energy can be obtained using the quasiharmonic approximation. In this approximation, anharmonic effects are included through the explicit volume dependence of the vibrational frequencies. Then thermal expansion and other thermal properties such as specific heat at constant volume (pressure) can be calculated. Several thermal expansion

calculations about cubic metals based on DFPT have been carried out [7–10], and they give good results about isotropic thermal expansion and related thermal properties for cubic metals. However, little attention has been paid to the calculation of the thermal expansion of anisotropic metals [11], because of the large computational cost of determining the complete phonon spectrum as a function of volume. In fact, anisotropic thermal expansion has seldom been studied even based on Debye–Grüneisen model. A complete specification of the anisotropic thermal expansion requires a knowledge of two or three expansion coefficients as functions of temperature over a wide range. These coefficients measure expansion along perpendicular axes. For hexagonal structure, which has the axis of rotational symmetry, only two coefficients are required. In this paper we apply quasiharmonic approximation with DFPT to the study of the thermal properties of hcp metals Be and Y, which have remarkable different anisotropic thermal expansion, though their axial ratios are almost the same (1.569 and 1.571, respectively). Another purpose of the present paper is to check the electronic contribution to specific heat which previous calculations often neglected. Our results demonstrate that anisotropic thermal expan-

*Corresponding author. School of Physics Science and Technology, Central South University, Changsha 410083, China.
Tel.: +86 7318660059.

E-mail address: yz_nie@163.com (N. Yaozhuang).

sion and other thermal properties of hcp metals can be well predicted by this approach in a wide range of temperature.

2. Theory

The equilibrium structural parameters, $\mathbf{a} = (a_1, a_2, \ldots)$, of a crystal, at any temperature T, are obtained by minimizing the Helmholtz free energy F of the system. The free energy F at temperature T and structural parameters $\mathbf{a}$ is given by

$$F(\mathbf{a}, T) = E_{stat}(\mathbf{a}) + k_B T \sum_{q\lambda} \ln \left\{ 2 \sinh \left(\frac{\hbar \omega_{q\lambda}(\mathbf{a})}{2 k_B T} \right) \right\}, \quad (1)$$

where $E_{stat}(\mathbf{a})$ is the static energy of the crystal, k_B is Boltzmann's constant, $\hbar$ is Planck's constant, and $\omega_{q\lambda}(\mathbf{a})$ is the frequency of the phonon with wave vector $\mathbf{q}$ and polarization λ, evaluated at lattice parameter $\mathbf{a}$. The sum is over all phonon branches λ and over all wave vectors $\mathbf{q}$ in the Brillouin zone. To calculate free energy F, one must be able to calculate frequencies all over the Brillouin zone, and this can be done exactly using DFPT. Furthermore this calculation must be performed at various values of the structural parameters. In the case of hcp structure, the system is described by two parameters a and c. One should compute phonon dispersions in a grid of points in the (a, c) space. Because of this, it is difficult from a computational point of view. The equilibrium lattice constants at temperature T are obtained by minimizing F with respect to a and c, for hexagonal structure. The coefficients of linear expansion (CTE) are given by

$$\alpha_a = \frac{1}{a_{293}} \left(\frac{\mathrm{d}a(T)}{\mathrm{d}T} \right), \quad (2)$$

$$\alpha_c = \frac{1}{c_{293}} \left(\frac{\mathrm{d}c(T)}{\mathrm{d}T} \right), \quad (3)$$

and the thermal expansions are described by

$$\varepsilon_a = \frac{a - a_{293}}{a_{293}}, \quad (4)$$

$$\varepsilon_c = \frac{c - c_{293}}{c_{293}}, \quad (5)$$

where a and c mean equilibrium lattice constants at corresponding temperatures. The subscript 293 means 293 K.

In order to compare theoretical results with the experimental data from Ref. [12], another coefficient of linear thermal expansion are defined as, $\alpha = (2\alpha_a + \alpha_c)/3$ for hexagonal structure. We call it mean coefficient of linear thermal expansion. We have similar definitions for mean linear thermal expansion ε.

Once phonon spectrum is obtained, we can easily evaluate the vibrational heat capacity at constant volume from next equation

$$C_V^{ph} = k_B T \sum_{q\lambda} \left(\frac{\hbar \omega_{q\lambda}(\mathbf{a})}{2 k_B T} \right)^2 \sinh^{-2} \left(\frac{\hbar \omega_{q\lambda}(\mathbf{a})}{2 k_B T} \right). \quad (6)$$

The electronic heat capacity can be obtained from

$$C_V^{el} = T \frac{\partial S_{el}}{\partial T} \bigg|_V, \quad (7)$$

where the electronic entropy S_{el} can be evaluated from the self-consistent DFT calculations using FD smearing. The heat capacity at constant pressure can be computed by using the relation

$$C_P = C_V + 9\alpha^2 BVT, \quad (8)$$

where B is bulk modulus, α is the mean coefficient of linear expansion, and $C_V = C_V^{ph} + C_V^{el}$.

3. Computational details

The calculations were performed using the ABINIT codes [13]. ABINIT is a package whose main program allows one to find the total energy, charge density and electronic structure of systems within density functional theory (DFT) [14,15], using pseudopotentials and a planewave basis. ABINIT also includes options to optimize the geometry according to the DFT forces and stresses, and to generate dynamical matrices, Born effective charges, and dielectric tensors within DFPT [16,17]. In our calculations, for both metals, the local density approximation [18] (LDA) was used for the exchange correlation. The interaction between the ions and valence electrons was described using norm-conserving pseudopotentials generated in the scheme of Troullier–Martins [19]. The Monkhorst–Pack [20] meshes used for sampling of the Brillouin zone were $12 \times 12 \times 8$. Phonon dynamical matrices were computed for $6 \times 6 \times 4$ q-point grids. Plane-wave basis sets with a cutoff of 20 Hartree were used. Convergence in the plane-wave basis sets and the Brillouin zone sampling for both Be and Y was confirmed by employing higher kinetic energy cutoffs and denser k meshes. These calculating parameters were chosen to guarantee the total energy error in 0.1 mHartree/atom.

4. Results

We first calculated ground properties of Be and Y. The lattice constants and bulk modulus are listed in Table 1. The calculated lattice constants and bulk modulus are about 1% and 10% errors compared with the experimental values, respectively.

To obtain the linear thermal expansion, 25 sets of ground-state and response-function calculations were

Table 1
Ground properties of Y

	a (Å)		c (Å)		B (GPa)	
	Calc.	Expt. [21]	Calc.	Expt. [21]	Calc.	Expt. [21]
Be	2.249	2.283	3.550	3.581	144	130
Y	3.645	3.647	5.659	5.731	44.3	41.0