



Thermal expansion coefficients of Mo–Si compounds by first-principles calculations

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[Received 16 February 2000 and accepted in revised form 19 June 2000]

ABSTRACT

Taking Mo–Si compounds as model systems, we show that the coefficients of thermal expansion (CTEs) of complex structures can be calculated precisely from first principles by incorporating the Debye model for acoustic response. Specifically, we obtain a nearly isotropic CTE in MoSi₂ but a highly anisotropic CTE in Mo₅Si₃. The CTE anisotropy in Mo₅Si₃ is due to an elastically more rigid basal plane and a higher anharmonicity along the *c* axis. As the structure of 5–3 compounds is modified from D8_m to D8₁ by boron substitutions (Mo₅SiB₂), we predict a significant decrease in the CTE anisotropy, which is confirmed by experiments.

§ 1. INTRODUCTION

In the synthesis and processing of non-cubic high-temperature materials, micro-cracks are often induced owing to the anisotropy in the coefficients of thermal expansion (CTEs). To minimize the thermal stresses in polycrystalline materials, a more isotropic CTE is desirable. The degree of the anisotropy, however, is not predictable by any empirical rules and can vary substantially within any specific material type. For example, among the transition-metal silicides, the CTEs are highly anisotropic for 5–3 silicides, but become nearly isotropic for disilicides (Shah *et al.* 1992). No *ab initio* theory has been developed to correlate the degree of the anisotropy with the nature of crystal and electronic structures. In this paper, taking the tetragonal Mo–Si alloys (MoSi₂, Mo₅Si₃ and Mo₅SiB₂) as model systems, we show that *ab initio* theory can precisely predict and elucidate the thermoelastic properties of these alloys.

That the CTEs are highly anisotropic in 5–3 transition-metal silicides is well documented. There is no exception for Mo₅Si₃. Measurements by Chu *et al.* (1999) show that the CTE in the [001] direction is more than twice the CTE in the [100] direction. We shall calculate the CTEs and address the origin of anisotropy in this class of compounds. One prominent feature of 5–3 Mo–Si is that the substitution by boron (Mo₅SiB₂) substantially improves the oxidation resistance (Meyer *et al.* 1996) but, at the same time, changes the crystal structure from D8_m (T1 phase) to

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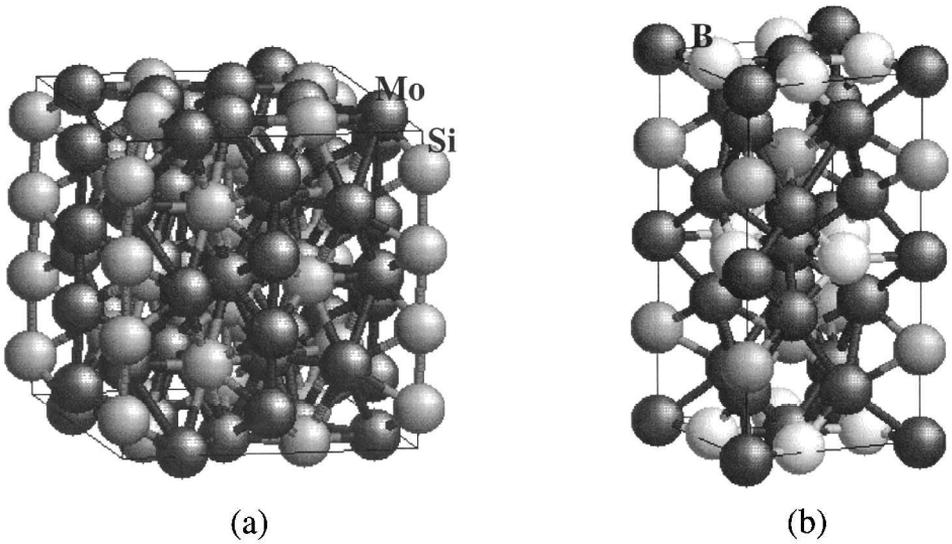


Figure 1. The crystal structures of the (a) $D8_m$ and (b) $D8_1$ structures.

$D8_1$ (T2 phase). An important basic question is whether or not the CTE anisotropy of the T1 phase is retained in the T2 phase. The answer provided by our investigation is that the CTEs of the T2 phase become nearly isotropic. This prediction is further confirmed by experiments. The structures of $D8_m$ and $D8_1$ are depicted in figure 1. Note the existence of prominent chain structures along the c axis shown at the cell boundaries in figure 1 (a).

§ 2. THE THEORETICAL MODEL

Although thermal expansion is a classic subject, the calculation of CTEs by first principles is still largely limited to simple cubic elements (for example Fleszar and Gonze (1990) and Quong and Liu (1997)). This is the situation because rigorous calculations of the entire phonon spectra become lengthy and difficult for complex multicomponent systems. The problem can be simplified by approximating the phonon contribution through the elastic acoustic response (i.e. the Debye model). The semiempirical approach based on this model has had quantitative success in describing the CTEs of monatomic cubic metals (Moruzzi *et al.* 1988). Generally, the use of a Debye model for thermal expansion tends to overestimate the hydrostatic pressure for multicomponent systems. For the present systems, however, we find that the use of a Debye model for the lattice anharmonicity in our formalism (see below) is adequate enough to give CTE values to within about 10% of the available measured values in most cases. On physical grounds, this is not surprising. The materials investigated here display strong covalent bonding characteristics (Fu *et al.* 1999), which imply high optical phonon energies. Because of their higher activation energies, optical phonons are not expected to modify significantly the results presented here. The good agreement between our results and the measurements on the prototype system MoSi_2 (see below) further confirms that optical phonons do not play significant roles.

To calculate the CTE of a tetragonal structure, we consider the free energy $F(T)$ in the presence of elastic strain components (uniform expansions or contractions) u_i as

$$F(T) = E_0 + \frac{1}{2} C_{\mu\nu} u_\mu u_\nu + \frac{1}{3!} C_{\mu\nu\sigma} u_\mu u_\nu u_\sigma + F_{\text{phonon}}(T), \quad (1)$$

where the Greek subscripts take values from 1 to 3 and the Einstein summation convention is implied. F_{phonon} is the phonon free energy (including zero-point motion), and E_0 is the total energy at 0 K. C_{ij} and C_{ijk} are second-order and third-order elastic constants respectively. The sound velocities are determined from the Christoffel equation (Ashcroft and Mermin 1976). A minimization of the free energy with respect to the strains ($\delta a/a$ and $\delta c/c$ in [100] and [001] directions respectively) yields the following equations for the change in lattice parameters at temperature T :

$$\frac{\delta a}{a} = \frac{2\tilde{C}_{13}^{(2)}\Gamma_c(T) - \tilde{C}_{33}\Gamma_a(T)}{2(\tilde{C}_{11} + \tilde{C}_{12})\tilde{C}_{33} - 4\tilde{C}_{13}^{(1)}\tilde{C}_{13}^{(2)}}, \quad (2)$$

$$\frac{\delta c}{c} = \frac{2\tilde{C}_{13}^{(2)}\Gamma_a(T) - 2(\tilde{C}_{11} + \tilde{C}_{12})\Gamma_c(T)}{2(\tilde{C}_{11} + \tilde{C}_{12})\tilde{C}_{33} - 4\tilde{C}_{13}^{(1)}\tilde{C}_{13}^{(2)}}. \quad (3)$$

Here, $\Gamma(T)$ and $\Gamma_c(T)$ are the derivatives of F_{phonon} with respect to $\delta a/a$ and $\delta c/c$, and the \tilde{C} values are given by

$$\tilde{C}_{11} + \tilde{C}_{12} = C_{11} + C_{12} + (C_{113} + C_{123})\frac{\delta c}{c} + \frac{1}{2}(C_{111} + 3C_{112})\frac{\delta a}{a}, \quad (4)$$

$$\tilde{C}_{33} = C_{33} + \frac{1}{2}C_{333}\frac{\delta c}{c} + 2C_{133}\frac{\delta a}{a}, \quad (5)$$

$$\tilde{C}_{13}^{(1)} = C_{13} + \frac{1}{2}(C_{113} + C_{123})\frac{\delta a}{a}, \quad (6)$$

$$\tilde{C}_{13}^{(2)} = C_{13} + \frac{1}{2}C_{133}\frac{\delta c}{c}. \quad (7)$$

The algebraic equations (2)–(7) are solved iteratively once $\Gamma_a(T)$ and $\Gamma_c(T)$ are obtained from first principles. Clearly, thermal expansion depends on both crystal elasticity and lattice anharmonicity. If the system is isotropic in lattice anharmonicity (i.e. $\Gamma_a = 2\Gamma_c$), the ratio of thermal expansions becomes inversely proportional to the ratio of elastic tensile stiffness in the basal plane and along the c axis.

The calculation of the CTEs for these complex structures imposes a tremendous challenge, since the CTE depends not only on the second-order elastic constants but also on higher-order elastic constants (dominated by third-order terms). For a tetragonal structure, there are six independent second-order elastic constants and ten independent third-order elastic constants. While the calculation of second-order elastic constants has become more common recently, the calculation of higher-order elastic constants remains challenging. This is because that the calculation of higher-order terms involves the *difference* in the elastic strain energies at a small change in lattice parameter. The higher-order elastic constants contribute to both crystal anharmonicity (through the dependence of the Debye temperature on the lattice parameter in our model) and the temperature dependence of elastic constants.

The elastic constants were calculated by the full-potential linearized augmented plane-wave (FLAPW) method (Wimmer *et al.* 1981) within the local-density-functional approach. The calculational details of the second-order elastic constants of a tetragonal structure have been described by Fu *et al.* (1999). The third-order elastic constants were determined through the derivative of second-order elastic constants with respect to lattice strains (i.e. $\delta a/a$ and $\delta c/c$). Within a range of 3–4% change in the lattice parameters, the dependence of the second-order elastic constants on lattice parameters is found to be linear, indicating that the third-order terms are dominant in the higher-order elastic constants. In calculations of the strained structure systems, the internal coordinates of the atoms within the unit cell were relaxed using the calculated FLAPW atomic forces.

§ 3. RESULTS AND DISCUSSION

The calculated second- and third-order elastic constants are listed in table 1 and table 2 respectively. We find excellent agreement between theory and experiments (Nakamura *et al.* 1990; Chu *et al.* 1999) in the second-order elastic constants for MoSi_2 and Mo_5Si_3 . The measured second-order elastic constants are $C_{11} = 446$ GPa, $C_{12} = 174$ GPa, $C_{33} = 390$ GPa, $C_{13} = 140$ GPa, $C_{44} = 110$ GPa and $C_{66} = 140$ GPa for Mo_5Si_3 , and $C_{11} = 417$ GPa, $C_{12} = 104.2$ GPa, $C_{33} = 514.5$ GPa, $C_{13} = 83.8$ GPa, $C_{44} = 204.2$ GPa and $C_{66} = 193.6$ GPa for MoSi_2 . However, we are not aware of any measurement of higher-order terms. For Mo_5SiB_2 , there is no experimental measurement to compare with, since single-crystal T2 phase is not currently available.

To examine the validity of our theory, we first consider MoSi_2 . It has the simplest structure studied here. There are two interesting features in the elastic properties of MoSi_2 .

- (1) $C_{11} + C_{12} \approx C_{33}$ (i.e. the same degree of elastic rigidity in the basal plane and along the c -axis).

Table 1. Theoretical second-order elastic constants of MoSi_2 , Mo_5Si_3 and Mo_5SiB_2 .

	C_{11} (GPa)	C_{12} (GPa)	C_{33} (GPa)	C_{13} (GPa)	C_{44} (GPa)	C_{66} (GPa)
MoSi_2^a	404	109	508	87	198	195
Mo_5Si_3^a	438	162	371	136	106	143
Mo_5SiB_2	483	154	419	188	179	127

^a At experimental lattice parameters.

Table 2. Theoretical third-order elastic constants of MoSi_2 , Mo_5Si_3 and Mo_5SiB_2 . Here $C_{111} + 3C_{112}$ and $C_{113} + C_{123}$ measure the ‘softening rate’ of the tensile modulus $C_{11} + C_{12}$ with [100] and [001] expansions respectively.

	$C_{111} + 3C_{112}$ (GPa)	$C_{113} + C_{123}$ (GPa)	C_{333} (GPa)	C_{133} (GPa)	C_{144} (GPa)	C_{344} (GPa)	C_{166} (GPa)	C_{366} (GPa)
MoSi_2	–4700	–1450	–4560	–950	–700	–600	–900	–750
Mo_5Si_3	–6520	–1540	–2830	–780	–370	–665	–820	–370
Mo_5SiB_2	–5700	–600	–2600	–200	–600	–770	–650	–200

- (2) $C_{166} \approx C_{366}$ and $C_{144} \approx C_{344}$ (i.e. the response of shear elastic constants with respect to lattice expansions in different directions are approximately equal), indicating a small difference between the lattice anharmonicities in the [100] and [001] directions.

Indeed, the calculated CTEs of MoSi₂ shown in figure 2 (a) are nearly isotropic with magnitudes of about 8–10 ppm K⁻¹ at high temperatures. The calculated CTEs are in good agreement with experiment (Thomas *et al.* 1985). The measured CTEs

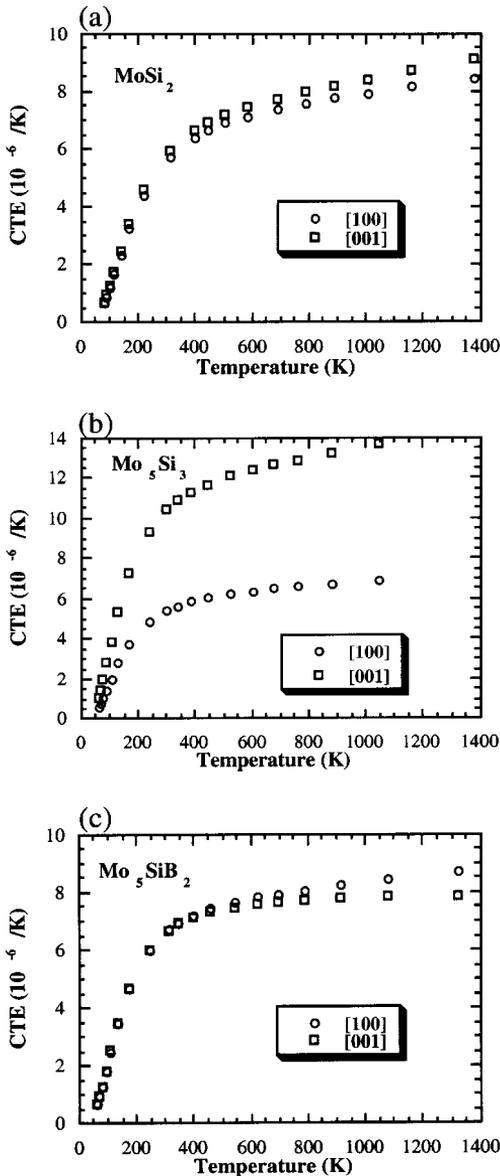


Figure 2. The calculated CTEs in the [100] and [001] directions for (a) MoSi₂, (b) Mo₅Si₃ and (c) Mo₅SiB₂.

are 8.2 and 9.4 ppm K⁻¹ in the [100] and [001] directions respectively. This good agreement confirms that our model is valid for these strong covalent Mo–Si systems. In the following, we report our theoretical predictions for the 5–3 Mo–Si compounds.

The calculation for the CTE of Mo₅Si₃ becomes far more demanding owing to the complexity of its structure. The bonding in Mo₅Si₃ is shown to have pronounced multicentred covalent components (Fu *et al.* 1999), characterized by the planar Mo–Si–Mo bonding units in the basal plane and by the unusually short Mo–Mo bonds along the *c* axis (shorter by about 10% relative to the Mo–Mo distance in the basal plane). While the basal plane is found to be elastically more rigid than the *c* axis ($C_{11} + C_{12} > C_{33}$), the Mo–Mo bonds along the *c* axis will be shown to play a more important role in determining the anisotropy of lattice anharmonicity. Anisotropy is found in the elastic response to lattice expansions, which is evidenced in the marked difference in the magnitudes of calculated third-order terms: $C_{344} > C_{144}$ and $C_{366} < C_{166}$ for [100](001) and [100](010) shears respectively.

The anharmonicity can be described by examining the volume dependence of Debye temperature θ_D , that is the Grüneisen constant ($\gamma = -\partial(\ln \theta_D)/\partial(\ln V)$). We find that γ is higher for the lattice expanded in the [001] direction ($\gamma_{[001]} = 2.55$) than in the [100] direction ($\gamma_{[100]} = 2.17$). In other words, the lattice vibration energy decreases more rapidly by [001] expansions than by [100] expansions. The calculated CTEs of Mo₅Si₃ shown in figure 2(b) are consistent with the experimental measurement by Chu *et al.* (1999). The CTE along the [001] direction is about twice that in the [100] direction. The measurements were made in the range from 300 to 700 K with fitted CTEs of 5.2 and 11.5 ppm K⁻¹ in the [100] and [001] directions respectively. It should be noted, however, that the calculated CTEs still increase linearly with increasing temperature at higher temperatures (in particular, in the [001] direction).

An examination of the third-order elastic constants of MoSi₂ and Mo₅Si₃ shows the difference between their elastic responses to lattice expansions. In MoSi₂, the response of either C_{44} or C_{66} to lattice expansions is nearly isotropic. By contrast, the corresponding shear elastic response in Mo₅Si₃ is anisotropic. Because of a planar covalent bonding in the basal plane in Mo₅Si₃, the finding that $C_{366} < C_{166}$ for (001) *intralayer* shear is not entirely surprising (i.e. C_{66} decreases more rapidly by [100] expansions than by [001] expansions). The large difference (by a factor of two) between C_{344} and C_{144} for (001) *interlayer* shear, however, is unexpected, since an increase in lattice spacing in either the [001] or the [100] direction has the same effect to decrease the [100](001) shear elastic strength.

Analysis shows that, as the lattice spacing is varied, the change in Debye temperature (i.e. lattice anharmonicity) is particularly sensitive to the variation in shear elastic constants. In the case of Mo₅Si₃, the major contribution to the anisotropy in anharmonicity comes from the anisotropy in C_{344} and C_{144} (i.e. C_{44} decreases more rapidly by [001] expansions than by [100] expansions). (Note that the response of [100](001) shear (i.e. C_{44}) is about twice as important as the response of [100](010) shear (i.e. C_{66}), since C_{44} and C_{55} are degenerate for tetragonal systems.) The physical origin for this anisotropy lies in the dominant role of the unusually short Mo–Mo [001] covalent bonds in coupling the (001) layers. These covalent Mo–Mo bonds, which characterize the [100](001) shear, are weakened more by [001] expansions than by [100] expansions. Increasing the [001] spacing reduces the Mo–Mo [001] bond strength and decreases the lattice vibrational energy (giving

higher lattice anharmonicity) more rapidly than in-plane expansions. This directional dependence of the Mo–Mo bond strength (in coupling the (001) layers) contributes significantly to the difference in the softening behaviour of the [100](001) shear characteristics.

Thus, for Mo₅Si₃, there are two physical sources contributing to a higher CTE along the [001] direction than along the [100] direction: a stronger bonding in the basal plane ($C_{11} + C_{12} > C_{33}$) and a higher lattice anharmonicity along the c axis (dominated by $C_{344} > C_{144}$). Both of these physical mechanisms can be understood in terms of electronic structure: the existence of planar multicentred Mo–Si–Mo covalent bonds in the basal plane, and the dominant role of directional Mo–Mo bonds along the c axis in the (001) interlayer coupling. In fact, we believe that the same mechanisms are also responsible for the observed CTE anisotropy in other 5–3 transition-metal silicides. For example, although Ti₅Si₃ has a different crystal structure (hexagonal D_{8h} structure) from the tetragonal D_{8m} structure discussed above, the interlayer coupling between basal planes is still dominated by atomic chains along the c axis with unusually short interatomic distance. As a result, the calculated CTEs of Ti₅Si₃ are also highly anisotropic. It follows that it is possible to reduce the CTE anisotropy if the interlayer coupling between basal planes is no longer dominated solely by the [001] bonding component. This can probably be achieved either by interstitial alloying additions (to modify bonding direction) or by alloying substitutions (to increase the interatomic distance along the chains). These suggestions are currently examined by experiments.

The substitution of boron in Mo–Si changes the crystal structure from D_{8m} (T1 phase) to D_{8h} (T2 phase). One notable feature of the T2 phase is the absence of transition-metal atomic chains along the c axis in this structure. The calculated lattice parameters are 6.027 and 10.97 Å for a and c respectively.

For Mo₅SiB₂, the averaged elastic moduli are higher than those of Mo₅Si₃. This increase is partly attributed to the formation of Mo–B covalent bonds. While the calculated second-order elastic constants for the T2 phase still indicate that the basal plane is elastically more rigid than the c axis ($C_{11} + C_{12} > C_{33}$), the effect of this difference on the CTE is balanced by a substantial increase in the elastic coupling (C_{13}) between the basal plane and c axis, presumably owing to the effect of boron at interstitial sites (cf. figure 1). Most significantly, the lattice anharmonicity for the T2 phase is found to be nearly isotropic in the [100] and [001] directions (with Grüneisen constants of 2.05 and 1.98 respectively). We identify this near isotropy in lattice anharmonicity as being due to the absence of a directionally bonded [001] chain structure characteristic of the T1 phase. Indeed, in this case, the difference between C_{344} and C_{144} becomes smaller and is balanced by a relatively larger difference between C_{166} and C_{366} .

As a result of decreased anisotropy in both the elastic (static) contribution and the lattice anharmonicity compared with the T1 phase, the CTEs for the T2 phase become nearly isotropic in [100] and [001] directions with the CTE in the [100] direction being slightly higher. The calculated CTEs for the T2 phase are presented in figure 2(c). Experimentally, it was observed that, in the processing of these alloys, grain-boundary cracking problems (characteristic of the T1 phase) are virtually eliminated in the T2 phase, indicating that the CTE anisotropy in the T2 phase is much less than that of the T1 phase, in agreement with theoretical prediction.

More recently, the CTEs of Mo₅SiB₂ were measured by neutron powder diffraction (Rawn *et al.* 2000) and by synchrotron X-ray diffraction (Kramer 2000) from

room temperature to 1400°C. The experiments confirm the theoretical prediction not only of the CTE values but also of a nearly isotropic CTE for Mo₅SiB₂.

In summary, we have shown that the CTEs of complex systems can be predicted by first-principles calculation. The high CTE anisotropy in 5–3 silicides is understood in terms of the anisotropy in lattice anharmonicity. The removal of atom chains (characteristic of the T1 phase) along the *c* axis by boron substitutions substantially decreases the CTE anisotropy in the T2 phase.

ACKNOWLEDGEMENTS

Research was sponsored by the Division of Materials Sciences, Office of Basic Energy Sciences, US Department of Energy under contract DE-AC05-96OR 22464 with Lockheed Martin Energy Research Corporation.

REFERENCES

- ASHCROFT, N. W., and MERMIN, N. D., 1976, *Solid State Physics* (New York: Holt, Rinehart and Winston), p. 443.
- CHU, F., THOMA, D. J., MCCLELLAN, K., PERALTA, P., and HE, Y., 1999, *Intermetallics*, **7**, 611.
- FLESZAR, A., and GONZE, X., 1990, *Phys. Rev. Lett.*, **64**, 2961.
- FU, C. L., WANG, X., YE, Y. Y., and HO, K. M., 1999, *Intermetallics*, **7**, 179.
- KRAMER, M. J., 2000 (to be published).
- MEYER, M. K., KRAMER, M. J., and AKINC, M., 1996, *Intermetallics*, **4**, 273.
- MORUZZI, V. L., JANAK, J. F., and SCHWARZ, K., 1988, *Phys. Rev. B*, **37**, 790.
- NAKAMURA, M., MATSUMOTO, S., and HIRANO, T., 1990, *J. Mater. Sci.*, **25**, 3309.
- QUONG, A. A., and LIU, A. Y., 1997, *Phys. Rev. B*, **56**, 7767.
- RAWN, C. J., HOFFMANN, C. M., SCHNEIBEL, J. H., and HUBBARD, C. R., 2000, *Intermetallics* (to be published).
- SHAH, D. M., BERCIK, D., ANTON, D. L., and HECHT, R., 1992, *Mater. Sci. Engng*, **A155**, 45.
- THOMAS, O., SENATEUR, J. P., MADAR, R., LABORDE, O., and ROSENCHER, E., 1985, *Solid St. Commun.*, **55**, 629.
- WIMMER, E., KRAKAUER, H., WEINERT, M., and FREEMAN, A. J., 1981, *Phys. Rev. B*, **24**, 864.