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Ab initio study of the phononic origin of negative thermal expansion

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Negative thermal expansion is an uncommon phenomenon of theoretical interest. Multiple hypotheses regarding its microscopic origins have been suggested. In this paper, the thermal expansion of a representative semiconductor, Si, and a representative metal, Ti, are calculated *ab initio* using density-functional perturbation theory. The phonon modes' contributions to the thermal expansion are analyzed and the negative thermal expansion is shown to be dominated by negative mode Grüneisen parameters at specific points on the Brillouin zone boundaries. Thus, the elastic (Debye) theory for negative thermal expansion is shown to be irrelevant for these phenomena. The anomalous behavior of these modes in Ti is shown to be unaffected by an electronic topological transition as previously suggested, instead it arises from complex interplay of atomic displacements of the anomalous mode.

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I. INTRODUCTION

Thermal expansion is an anharmonic property of materials that reflects the evolution of the phonon spectrum with volume and temperature. For most materials, across a wide range of conditions, the thermal expansion coefficient is positive. Anisotropic thermal expansion reflects the anisotropic anharmonic nature of certain crystals, i.e., mainly the change in the phonon spectra as they undergo an anisotropic deformation in response to temperature variations at constant pressure.

Negative values of the coefficient of thermal expansion (both isotropic and anisotropic) have been measured in several materials at low temperatures [1]. Focusing for simplicity on elemental solids, the semiconductors silicon and germanium exhibit negative thermal expansion at low temperatures [2,3] in contrast to diamond which does not present such behavior [4]. Titanium has a negative coefficient of anisotropic thermal expansion at low temperatures [5] although the bulk thermal expansion remains positive. Pawar *et al.* [6] measured the anisotropic thermal expansion of titanium in the hexagonal closed-packed (hcp) α phase. They found that at room temperature and above, the coefficient of thermal expansion along the c axis of the hexagonal structure is smaller than the coefficient of thermal expansion along the a axis. Nizhankovskii *et al.* [5] measured the thermal expansion of single crystal titanium along both axes, and they found that the thermal expansion along the c axis is negative in the temperature range 0–165 K.

Several theories have been advanced for the origin of negative thermal expansion [7–9]. In general, the thermal expansion is dominated by lattice vibrations. Thus, negative thermal expansion requires at least one vibrational mode that has a negative Grüneisen coefficient, which is equivalent to anomalous volume dependence of the mode frequency ($\partial\omega/\partial V > 0$). At low enough temperatures, the phonon spectrum is dominated by acoustic modes and this anomaly would be presented as an increase in the sound velocity with volume [9]. It has also been suggested that the negative thermal expansion originates in thermal fluctuations due to the existence of a nearly degenerate metastable state [10].

Ab initio studies of negative thermal expansion have mostly focused on analysis of the phonon spectra. Methods for phonon calculations have been reviewed in Refs [11,12]. In particular, for the semiconductors silicon, germanium and gallium arsenide, Dolling *et al.* [13] suggest that the negative coefficient of thermal expansion is caused mainly by the negative Grüneisen parameter of the transverse acoustic modes. They calculated the Grüneisen parameter in two symmetry directions: Λ ($\Gamma \rightarrow L$) and Δ ($L \rightarrow K$). Negative Grüneisen parameters were found in specific directions and branches but it was not shown that these modes form the main contribution to the thermal expansion or that such negative Grüneisen parameters are not present in other directions. Similar results were obtained by Biernacki *et al.* [14].

In addition to the phonon contribution, thermal expansion in metals can also be affected by thermal electronic excitations. Lifshitz [15] discussed the effect of electronic topological transitions (ETTs) on the electronic properties of materials, and showed that an ETT leads to a discontinuity in the pressure derivative of the thermal electronic properties of materials, such as the electronic heat capacity. In this work the properties of phonons were not investigated. Vaks *et al.* [16] discuss the influence of van Hove singularities on the phonon frequencies. They showed that the phonon frequencies change significantly where the Fermi level is in the vicinity of a van Hove singularity. Therefore, a singular point in the electronic density of states can cause anomalies in both electronic and phononic contributions to thermodynamic properties such as free energy, entropy, heat capacity, and thermal expansion.

It has been proposed that the negative anisotropic thermal expansion in titanium arises due to an ETT which appears under anisotropic deformation [5]. In this work it was suggested that the contribution of electronic excitations to the entropy is the reason for the anomaly in the anisotropic thermal expansion. This anomalous behavior of the anisotropic thermal expansion was also studied by Souvatzis *et al.* [9] who showed that titanium has an ETT under compression of the c axis at constant volume. In addition, they calculated the derivative of the electronic density of states and showed that it has a different sign with respect to $\epsilon_v \equiv d[\ln(V)]$ and $\epsilon_c \equiv d[\ln(c/a)]$ where a and c are the lattice parameters and V is the volume. They concluded that the anomaly in the thermal expansion is caused by the ETT because it affects the elastic moduli, and thus the Debye temperature. However, no analysis of the phonon spectrum was performed and no direct relation between the proximity of the Fermi level to a van Hove singularity and negative thermal expansion was demonstrated.

Very recently, the low-compressibility metal osmium was compressed to multi-megabar pressures using both conventional and double-stage diamond anvil cells [17]. X-ray diffraction measurements of the c/a ratio of the hcp structure discovered a kink at 150 GPa. Theoretical calculations identified two ETTs at 100 and 180 GPa. However, these zero Kelvin calculations do not predict a kink in the c/a ratio. The authors explain the differences between the calculations and the experiment by the anisotropy in the thermal expansion present in hcp metals. Their explanation is based on the phonon modes at small wave vectors that are determined by the elastic constants, as argued by Souvatzis *et al.* [9] for titanium.

Theoretical studies in *ab initio* methods predict that, with increasing pressure, the thermal expansion in many materials decreases and becomes negative, or more negative at higher temperatures. For example, at pressures above 3.5 GPa, the coefficient of thermal expansion of cesium is predicted to be negative at all temperatures [18]. In silicon, the negative coefficient of thermal expansion decreases with pressure and the temperature range across which the coefficient is negative increases [19]. Finally, the coefficient of thermal expansion of diamond becomes negative at very high pressures [20]. The thermal expansion in titanium under hydrostatic pressure has not yet been investigated either in experimental or in theoretical studies to the best of our knowledge.

The aim of the present work is to explore the origins of negative thermal expansion by *ab initio* calculations in two elemental test systems, a semiconductor and a metal, silicon and titanium, as a function of temperature and pressure. The free energy is calculated *ab initio* and the phonon contribution is analyzed in the entire Brillouin zone within the quasiharmonic approximation. The thermal expansion as a function of temperature and pressure is obtained. Our results allow us to test the several hypotheses put forward for the origin of the negative thermal expansion.

The rest of the paper is organized as follows: In Sec. II we present the details of the electronic, phononic, and thermodynamic calculations. In Sec. III we consider the origins of the anomalous thermal expansion. In Sec. III A we analyze silicon as an example of anharmonic effects in an isotropic case. In Sec. III B we present an analysis of the anharmonic effects leading to the negative coefficient of anisotropic thermal expansion of titanium at zero pressure as well as the effect of pressure. In Sec. IV we discuss the effect of the negative Grüneisen parameter on the thermal expansion and the effect of ETT on the phonon modes. Sec. V includes a summary of our results and conclusions.

II. THEORY

A. Thermodynamics

1. Isotropic

The volume thermal expansion is proportional to the derivative of the entropy with respect to the volume:

$$\alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{B}\left(\frac{\partial S}{\partial V}\right)_T \tag{1}$$

where V is the volume, T is the temperature, P is the pressure, S is the entropy, and B is the bulk modulus. The linear thermal expansion is defined as

$$\alpha_L = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_P = \frac{1}{3}\alpha_V, \tag{2}$$

where L is the length of an isotropic material. The pressure dependence of the thermal expansion is given by the thermodynamic relation

$$-\frac{\partial K_T}{\partial T} = \frac{\partial \alpha_V}{\partial P}, \tag{3}$$

where K_T is the isothermal compressibility. This relation implies that if the material becomes softer as temperature increases then the thermal expansion decreases with pressure.

2. Anisotropic

To calculate the anisotropic coefficient of thermal expansion, the thermodynamic quantities and their derivatives are calculated as a function of the lattice parameters, two in the hexagonal case.

The expressions for $\partial a/\partial T$ and $\partial c/\partial T$ at the equilibrium volume, where the partial derivatives of the free energy with respect to the lattice parameters vanish, are [5,7,9]

$$\left(\frac{\partial a}{\partial T}\right)_P = \frac{A_{cc}(T)\big(S_a(T) - \frac{A_{ac}(T)}{A_{cc}(T)}S_c(T)\big)}{A_{ac}^2(T) - A_{aa}(T)A_{cc}(T)}, \tag{4}$$

$$\left(\frac{\partial c}{\partial T}\right)_P = \frac{A_{aa}(T)\big(S_c(T) - \frac{A_{ac}(T)}{A_{aa}(T)}S_a(T)\big)}{A_{ac}^2(T) - A_{aa}(T)A_{cc}(T)}, \tag{5}$$

where the subscripts a or c denote partial derivatives with respect to the lattice parameters. The coefficients of anisotropic thermal expansion are defined by [9]

$$\alpha_a \equiv \frac{1}{a}\left(\frac{\partial a}{\partial T}\right)_P, \tag{6}$$

$$\alpha_c \equiv \frac{1}{c}\left(\frac{\partial c}{\partial T}\right)_P. \tag{7}$$

From expressions (4) and (5) it is clear that a negative coefficient of anisotropic thermal expansion can appear in a material even though the two directional derivatives of the entropy, S_a and S_c, are positive. In such cases an anomaly may occur solely due to the coupling between these directional derivatives. This is in contrast to the isotropic case where the volume derivative of the entropy must be negative for a thermal expansion anomaly.

B. Quasi-harmonic approximation

The Helmholtz free energy A can be represented as a sum of a temperature independent term, E, and a thermal contribution, F. The thermal contribution to the free energy F can be decomposed into a sum of electronic excitations and phonon terms, F_{el} and F_{ph} respectively. In the quasiharmonic approximation both electronic and phononic densities of states (DOS) are approximated by their values at zero Kelvin at the appropriate volume; i.e., they are assumed to be independent of temperature at constant volume.

1. Isotropic

The vibrational contribution to the entropy of a harmonic mode with frequency ω at temperature T is

$$s = -k_B\left[\ln\left\{2\sinh\left(\frac{\hbar\omega}{2k_BT}\right)\right\} - \frac{\hbar\omega}{2k_BT}\coth\left(\frac{\hbar\omega}{2k_BT}\right)\right] \quad (8)$$

and the total vibrational entropy is obtained by an integral over all the modes of the crystal. The total contribution of the phonons to the volume derivative of the entropy is the derivative of this integral:

$$\frac{\partial^2 F_{ph}}{\partial V\partial T} = \left(\frac{\partial S_{ph}}{\partial V}\right)_T = \frac{V}{(2\pi)^3}\sum_i\int_{BZ}\frac{\partial s}{\partial\omega_i}\frac{\partial\omega_i}{\partial V}d\vec{q}, \quad (9)$$

where the integral is taken over the entire Brillouin zone. The Grüneisen parameter of a vibrational mode $\omega_i(\vec{q})$ is defined as

$$\gamma_i(\vec{q}) = -\frac{V}{\omega_i(\vec{q})}\frac{\partial\omega_i(\vec{q})}{\partial V}, \quad (10)$$

where $\vec{q}$ is a wave vector and i is the branch index. Since $\partial s/\partial\omega_i$ is always negative [as can be seen from Eq. (8)] some of the modes must have a negative Grüneisen parameter if the material is to have a negative volume thermal expansion, as previously noted [21]. We can also consider the derivative $\partial s/\partial\omega_i$ as a temperature dependent weighting function of the contribution of the derivatives $\partial\omega_i/\partial V$ to the thermal expansion α_V.

2. Anisotropic

The anisotropic derivative of the phonon entropy in the quasiharmonic approximation is calculated as

$$S_a = \left(\frac{\partial S_{ph}}{\partial a}\right)_{c,T} = \frac{V}{(2\pi)^3}\sum_i\int_{BZ}\frac{\partial s}{\partial\omega_i}\frac{\partial\omega_i}{\partial a}d\vec{q}, \quad (11)$$

$$S_c = \left(\frac{\partial S_{ph}}{\partial c}\right)_{a,T} = \frac{V}{(2\pi)^3}\sum_i\int_{BZ}\frac{\partial s}{\partial\omega_i}\frac{\partial\omega_i}{\partial c}d\vec{q}. \quad (12)$$

In the anisotropic case the phonon spectrum at fixed lattice parameters (a and c in our case) is assumed to be independent of temperature; i.e., the curvature of the free energy surface is to be assumed identical to that of the ground state energy. The validity of this approximation is expected to decrease as the temperature increases.

The quasiharmonic approximation (QHA) may be sufficient to calculate thermodynamic properties of materials. However, anharmonic effects are also important for transport properties. In particular, lattice thermal conductivity of insulators are calculated by anharmonic force constants within the framework of the Boltzmann transport equation [22–24].

C. Computational methods

The electronic calculations were performed using a pseudopotential plane-waves method [25]. Phonon spectra were calculated using density functional perturbation theory [12]. All calculations were performed with the QUANTUM ESPRESSO package [26]. The exchange-correlation functional was approximated by the Perdew-Burke-Ernzerhof (PBE) general gradient approximation (GGA) [27]. For silicon, the kinetic energy cutoff applied to the wave function expansions was 40 Ry. The cutoff for the charge density and potential expansions was 200 Ry. The number of k points in each direction of the reciprocal lattice vectors (Monkhorst-Pack algorithm) was 18, centered at the Γ point. For titanium, the corresponding energy cutoffs were 50 Ry for the kinetic energy and 300 Ry for the charge density and potential expansion and a 16 k-point grid was applied. The Methfessel-Paxton smearing scheme [28] with a Gaussian spreading of 0.01 Ry was used to determine the occupation number. These numerical parameters led to convergence of the total energy to 10^{-5} Ry/atom for both titanium and silicon. The pseudopotentials employed were si_pbe_v1.uspp.F.UPF, with 4 valence electrons, for silicon and ti_pbe_v1.4.uspp.F.UPF, with 12 valence electrons, for titanium, both from the GBRV (Garrity, Bennett, Rabe, and Vanderbilt) pseudopotential database [29]. Phonon calculations were performed with four q points in each direction of the reciprocal lattice vectors, after it was determined that this choice produces convergence of the entropy to 10^{-2} J/mol K.

The electronic and phononic DOS were evaluated at zero Kelvin within the quasiharmonic approximation (QHA) where they depend explicitly only on the volume. In the anisotropic case, the volume dependence is replaced by explicit dependence on the lattice parameters of the hexagonal structure (a,c). The values of these lattice parameters are found by minimization of the free energy at fixed pressure and temperature.

III. RESULTS

A. Silicon

1. Thermal expansion

In a semiconductor the electronic contribution to the free energy and its derivatives is negligible. Therefore, only the phonon contribution needs to be considered. Employing Eqs. (1) and (9), the thermal expansion of silicon, in the thermodynamically stable diamond structure, was calculated in the GGA. The results are presented in Fig. 1. The major features and magnitude of the thermal expansion observed

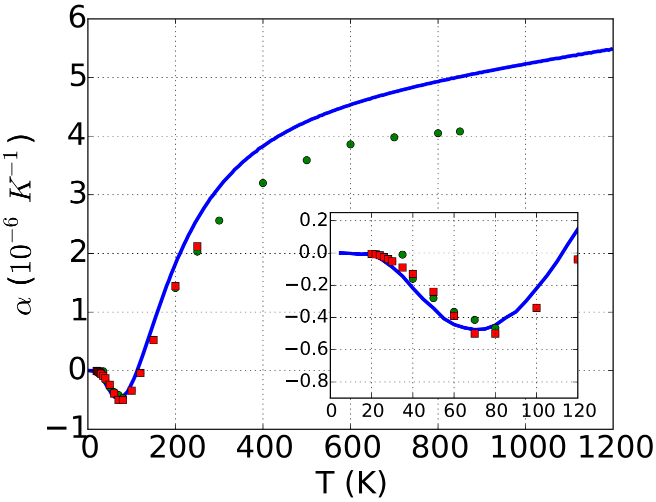

FIG. 1. Linear thermal expansion coefficient of silicon calculated using GGA. The dots are experimental data from Refs. [2] (red squares) and [3] (green circles).

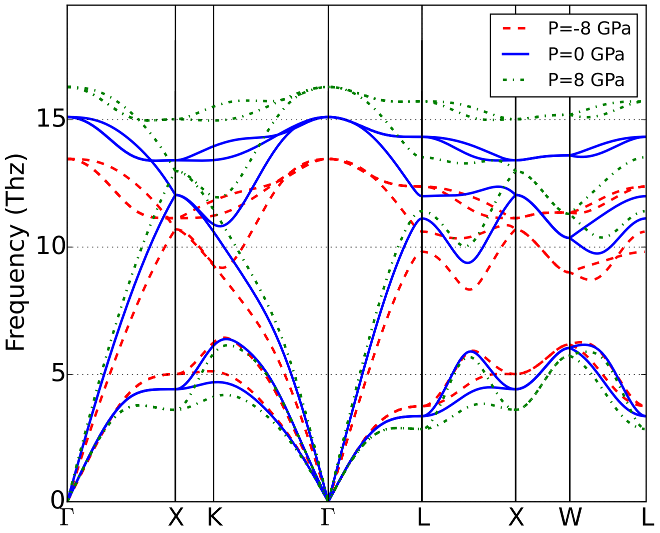

FIG. 2. Phonon spectra of silicon calculated at the volumes corresponding to $P = 0, \pm\ 8$ GPa at zero Kelvin.

experimentally are reproduced in both approximations. At low temperatures, where negative thermal expansion is observed, the GGA calculation fits well the experimental data. As the temperature is increased, the calculation and experiment deviate.

2. Volume dependence of the phonon spectrum

To explore the mode Grüneisen parameter across the Brillouin zone, the phonon spectrum of silicon was calculated at several volumes corresponding to positive, negative, and no compression. The results are presented in Fig. 2, where it can be seen that an anomaly in the phonon spectrum (negative mode Grüneisen parameter) is present in the acoustic transverse modes. The anomaly is most pronounced at the X, K, and L symmetry points and is absent near the Γ point. A weaker anomaly appears at the symmetry point W. It is thus clear that the dominant anomalous contribution to the thermal expansion arises on the boundaries of the Brillouin zone at low temperatures, not on the acoustic area near the Γ point which determines the elastic coefficients of the materials. Thus application of the Debye model would not predict anomalous thermal expansion in silicon.

3. Entropy of the modes

To investigate the contribution of specific phonon modes to the thermal expansion we calculated the contribution of each mode to the volume derivative of the entropy, which is the integrand of the right-hand side of Eq. (9). The results of these calculations at selected temperatures are presented in Fig. 3. Negative values of this integrand are represented in blue and positive ones in red. At 50 K the integrand is negative over most of the irreducible Brillouin zone (IBZ), shown in Fig. 3(a), and the total derivative of the entropy is negative. At higher temperatures the derivative of the entropy becomes positive at gradually expanding regions of the IBZ until the anomalous contribution becomes concentrated at the X and L points before disappearing completely. It is interesting to note that the X point is the center of the rectangle and L is the center of the hexagon on the boundaries of the Brillouin zone [see Fig. 4(a)]. The contribution to the thermal expansion at low temperatures at a particular wave vector $\vec{q}$ is a competition between the anomalous $\partial\omega/\partial V$ of the lower frequency branches and the normal contribution of the higher frequency branches. As the temperature increases, the contribution of the higher branches become dominant and the anomaly disappears.

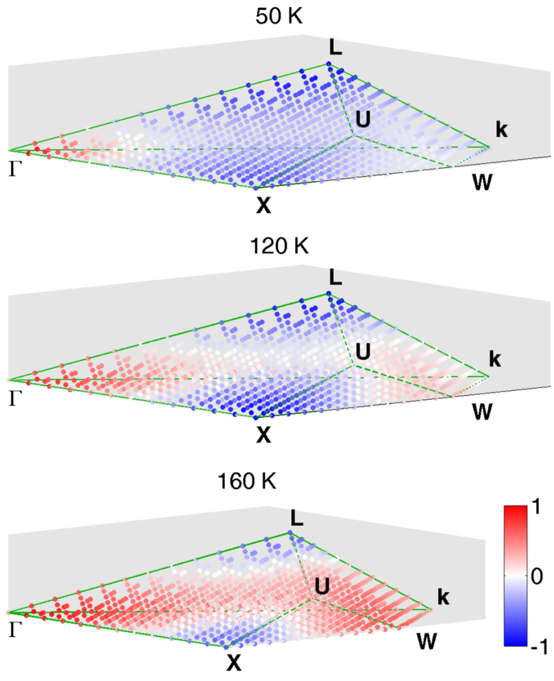

FIG. 3. The derivative of the entropy with respect to the volume, $\partial s(\omega(\vec{q}))/\partial V$, at each wave vector in the irreducible Brillouin zone (sum over all branches) of silicon, blue for anomalous contributions and red for normal contributions. The values (shown in the color bar) are normalized to the maximum absolute value. This derivative (the total contribution from the entire IBZ) has the same sign as the coefficient of thermal expansion [see Eq. (1)].

B. Titanium

1. The anisotropic thermal expansion

The coefficients of anisotropic thermal expansion of the α phase of titanium were calculated *ab initio* using Eqs. (6)

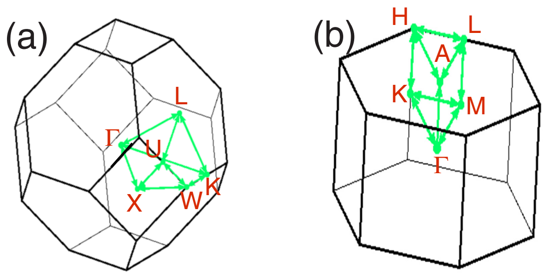

FIG. 4. The Brillouin zone of the fcc (a) and hexagonal (b) lattices. The polyhedron indicated by the high symmetry points is the irreducible Brillouin zone.

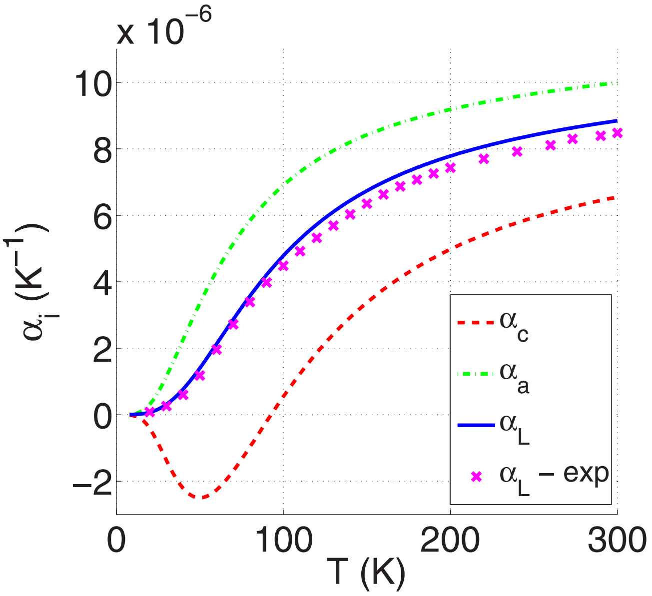

FIG. 5. The coefficients of thermal expansion of α-titanium at zero pressure along the a axis, α_a, along the c axis, α_c, and the linear thermal expansion, α_L, calculated from the anisotropic coefficients. The experimental data are from Ref. [30].

and (7). It was verified that the contribution of electronic excitations to these coefficients is negligible. The results are presented in Fig. 5. In this calculation, the free energy was minimized with respect to a and c at each temperature at a constant hydrostatic pressure $P = 0$. An anomaly in the thermal expansion along the c axis is observed, in contrast to the thermal expansion along the a axis which is positive at all temperatures. The bulk thermal expansion, α_L, calculated from these anisotropic coefficients, agrees very well with the experimental data as can be seen in Fig. 5.

2. *Thermodynamics analysis*

Figure 6 shows the total energy of α-titanium in the plane of lattice parameters a and c. The isoenergy lines are ellipses slightly rotated with respect to the lattice parameter axes. Thus, the second derivative A_{ac} is nonzero, causing a coupling between the directional derivatives of the entropy along the two lattice parameters. The elliptical shape reflects the anisotropy of the material where there exist both hard and soft directions. The second derivative A_{aa} is therefore much larger than A_{cc}. The ratios A_{ac}/A_{aa} and A_{ac}/A_{cc} are dominated by the zero temperature energy and are almost independent of temperature and hydrostatic pressure. The numerators of Eqs. (4) and (5) determine the sign of the anisotropic thermal expansion coefficients. Their components are shown in Fig. 7(a) for α_c and Fig. 7(b) for α_a. In Fig. 7(a) the two components intersect, thus the coefficient α_c changes sign, whereas the curves in Fig. 7(b) do not intersect so α_a remains positive at all temperatures. The derivative of the entropy S_a is positive at all temperatures and pressures in contrast to S_c which is negative below 45 K at zero pressure as shown in Fig. 7(a). It should be noted that α_c would have been negative at low temperatures even if S_c was positive at all temperatures, provided it remained small enough to preserve the curve intersection in Fig. 7(a).

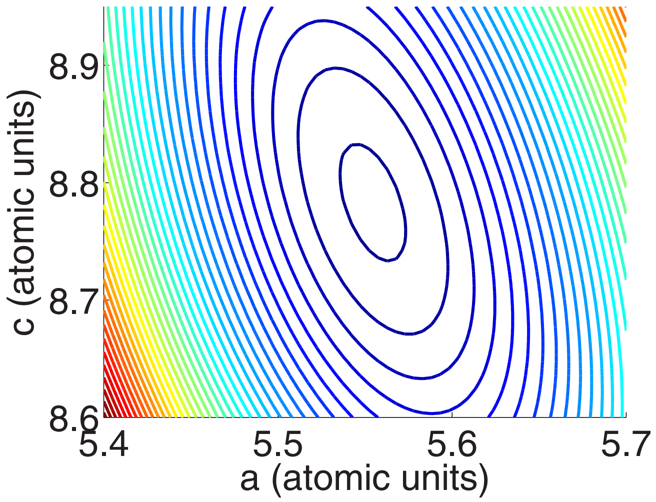

FIG. 6. Isocurves of the total energy of α-titanium (without phonon contribution) in the plane of the lattice parameters around the equilibrium point $a = 5.55$ atomic units and $c = 8.78$ atomic units.

From these results, we learn that there are two contributions to the anomaly in the coefficient of thermal expansion along the c axis. One is the negative entropy derivative with respect to the lattice parameter c, S_c. This derivative is negative below 45 K at zero pressure. However, the anomaly in α_c persist up to approximately 100 K. This is due to the second contribution arising from the coupling with S_a.

3. *Phonon analysis*

Figure 8 displays the phonon spectra at 3 points in the (a,c) plane: at equilibrium ($a = 5.55$ atomic units, $c = 8.78$ atomic

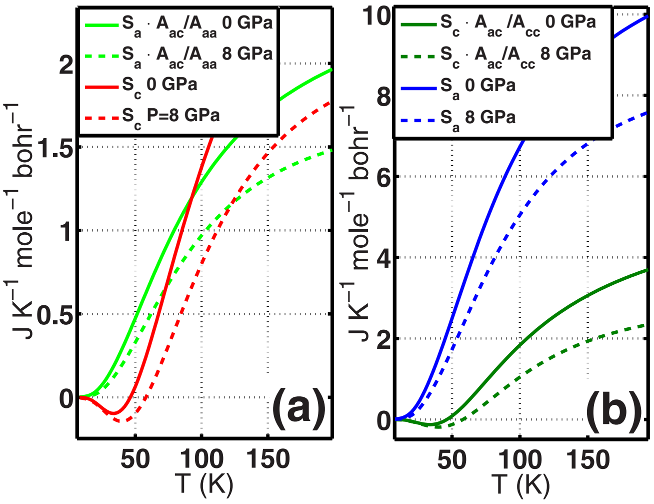

FIG. 7. The derivatives of the entropy with respect to the lattice parameters and their coupling terms in Eqs. (4) and (5). The intersections in (a) of the two solid or dashed curves denote the temperatures where the thermal expansion along the c axis changes its sign. The absence of such intersections in (b) shows that the expansion along the a axis is always positive.

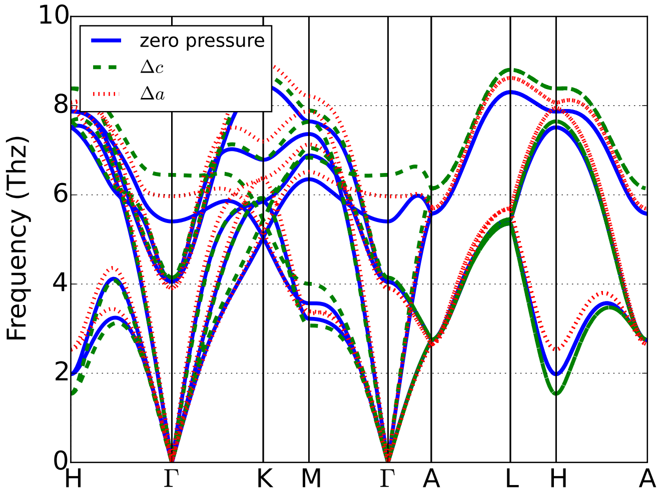

FIG. 8. Phonon spectra at several lattice parameters for α-titanium around zero pressure. The curves denoted by Δc and Δa represent compressions of 2% in the c and a directions, respectively.

units) and at compression of the unit-cell of both a and c lattice parameters. We note that our results agree with and extend recent calculations by Togo and Tanaka [22]. At the H point on the edge of the Brillouin zone, shown in Fig. 4(b), there is a soft transverse acoustic mode whose frequency decreases under compression in the c direction. This anomaly in the phonon spectrum does not appear under compression in the a direction. Most of the spectrum exhibits normal behavior under compression in both directions and the anomaly is observable mainly at the H point and its neighborhood. We find that this soft mode is associated with a mechanical structural instability of the α phase under sufficient shear deformation, as shown in Fig. 12(b) below.

In Figs. 9 and 10 we present the the integrands of Eqs. (11) and (12). A positive contribution is represented by the red color and a negative one is represented by blue. The main contribution to the derivative of the entropy at very low temperatures (around 30 K) comes from the vicinity of the H point. It is positive in the a direction, Fig. 9, and negative in the c direction, Fig. 10. A weaker negative contribution in the c direction also appears around the Γ point. As the temperature rises, more modes contribute to the thermal expansion. In the a direction the contribution is positive over the entire IBZ, whereas in the c direction it remains negative near the H point, at the corner of the Brillouin zone [Fig. 4(b)]. At high temperatures, the thermal expansion in the c direction becomes positive due to the increased positive contributions to S_c over most of the IBZ. The coefficients of thermal expansion α_a and α_c both decrease as pressure increases for temperatures above 50 K; see Fig. 11. The temperature range in which α_c is negative increases with pressure. This is due to the increase in the frequencies of the optical branches under pressure which reduces their relative contribution to the entropy at low temperatures. Their contribution to the positive thermal expansion thus becomes dominant at increasingly higher temperatures as the pressure increases. At temperatures below 50 K the compression reduces the negative anisotropic coefficient α_c.

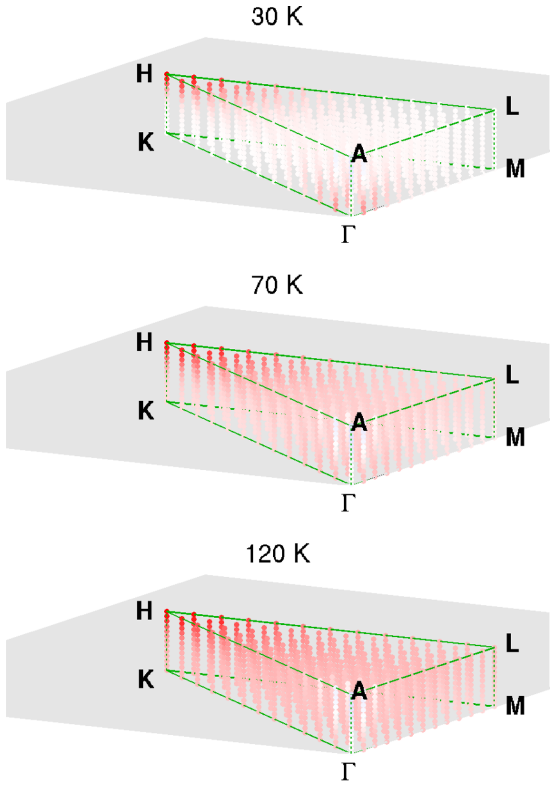

FIG. 9. The integrand of Eq. (11), s_a, over the IBZ of titanium at different temperatures. The red color denotes $s_a > 0$. The color bar is the same as in Fig. 3.

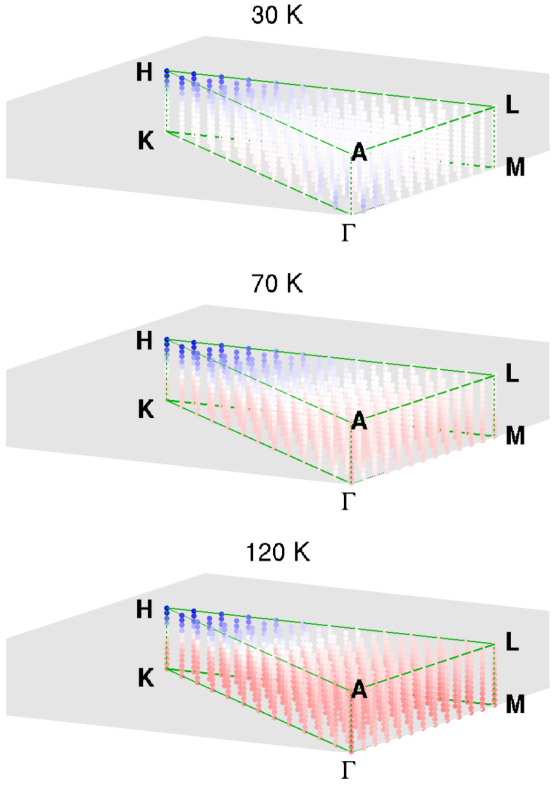

FIG. 10. The integrand of Eq. (12), s_c, over the IBZ at different temperatures. The red and blue colors denote $s_c > 0$ and $s_c < 0$, respectively. The color bar is the same as in Fig. 3.

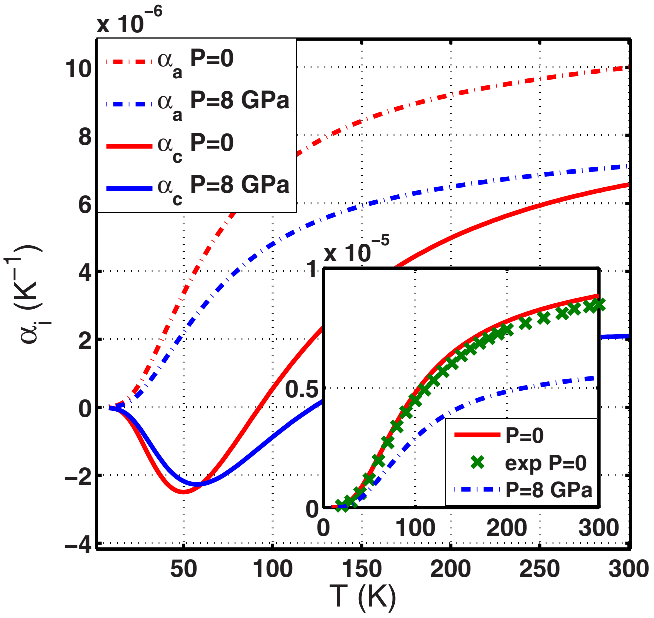

FIG. 11. The anisotropic thermal expansion coefficients and bulk thermal expansion (inset) of α-titanium at different pressures. The experimental data is taken from Ref. [30].

IV. DISCUSSION

The anomaly of the bulk thermal expansion in silicon was studied by *ab initio* calculations in the QHA. The magnitude and extent of this anomaly obtained are in good agreement with experiments. The origin of the anomaly is clarified by an analysis of the phonon spectra at different volumes and temperatures. It is found that it is due to negative Grüneisen parameter of the low frequency transverse acoustic modes over most of the Brillouin zone. As the temperature is increased, the normal high frequency longitudinal acoustic and optical modes, that have positive Grüneisen parameters, become dominant, thus leading to the disappearance of the anomaly. At the vicinity of the Γ point the behavior is normal at all temperatures, thus the anomalous thermal expansion is not reflected by an anomalous behavior of the elastic constants.

The anisotropic thermal expansion of titanium in the α phase is obtained by similar quasiharmonic calculations. A quantitative comparison to experimental data is complicated by large differences between different experimental studies in the literature even at higher temperatures. Pawar *et al.* [6] reported the values $\alpha_a = 9.5 \times 10^{-6}\ K^{-1}$ and $\alpha_c = 5.6 \times 10^{-6}\ K^{-1}$ in the temperature range of 28–155° C. The values reported by McHargue *et al.* [31] are $\alpha_a = 11 \times 10^{-6}\ K^{-1}$ and $\alpha_c = 8.8 \times 10^{-6}\ K^{-1}$ at $T = 25$–255° C. These coefficients were measured also by Nizhankovskii *et al.* [5], who reported a value of $18 \times 10^{-6}\ K^{-1}$ for α_a at room temperature, which is very different from other experimental studies. In addition, they reported the value $10 \times 10^{-6}\ K^{-1}$ for α_c. There is also a large variation between the calculated values of the thermal expansion coefficients. At room temperature, Souvatzis *et al.* [9] reported values of $\alpha_a = 12 \times 10^{-6}\ K^{-1}$ and $\alpha_c = 2 \times 10^{-6}\ K^{-1}$. Their value for α_c at room temperature is smaller than the value calculated in the present contribution. It should be noted that their calculation was constrained by the use of a relatively small supercell.

Analysis of the phonon spectrum and the derivative of the entropy reveals that an anomaly in a soft transverse acoustic mode at the H point is the main contribution to the anomaly in the derivative of the entropy (Figs. 9 and 10). This again shows that the Γ point is not the dominant region in determining the thermal response even at very low temperatures. Instead, we show that a high symmetry point on the boundary of the Brillouin zone provides the main contribution to the derivative of the entropy that is the origin of the negative thermal expansion along the c axis. This analysis precludes explanations of the negative thermal expansion in terms of the simple Debye model, contrary to suggestions in previous work [9]. In both titanium and silicon, the modes near the Γ point are weakly dependent on compression, compared to points on the boundary of the Brillouin zone. Their contribution to the thermal expansion is thus negligible.

It should be noted that the measured phonon spectra of titanium [32] does not include the H point. Thus, the present conclusion could not be obtained by these experimental studies.

Equations (4) and (5) show that the anomaly in the anisotropic thermal expansion can arise from two sources: first, the derivatives of the entropy with respect to the lattice parameters, $\partial S/\partial a$ and $\partial S/\partial c$, might be negative, and second, the coupling coefficients A_{ac}/A_{cc} and A_{ac}/A_{aa} might be large enough to give a negative thermal expansion even when both directional derivatives of the entropy are positive. This is in contrast to the isotropic case, Eq. (1), where a negative derivative of the entropy is a necessary condition for negative thermal expansion. The first source is determined mostly by the phonons and the second one is determined mostly by the second derivative, with respect to the lattice parameters, of the total energy. In other words, it is determined by the c/a anisotropy and tilt of the total energy surface. Generally speaking, it turns out that negative thermal expansion along one of the axes should be observed in anisotropic materials where $S_a > S_c$ and the coupling coefficient is positive and not too small.

Nizhankovskii *et al.* [5] and Souvatzis *et al.* [9] found an electronic topological transition (ETT) in titanium under anisotropic deformation near zero pressure. Souvatzis *et al.* showed that this ETT occurs on a point between Γ and A on the edge of the IBZ. We find the locus of this ETT, on the same point in the Brillouin zone, in the (a,c) plane, as shown by black solid lines in Fig. 12. The band structure at two representative points in the two different zones is shown in Fig. 13. Figure 12 shows that the ETT affects the frequencies between Γ and A, as expected because these modes are in the same direction as the ETT. In contrast, the frequencies at the H point do not exhibit the same effect. Thus the ETT present in α-titanium between the Γ and A points is not related to the anomaly in the anisotropic thermal expansion.

The low frequency degenerate acoustic normal mode at the H symmetry point dominates the anomalous thermodynamic behavior and can be further understood by considering the motion of the atoms in this mode. Based on the phonon polarizations obtained in our calculations we determined the nature of this mode, which is neither pure transverse nor

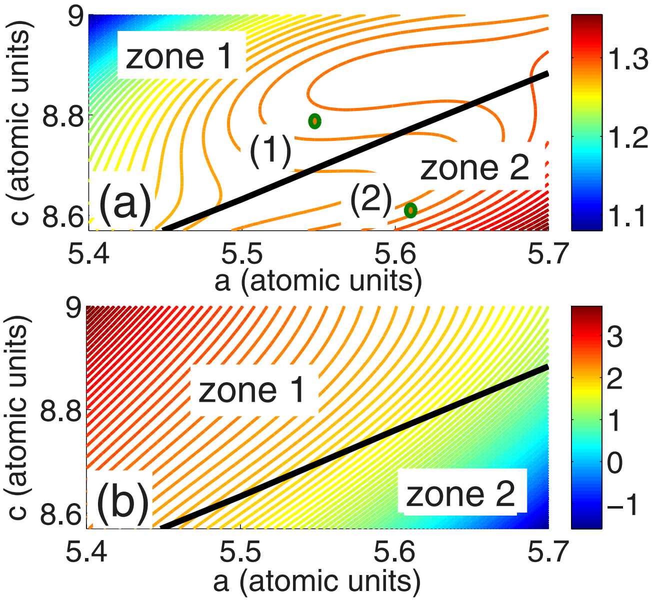

FIG. 12. Isofrequency curves at (a) a point on the acoustic branch between Γ and A on the surface of the IBZ of titanium and (b) at the H point. The solid black lines are the loci of the electronic topological transition. The points (1) and (2) in (a) correspond to the band structures shown in Fig. 13. The negative values in (b) show that the structure loses its mechanical stability under large enough compression along the c axis or expansion along the a axis.

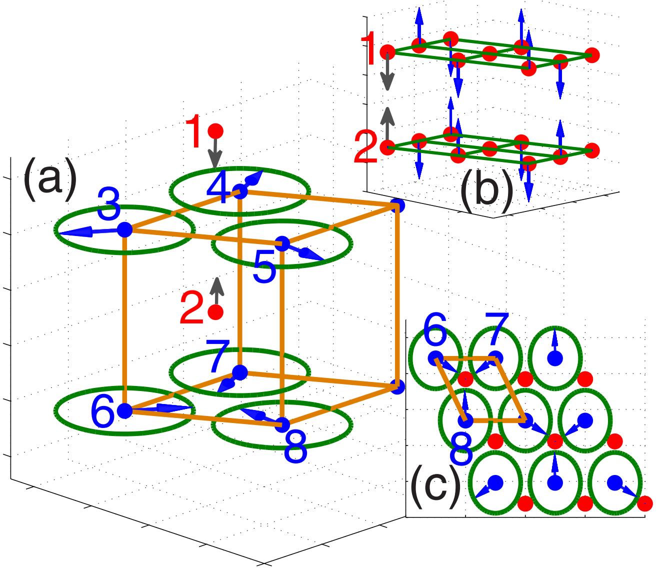

FIG. 14. Illustration of the acoustic mode with the lowest frequency at the H symmetry point. The blue and red dots represent the ideal atomic positions without vibrations at alternating basal planes. The blue arrows denote the direction of the instantaneous displacements of the atoms in this mode and the black arrows show the direction of the velocity of atoms 1 and 2, which are at their equilibrium position at the same instant. The blue atoms have a circular polarization in the basal plane with orbits denoted by green circles. The red atoms have a linear polarization in the z direction (perpendicular to the basal plane). (a) One primitive unit cell with one atom outside of it (atom 1). (b) Two parallel basal planes with red atoms shown. The green lines are a guide to the eye. (c) Top view of two adjacent basal planes denoted by red and blue atoms. At the instant depicted, triplets of blue atoms such as 6–8 are at their maximal contraction, and atoms 1 and 2 are in their ideal atomic positions [as are all the atoms on the basal diagonal in (b)].

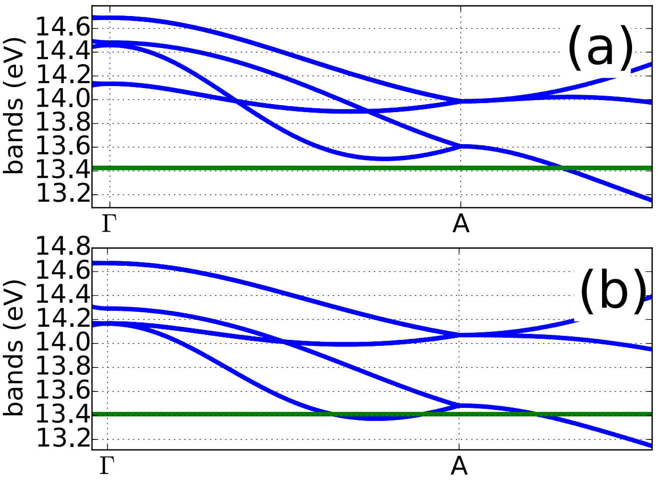

FIG. 13. α-titanium band structure at points (1) and (2) marked in Fig. 12(a). The green line marks the Fermi level.

pure longitudinal but is a mixed mode. The periodicity of this mode, on the corner of the Brillouin zone, requires a 36 atom supercell, spanning 3 unit cells along the two equivalent hexagonal directions and 2 unit cells along the z axis. Figure 14 presents a snapshot of the atomic motion in this mode. In the Supplemental Material [33] we present a movie of the complex vibrational motion in this mode. The hcp lattice consists of a two-atom basis, each of which forms a set of (001) planes. In the vibrational mode considered one plane of atoms (e.g., atoms 1 and 2 in Fig. 14) has only vertical (c-axis) motion and the other plane of atoms move only on the plane, contracting (atoms 6–8) or expanding (atoms 3–5) locally. In this mode, atoms (such as 1 and 2) that vibrate only perpendicular to the basal plane move towards lower density regions as the triangle formed by atoms 3–5 is expanding. In contrast, the triangle formed by atoms 6–8 is contracting and atom 2 is moving away from it.

The mode with the highest frequency at the H point is very similar to the mode with the lowest frequency shown in Fig. 14, but atoms of type 1 and 2 move in the opposite phase. The consequence of this phase shift is that the red atoms move in the opposite direction to that shown in Fig. 14, towards positions with high density. The frequency of this mode is higher by approximately a factor of 4 from the low frequency mode due to the excess repulsion from the contraction in the neighboring plane.

The geometry of this mode can also explain the anomaly of the anisotropic Grüneisen parameter in the z direction. Considering only the planes of atoms having vertical motion in this mode, shown in Fig. 14(b), we see that this is a shearing (bond-bending) mode. As the c lattice parameter decreases, the interactions between nearest neighbors in this plane are screened by the atoms in the alternate hcp planes, weakening the interaction and reducing the frequency, thus leading to the anisotropic Grüneisen parameter anomaly. In addition, as the c lattice parameter decreases, the component of the motion in the direction perpendicular to the chemical bond of the atoms denoted by 2 in Fig. 14 becomes larger, which signifies bond bending. We note that bond-bending geometrical explanations of negative thermal expansion are present in the literature, e.g., for silicon [21], which has a cubic structure.

V. SUMMARY

In the present work we show, by a detailed analysis of the phonon spectra, that the negative Grüneisen parameter of specific phonon modes located on the boundaries of the Brillouin zone is the origin of the negative thermal expansion in both titanium and silicon. In silicon, the negative Grüneisen parameters appear at low frequencies in the transverse acoustic modes over most of the Brillouin zone, except in the vicinity of the Γ point, and gradually turn positive with increasing temperature. In contrast, in titanium, the negative Grüneisen parameters are localized in the vicinity of the H point, the farthest point from Γ on the boundary of the Brillouin zone. In both materials it is thus found that the elastic modes do not contribute to the thermal anomalies even at low temperatures.

The phonon spectra of titanium have not yet been measured in the vicinity of the H point and verifying our prediction would thus be an interesting experimental challenge. According to this prediction, the negative anisotropic thermal expansion in titanium is unrelated to the ETT in the $\Gamma \rightarrow A$ direction, as previously conjectured, since this transition does not affect the phonon spectrum in the region of negative Grüneisen parameters near the H point.

The anisotropic negative thermal expansion in the c direction in titanium extends beyond the temperature range of the negative directional derivative of the entropy due to the thermoelastic coupling between the two directional derivatives of the entropy. This coupling may give rise to a negative thermal expansion along one of the principal axes even when none of the directional derivatives of the entropy is negative. Such conditions may be easily fulfilled in anisotropic materials. This raises the prospect that anisotropic negative thermal expansion is not a rare phenomenon in anisotropic materials at low temperatures. The scarcity of reports of such behavior may therefore simply reflect gaps in the experimental studies on these materials.

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