Local Bond Average for the Thermally Induced Lattice Expansion

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An approach of local bond average (LBA) has been developed by extending the bond-order-length-strength correlation (Sun, C. Q. Prog. Solid State Chem. 2007, 35, 1–159) to temperature domain for the mechanism of the thermally driven bond expansion in a solid specimen. It is shown that the detectable quantities of a solid can be connected directly to the bonding identities and the response of the bonding identities to the stimulus of temperature change, being free from using the concepts in classical thermodynamics or hypothetical constants. The success of the LBA approach has been evidenced by fitting the observations from a number of specimens with derived information of atomic cohesive energy, which may go beyond the currently available approaches.

I. Introduction

Thermal expansion coefficient (TEC or α(t)) is one of the key parameters in material science, which is of great importance to the performance of a material for devices or engineering structures with temperature variation. For example, when a sample layer is grown on a substrate, residual stresses can be built up at the interface between the film and the substrate because of the TECs mismatch.1,2 Likewise, the thermal stress can also be developed in the sample during annealing3 and hence affects the performance of the devices.4 The TECs of different materials have been well studied experimentally during the past decades; however, even for the same material such as diamond,5–8 silicon,9–12 and GaN,13–16 the available experimental data was found to be scattered significantly depending on the measuring techniques and processes.

The mechanism behind the temperature dependence of the lattice thermal expansion has long been a puzzle despite various sophisticated modeling considerations.17–20 From microscopic point of view, the temperature dependence of the bond relaxation is usually attributed to the anharmonicity of the interatomic potential. The T-dependent trends of the TECs have been found analogous to the temperature dependent profiles for specific heat,14,19,21 and they have been described by a number of models,13,18,21–24 from the perspectives of classical thermodynamics and lattice quantum vibrations, as summarized in eq 1 where $A_n$, $B_n$, $X_n$, and $\theta_i$ are adjusting parameters for best fitting to the measurement; $B_0$ and $V_0$ are the bulk modulus and the volume, respectively; $\gamma_n$ is the mode Grüneneisen parameter, and $\xi = \hbar \omega_n/k_B T; \theta(\theta_B T)$ is the Debye function given by $f(\chi) = 3/x^3 \exp(x) - 1$.14 Numerically, all the models could reproduce the general trends of the measured temperature dependence of the TECs despite the adjustable parameters needing physical indication. As indicated by Brulex21 and Garai,22 the temperature dependent bond length $l$ could be well fitted by a polynomial $\sum \delta A_i l^{\alpha_i}$, and hence the TECs could be represented by a polynomial empirically.5,21,22 The observed TECs sometimes could also be fitted using exponential terms.12,22 The ab initio method, which computed the total energy for the equilibrium and distorted atomic configuration, was also used to calculate the temperature dependent TECs for Al and W, with the involvement of bulk modulus, mode Grüneneisen constant, and the concave parameter as adjustable variables.24 Phenomenological lattice dynamics theory in quasiharmonic approximation is also well applied to describe the temperature dependence of the TECs.19 However, deeper insight into the atomistic origin of the thermal expansion and a unified form of expression remains yet a great challenge. The objective of this work is to show that a simple and straightforward analytical solution can be developed from the perspective of local bond average (LBA) and that the TECs follow closely the temperature dependence of the specific heat without involvement of empirical parameters or concepts in classical thermodynamics.

II. Principle: Local Bond Average

As we know, a piece of solid is formed by numerous atoms with bonds connecting one to another. The interatomic bonding makes the bulk to perform differently from the isolated...
An Approach for Local Bond Average

Figure 1. Comparison of the predictions (curves) to the measured (scattered) temperature dependence of the TECs of (a) AlN, (refs 21), Si,N (ref 21), and GaN (refs 13, 33); (b) Si (refs 4, 11, 12, 18), Ge (ref 34, 35) and Diamond (refs 5, 6, 7, 8, 9, 18); (c) Au, Cu, and Al (ref 36); (d) Ni and Fe (ref 36).

constituent atoms. For a given specimen, no matter whether it is crystal, noncrystal, or with defects or impurities, the nature and the total number of bonds do not change under external stimulus, such as temperature or pressure, before phase transition occurs. However, the length and strength of all the bonds involved will respond to the stimulus. If the functional dependence of a detectable quantity, like the thermal expansion coefficient in current discussion, on the bonding identities (nature, order, length, and strength) is established, one would be able to predict the performance of the solid by focusing on the response of the length and energy of the representative bonds, or their average, to the specified external stimulus. Therefore, the performance of such representative bonds can represent the performance of the specific sites, or their average can represent the performance of the entire body of the specimen. This LBA approach may represent the real situations of measurements or theoretical computations that collect statistical information from large number of bonds of the given specimen. Furthermore, compared with the measurement and numerical computation, the LBA could distinguish the behavior of local bonds at different sites.

Generally, the material dimension expands upon temperature increase. The bond length of a specimen has the following relation with respect to the temperature under consideration,

\[ l = l_0 \left[ 1 + \int_0^T \frac{\alpha(t)}{l_0} \, dt \right] \]  

where \( \alpha(t) \) is the thermal expansion coefficient. From bonding energetics and the LBA point of view, the thermal expansion coefficient \( \alpha(t) \) can be calculated as follows:

\[ \alpha(t) = \frac{1}{l_0} \left( \frac{dl}{dr} \right) = \frac{1}{l_0} \left( \frac{du}{dr} \right) \frac{du}{dr} = -\frac{C_r(t/\theta_D)}{l_0 F(r)} \]  

because \( du/dr = -F(r) > 0 \) and \( du/dr \approx C_r(t/\theta_D) \) where \( u(r) \) is the pairing potential and \( F \) represents the restoring force at a nonequilibrium point when \( r \approx r_0 \). With the Leonard-Jones potential, for instance, the term \(-F(r)\) takes a value from 0 to a positive value of finite small. Since the thermally induced bond expansion deviates from the equilibrium distance by a maximal amount of 3% at the melting point, \( F(r) \) is limited and deviates slightly from the linear relation because of the anharmonic contribution. \( C_r \) is the specific heat per atom, which is assumed to follow Debye model, \( C_r(t) = 9RN_\Lambda d(\theta_D)^2 \int_0^{\theta_D} x^2 \exp(x)/[\exp(x) - 1]^2 \, dx \) or Einstein model, \( C_r(t) = 3RN_\Lambda \theta_E^2/ t^2 \times \exp(\theta_E/t)/[\exp(\theta_E/t) - 1]^2 \). \( \theta_D \) and \( \theta_E \) are the Debye and Einstein temperature, respectively, and \( N_\Lambda \) is the Avogadro's constant. There is no substantial difference between the Debye's and Einstein's approximation of the specific heat numerically. Both models match each other very well at high temperature. It is therefore acceptable to assume the Debye approximation as there exists no better alternatives. The Debye approximation will be used in subsequent discussions. The integration of the specific heat gives the specific internal energy, which rises with temperature due to the thermally excited lattice vibration in all possible phonon modes.

By considering the fact that the product of bond length \( (l_0) \) at 0 K and the force \( F(r) \) is in the dimension of atomic bonding energy, we let \( -l_0 F(r) = A_r(t)E_0(0) \), where \( E_0(0) \) is the intrinsic atomic bonding energy at 0 K, and \( A_r(t) \) is a \( r \)-dependent coefficient similar to \( F(r) \). The \( T \)-dependent TEC can then be rewritten as,

\[ \alpha(t) = -\frac{C_r(t)}{l_0 F(r)} \approx \frac{C_r(t)}{A_r(t)E_0(0)} = A_r(t)C_r(t) \]  

Hence, \( A_r = [-l_0F(r)]^{-1} = [A_r(t)E_0(0)]^{-1} \) is related to the restoring force at nonequilibrium position \( r, F(r) \). In reality, the measurement was conducted under constant pressure. Therefore, the specific heat under constant pressure \( C_p \) should be considered instead. However, for solid state, \( (C_p - C_V)/C_V \approx 3\% \) or less. The replacement of \( C_p \) with \( C_V \) may compensate for the effect of \( F(r) \) linear dependence in the range of 1% lattice expansion. In addition, the \( C_V \) at extremely low temperatures approaches to zero, the contribution of the nonconstant term \( l_0 F(r) \) becomes unapparent.
On the other hand, based on eqs 2 and 4, the bond length $l$ can be expressed as,

$$l = l_0 \exp \left[ A(r) \times \int_0^T C_v(t) \, dt \right]$$  \hspace{1cm} (5)

We have thus derived for the temperature dependence of TEC and thermally induced bond expansion from the perspective of LBA approximation. The only parameter $A(r)$, in unit of (eV/atom)$^{-1}$, is slightly $r$-dependent, being related to the bond energy at equilibrium and determines the slope of the TECs at higher temperature; the Debye temperature, $\theta_D$, determines the width of the shoulder at low temperature in the $R(T)$ curve (See Figure 1).

### III. Results and discussion

Generally, the specific heat approaches a constant at high temperatures. Hence, in order to reproduce the experimentally measured $T$-dependent TECs, first of all, $\alpha(T)$ at high temperature is used to estimate the value of $A$ in eq 4. This $A$ is then used as an initial input in the subsequent fitting iteration. By carefully reproducing the available experimental data, $A$ and $\theta_D$ can be obtained and are tabulated in Table 1 for the samples under consideration. With the obtained $A$ and $\theta_D$, we can also fit the $T$-dependent lattice parameter using eq 5. Fine tuning of $A$ and $\theta_D$ is necessary because of the difference in the data sources and errors in the measurement. The refined $A$ and $\theta_D$ are also given in Table 1 for comparison. The current $\theta_D$ values derived from fitting to the $T$-dependent lattice parameter and $T$-dependent TECs are in nice agreement with the findings of Redor.$^{14}$ As the fitting parameter $A$ relates to $E_B(0)$, it can be obtained from fitting to the temperature dependent Young’s modulus and Raman optical phonon shift.$^{27,28}$ With the given atomic bonding energy $E_B(0)$, the value of $A_1$ can readily be obtained. For example, the $E_B(0)$ was estimated to be 3.58, 2.58, and 6.18 eV for Si, Ge, and diamond,$^{28}$ respectively, and the corresponding $A_1$ values are 0.482, 0.374, and 0.204, meaning that $-F_{0\text{lo}}$ is $A_1$ portion of the atomic bond energy. The $A(r)$ is indeed $r$ insensitive, which may be the compensation for the $C_v$, replacing the $C_p$.

Figure 1 shows the reproduction of the measured temperature dependence of TECs using eq 4 of some specimens. Encouragingly, the current approach covers the general trend for $T$-dependent $R(T)$. Exceedingly good agreement with the measured data has been obtained for AlN, Si$_3$N$_4$, and GaN. However, the observed negative TECs in group IV elements at extremely low temperatures could not be reproducible. Generally, most materials expand upon heating, although very rarely some materials expand upon cooling. The unusual behavior of materials having negative TECs have been considered arising from the negative Grüneisen parameters of the transverse acoustic phonons near the Brillouin-zone boundary.$^{17,18,29}$ In metals, in addition to the phonon contribution to the thermal expansion, free electrons also play a role in $T$-dependent change of lattice constant.$^{30}$ The current model gives better prediction

<table>
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<tr>
<th>Reference</th>
<th>$\theta_D$ (K)</th>
<th>$\alpha(t)$</th>
<th>$\theta_D$ (K)</th>
<th>$A$</th>
<th>$l(t)$</th>
<th>$l_0$ (Å)</th>
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<tr>
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<tr>
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</table>

$^a$ The documented Debye temperature is obtained from ref 32 $^b$ a-axis. $^c$ c-axis.

![Figure 2](image-url)
for the lattice behavior at low temperatures than that at high temperatures for some pure metals, such as Au, Cu, and Al. The TECs of these pure metals still keep increasing with temperature even at very high temperature \( T \gg \theta_b \). This deviation may arise from the thermal contribution from electrons. For the ferromagnetic Ni and Fe, the measured TECs exhibit an abrupt feature at the Curie temperature \( T_c \), which corresponds to a phase transition from ferromagnetic to paramagnetic, and this abrupt feature may arise from spin contribution to the specific heat.\(^\text{31}\) It is not surprising that these unexpected features are beyond the scope of the current model because we used an ideal case of the phonon density-of-states derived from long wavelength at the Brillion zone center and only the phonon contribution is considered. The contribution from electrons, spins, or phase transition is not included. The Debye approximation of the specific heat assumes that the phonon density-of-states in an elastic medium is ideally proportional to \( \omega^2 \). In reality, one has to consider the exact form of the phonon density-of-states that is a quantity of measurement using neutron diffraction, and it is beyond the scope of theory.\(^\text{17}\) Nevertheless, the phonon contribution to the thermal properties is dominant, and a precise prediction of the \( T \)-dependent TECs can be made if the exact density-of-states \( g(\omega) \) vs \( \omega \) is given. The reproduction of the general trend of \( T \)-dependent TECs may provide evidence that the validity of the current LBA approach in describing the thermally induced bond expansion.

Figure 2 shows the reproduction of the \( T \)-dependent lattice parameters of various materials. The fact that much better match of the lattice constants compared to the match of the TECs for the same elements indicate that experimental errors can not be ignored in practice. The agreement of the LBA approach to the available experimental data justifies the validity of the LBA approach and the assumption of the slight \( r \)-dependent on \( A(r) \). The derived form is numerically consistent with most of the existing models.\(^\text{14,19,21}\) If the Einstein’s model of specific heat is applied, the exponential terms in Reeber’s model\(^\text{13}\) can be obtained. If the exponential term is expanded in Taylor’s sour, the temperature dependent polynomial TECs is quite obvious.\(^\text{21,22}\) Therefore, with the current justification, the previous models discussed\(^\text{23-24}\) are all numerically correct.

IV. Conclusion

An approach of local bond average has led to an improved understanding of the temperature dependence of the TECs that follow closely the general trend of the specific heat of a solid. The slopes of the TECs at high temperature are related to the atomic cohesive energy. No concepts in classical thermodynamics are involved. Neither the bulk modulus nor the Grüneisen parameter is needed in the current LBA approach. Exceedingly good agreement to the measured TECs for nitrides and the general trends for metals and diamond structures may provide evidence that LBA approach and our modeling considerations can predict the true situation of observations, though refinement can be made by using the real phonon density-of-states for a particular specimen.

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Note Added in Proof. While proofing this article, we have become aware of the measurement\(^\text{28}\) of the size dependence of the thermal expansion of Ni bulk and Ni nanowire array, showing that the interatomic distance of Ni bulk increases more rapidly with temperature than the wires, indicating the stronger bond of the less-coordinated atoms in the nanowires. This finding provides further evidence for the BOLS theory, indicating that if one bond breaks, the remaining ones will be shorter and stronger.

Note Added after ASAP Publication. This paper was published ASAP on June 12, 2008. Equation 2 was changed. The revised paper was reposted on June 19, 2008.

References and Notes


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