Temperature dependence of the elastic and vibronic behavior of Si, Ge, and diamond crystals

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The thermally induced softening of the elastic and vibronic identities in crystals and their correlations have long been a puzzle. Analytical solutions have been developed, showing that the detectable elastic and vibronic properties could be related directly to the bonding parameters, such as bond length and strength, and their response to the temperature change. Reproduction of measured T-dependent Young’s modulus and Raman shift of Si, Ge, and diamond reveals that the thermally driven softening of the elasticity and the optical Raman frequency arises from bond expansion and vibration, with derived information about the atomic cohesive energy and clarification of their interdependence. © 2007 American Institute of Physics.

I. INTRODUCTION

The elastic and vibronic behavior of a bond in a specimen is of fundamental significance to the processes such as electron-phonon coupling, phonon-phonon interaction, phonon transport and thermal conductivity in addition to the thermal stability of engineering materials. Better understanding of the thermally induced elastic and vibronic behavior is fundamentally important to materials science. However, the correlation between the elastic modulus and the vibronic frequency and the mechanism behind the thermally driven softening of these physical quantities upon the increase of temperature of measurement have long been a puzzle. For example, the thermally induced softening of Young’s modulus was attributed to anharmonic effects of the lattice vibrations and expressed in the following semiempirical models:2–5

\[
\Delta Y(T) = \frac{-A_0T \exp(-\theta_0/T)}{Y(0)} - \frac{3R\gamma\delta T}{Y_0V_0}H(T/\theta_0) \quad \text{(Wachtman et al.)}
\]

\[
\Delta \omega(T) = \frac{\Delta \omega_0}{\omega_0} = \Delta_1(T) + \Delta_2(T) + \Delta_3(T) + \Delta_4(T),
\]

where \(Y(0)\) is Young’s modulus measured at 0 K. The constants \(A_0\) and \(\theta_0\) are temperature independent parameters for data fitting. In Anderson’s model, \(R\) is the ideal gas constant, \(\theta_0\) is the Debye temperature, \(V_0\) is the specific volume per average atom at 0 K, \(\gamma\) is the Grüneisen parameter, and \(\delta\) is a parameter analog to \(\gamma\). The product \(\gamma\delta\) is assumed to be temperature independent. Anderson’s model in Eq. (1) satisfies Nernst’s theorem that the temperature derivatives of the elastic constants must vanish at 0 K. The model of Wachtman et al. describes well the elastic behavior at high temperature, whereas Anderson’s model could reproduce the measured \(Y(T)\) curves reasonably well at the whole temperature range by taking the \(\gamma\delta\) as an adjusting parameter.

The thermally softened Raman optical mode was attributed to the anharmonic-phonon decay to the third order in addition to the effects of thermal expansion and/or interface effect, as shown by

\[
\Delta_1(T) = A_1 \left[ 1 + \frac{1}{e^x - 1} \right] \quad \text{(anharmonic-phonon decay)},
\]

where \(x\) is

\[
H(T/\theta_0) = 3(T/\theta_0)^3 \int_0^{\theta_0/T} \frac{x^3 dx}{e^x - 1},
\]
\[ \Delta_2(T) = A_2 \left[ 1 + \frac{1}{e^\gamma - 1} + \frac{1}{(e^\gamma - 1)^2} \right] \]  
(high-order-phonon decay),

\[ \Delta_3(T) = \exp \left[ -3 \gamma \int_0^T \alpha(t) \, dt \right] - 1 \]  
(thermal expansion),

\[ \Delta_4(T) = 2 \left( a - b \frac{C_{13}}{C_{33}} \right) \times \left[ 1 + \frac{1}{(1 + e_x) \frac{\alpha_x(t) \, dt}{1 + \alpha_x(t) \, dt}} - 1 \right] \]  
(interface effect),

where \( \omega_0 \) is the specific Raman phonon frequency measured at 0 K, and \( x = \hbar \omega_0 / 2k_B T \) and \( y = 2x / 3 \), which correspond to the third and the fourth order of phonon decay, respectively. The constants \( A_1 \) and \( A_2 \) are freely adjustable parameters for fitting purpose. The \( \gamma_i \) is the mode Grüneisen parameter, \( \alpha(T) \) and \( \alpha_x(T) \) are the coefficients of thermal expansion of the specimen and the substrate, respectively, when the interface interaction is involved. \( e_x \) is the residual strain in the sample at the growth temperature \( T_x \). The \( C_{13}/C_{33} \) is the elastic constant ratio of the 13 and 33 elements in the elastic tensor. The parameters \( a \) and \( b \) in \( \Delta_4 \) are phonon deformation potentials.\(^{15} \) The sophisticated models could reproduce the temperature dependence of the softening of Raman optical modes at the expense of increasing the number of adjustable parameters.

However, the atomistic origin of the temperature dependence of Young’s modulus and Raman frequency shift remains yet unclear. It seems that the elastic modulus and the vibronic frequency are independent of each other. Here, we present an analytical solution to correlate the elastic modulus and vibration frequency as well as their temperature dependence. Agreement between the predictions and the measured temperature dependence of the elastic modulus and vibronic frequency of Si, Ge, and diamond samples reveals that the thermal softening of Young’s modulus and optical Raman phonon frequency arises from bond expansion and bond vibration with derived information about the atomic cohesive energy.

\[ Y(0) \propto \frac{E_B(0)}{d^3(0)}, \quad \omega(0) \propto \left[ \frac{zE_B(0)}{m^*} \right]^{1/2}, \]  
(3)

where \( m^* \) is the reduced mass of the pair of bonding atoms. By using the core-shell configuration for nanostructures, this approach has allowed us to reproduce the size dependence of elastic modulus of ZnO and polymers\(^{18} \) and the size-dependent optical frequency shift in the Raman spectrum with derived information on the vibration frequency of an isolated dimer in InP, CeO2, SnO2, CdS, and Si nanostructures at temperature far below the melting point.\(^{17} \)

Considering the effect of thermal expansion and the bond energy weakening due to vibration, the atomic bonding energy \( E_B(T) \) and the bond length \( d(T) \) follow the relations

\[ E_B(T) = E_B(0) - \int_0^T C_v(t) \, dt, \]

\[ d(T) = d_0 \left[ 1 + \int_0^T \alpha(t) \, dt \right], \]  
(4)

where \( \alpha(t) \) is the temperature dependent thermal expansion coefficient. \( d_0 \) and \( E_B(0) \) is the bond length and atomic bond energy at 0 K, respectively. The specific heat \( C_v(T) \) and the integration of \( C_v(t) \) from 0 K up to \( T \) or the conventionally termed specific internal energy \( U(T/T_{\theta_B}) \) follow the relations

\[ C_v(T/T_{\theta_B}) = 9R(T/T_{\theta_B})^3 \int_0^{\theta_B T} x^4 \exp(x) \frac{dx}{(e^x - 1)^2}, \]

\[ U(T/T_{\theta_B}) = \int_0^T C_v(t) \, dt = 9R(T/T_{\theta_B})^3 \int_0^{\theta_B T} \frac{x^3 \, dx}{e^x - 1} = 3TH(T/T_{\theta_B}). \]  
(5)

By extending Eq. (3) to temperature domain, it gives

\[ \frac{Y(T)}{Y(0)} = \left[ 1 + \int_0^T \alpha(t) \, dt \right]^{-3} \left[ 1 - \int_0^T \frac{C_v(t) \, dt}{E_B(0)} \right], \]

\[ \frac{\omega(T)}{\omega(0)} = \left[ 1 + \int_0^T \alpha(t) \, dt \right]^{-1} \left[ 1 - \int_0^T \frac{C_v(t) \, dt}{E_B(0)} \right]^{1/2}, \]  
(6)
TABLE I. List of the input data, such as melting temperature \( T_m \), the Debye temperature \( \theta_D \), \( T \)-dependent thermal expansion coefficient \( \alpha(T) \), and the derived atomistic cohesive energy \( E_p(0) \) from fitting to the temperature dependence of \( Y \) and \( \omega \) for Si, Ge, and diamond.

<table>
<thead>
<tr>
<th></th>
<th>( T_m ) (K)</th>
<th>( \theta_D ) (K)</th>
<th>( \alpha(T) ) (Ref.)</th>
<th>( E_p(0) ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Raman ( Y )</td>
</tr>
<tr>
<td>Si</td>
<td>1647</td>
<td>647</td>
<td>29</td>
<td>2.83</td>
</tr>
<tr>
<td>Ge</td>
<td>1210</td>
<td>360</td>
<td>30</td>
<td>2.52</td>
</tr>
<tr>
<td>C</td>
<td>3820</td>
<td>1860</td>
<td>31</td>
<td>6.64</td>
</tr>
</tbody>
</table>

with \( E_p(0) \) being the only fitting parameter for both the \( Y(T) \) and \( \omega(T) \).\(^{20}\) For the same material and the same coordination environment, the relative \( Y \) relates to the relative \( \omega \) in the form of

\[
\frac{Y(T)}{Y(0)} = \left[ \frac{\omega(T)}{\omega(0)} \right]^2 / \left[ 1 + \int_0^T \alpha(t) dt \right] \equiv \left[ \frac{\omega(T)}{\omega(0)} \right]^2 . \tag{7}
\]

III. RESULTS AND DISCUSSIONS

In calculations, the melting temperature \( T_m \), Debye temperature \( \theta_D \), and the \( T \)-dependent thermal expansion coefficient \( \alpha(T) \) are taken as the known data for input with derived value of \( E_p(0) \) as output, and these data are tabulated in Table I. We selected a few sets of experimental data for the optical Raman shift of Si, Ge, and diamond and Young’s modulus of Si, Ge, and diamond, and normalized them with the extrapolated values to the \( T=0 \) K. Experimental observation shows that Young’s modulus and Raman frequency shift decrease linearly with increasing \( T \) at a higher temperature. When \( T \gg \theta_D \), the specific heat \( C_v \) can be considered as a constant approaching \( 3R \), and since the thermal expansion coefficient \( \alpha \) is normally in a range of \( 10^{-6} \), \( 1+\alpha T \) can be ignored in rough calculation. Hence, when \( T \gg \theta_D \), Eq. (6) can be simplified as

FIG. 1. Agreement between predictions and the measured temperature dependence of the relative Raman frequency shift and Young’s modulus of Ge [(a) and (b)], Si [(c) and (d)], and diamond [(e) and (f)] with derived information of \( E_p(0) \) given in Table I. Scattered symbols represent experimental data in (a) Ref. 11, (b) Ref. 27, (c) Si 1 (Ref. 26), Si 2 (Ref. 7), and Si 3 (Ref. 11), (d) Ref. 1, (e) diamond 1 (Ref. 22), diamond 2 (Ref. 23), diamond 3 (Ref. 24), and diamond 4 (Ref. 25), and (f) Ref. 28.
I. The literature data for atomic cohesive energy possible with caution of measurement of pure samples. For instance, in Fig. 1 small values because of the iteration of refinement and it can be further refined by carefully fitting the experimental data at the whole temperature range with the consideration of the $T$-dependent thermal expansion coefficient. The $T$-dependent thermal expansion coefficient for Si is $\alpha(T) = (3.725 \times 10^{-3})T + 5.548 \times 10^{-3}T - 6.05 \times 10^{-6} + 34.22 \times 10^{-9}T - 7.795 \times 10^{-6} exp(-0.003528T)$ (fitting to Ref. 31) in unit of $K^{-1}$.

Figure 1 shows the agreement between theoretical predictions and the measured temperature dependence of Raman shifts and Young’s modulus with derived data given in Table I. The literature data for atomic cohesive energy $E_B(0)$ from Kittel are also listed in Table I for comparison. The slow decrease of $\omega$ and $Y$ at very low temperatures arises from the smaller $\int_0^T \Delta E_B(t)dt$ values because of the $T^3$ approximation at low $T$. The difference in the $E_B(0)$ values in Table I, derived from Young’s modulus measurement and from Raman spectroscopy, is subject to the accuracy of measurement. This difference shows the sensitivity of this approach and extra caution is needed in calibrating the equipment and collecting the data. One needs to note that artifacts in experiment such as the defect, crystal orientation, and even the measurement method used may affect the accuracy of experimental data and, hence, this approach provides the estimated $E_B(0)$ values. Furthermore, this method is very sensitive to the experimental data obtained. For instance, in Fig. 1(e), the atomic cohesive energy obtained from Ref. 23 is about 30% larger than that obtained from Ref. 22. High accuracy would be possible with caution of measurement of pure samples.

IV. CONCLUSION

In conclusion, we have presented simple and straightforward analytical solutions from the perspective of bonding energetics to describe the temperature dependence of thermally driven softening of Young’s modulus and optical Raman frequency shift and their interdependence. We have clarified the correlation between the elasticity and the vibronic frequency of atomic bonds in a specimen. Exceedingly good agreement between the measured $T$-dependent Young’s modulus and Raman shift of Si, Ge, and diamond with the current approach has led to estimated information about the atomic cohesive energy, which is beyond the scope of conventional approaches. The agreement between calculation and experimental data without involving other freely adjustable parameters may demonstrate that the current expression could represent the true situation of the thermally driven softening of Young’s modulus and Raman frequency shift, which may extend to other thermally induced property change such as mechanical strength, photoluminescence, etc.