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HARMONIC AND ANHARMONIC PROPERTIES OF SILICON

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Abstract.—Silicon has interesting harmonic and anharmonic properties such as the low-lying transverse acoustic modes at the X and L points of the Brillouin zone, negative Gruneisen parameters, negative thermal expansion and anomalous acoustic attenuation. In an attempt to understand these properties, we have developed a lattice dynamical model for silicon employing long-range, non-local, dipole-dipole interactions. Several interesting features of this interaction are found and discussed. We present analytic expressions for the Gruneisen parameters that explain how the negative Gruneisen parameters arise. Application of this model to the calculation of the thermal expansion of silicon is made.

It is well known that comparatively long range interactions are necessary to explain the elastic constants as well as the low-lying TA[100] and [111] modes in silicon. Several models have been developed to explain this behavior. Attempts \(^1,2\) to compute anharmonic properties have utilized first neighbor anharmonicity or first and second neighbor anharmonicity, one of the authors\(^2\) concluding that this was sufficient to explain the mode Gruneisen parameters and thermal expansion coefficient. That this is not the case can be seen from the fact that the Gruneisen parameters for these models are in major disagreement with experiment for several modes.

The model we use employs first thru fourth neighbor central potentials, nearest neighbor angle bending and displacement induced non-local dipoles. An interesting feature of the non-local dipole interaction is that it does not affect the elastic constants or the Raman frequency. This is in contrast to the local quadrupoles used by Lax.\(^3\)

A ten independent parameter preliminary fit of our model to the experimental data is shown in Fig. 1. The major feature of this dipole model is the dramatic lowering of the TA modes at the X point.

Proceeding to the anharmonic properties, we note that silicon has negative thermal expansion and thus negative Gruneisen parameters for some modes. The volume thermal expansion coefficient is given to
lowest order in the anharmonicity by
\[
\alpha = \frac{1}{B V_0} \sum_k n_k \gamma(k_k) C_B(\omega(k_k)) \tag{1}
\]

Here \(B\) is the bulk modulus, \(V_0\) the volume of the bare crystal, \(\omega(k_k)\) the bare harmonic frequency, \(C_B(\omega)\) is the Einstein specific heat function and \(\gamma(k_k)\) the mode Gruneisen parameter.

To illustrate the origin of the negative mode gammas, consider the analytic expressions we have found at the X point.

\[
\gamma_{\text{TAX}} = -\frac{1}{3 M \omega_{\text{TAX}}} \left[ \frac{2 \phi'_1(r_0) - 2 \phi'_1(r_0)}{r_0} + 2 r_2 \phi''_2(r_2) + 6 \phi''_2(r_2)
\right.
\]
\[
- \frac{6 \phi'_2(r_2)}{r_2} + \frac{32}{11} r_3 \phi''_3(r_3) + \frac{34}{11} \phi''_3(r_3)
\]
\[
- \frac{34 \phi'_3(r_3)}{11 r_3} + 6 \sigma(1)
\]
\[
- \frac{16 \pi}{\varepsilon_3} (16.28143)(p_1 - p_2)(p_1^{(1)} - p_2^{(1)})
\]
\[
(2a)
\]

\[
\gamma_{\text{TOX}} = -\frac{1}{3 M \omega_{\text{TOX}}} \left[ \frac{4 r_0 \phi'_1(r_0) - 2 \phi''_1(r_0)}{3 r_0} - \frac{2 \phi'_1(r_0)}{3 r_0}
\right.
\]
\[
\left. + 2 r_2 \phi''_2(r_2) + 6 \phi''_2(r_2)
\right]
\[
+ \frac{6 \phi'_2(r_2)}{r_2} + \frac{12}{11} r_3 \phi''_3(r_3)
\]
\[
+ \frac{54}{11} \phi'_3(r_3) - \frac{54 \phi'_3(r_3)}{11 r_3} + 2 \sigma(1)
\]
\[
\left. + \frac{16 \pi}{\varepsilon_3} (10.76338)(p_1 + p_2)(p_1^{(1)} + p_2^{(1)})
\right]
\]
\[
(2b)
\]

In Eqs. (2) \(a\) is the conventional cube edge, \(\varepsilon\) the static dielectric constant, \(p_1\) and \(p_2\) are harmonic dipole parameters, \(p_1^{(1)}\) and \(p_2^{(1)}\) are anharmonic dipole parameters, \(\sigma^{(1)}\) is an anharmonic angle-bending parameter and \(\phi''_1(r_0), \phi''_1(r_0), \phi''_1(r_0)\) are the derivatives of the
first neighbor potential function etc. The fourth neighbor interaction does not contribute at the X point. The interesting feature of Eqs. (2) is that the nearest neighbor third derivative is not present in Eq. (2a) but is in Eq. (2b). This is the explanation for why the TAX mode has a negative mode gamma and the TOX mode does not. It is due to the fact that the diamond structure has a nearest neighbor central force instability. In fact, it is just those modes that have the instability that exhibit the negative mode gamma. This point has not been recognized in the literature previously. We emphasize again that since $\phi''(r_0)$ is of opposite sign to $\phi_1''(r_0)$, the cancellation of $\phi''_1(r_0)$ in certain modes makes the mode gamma extremely likely to be negative.

A preliminary calculation of the thermal expansion is shown in Fig. 2. In this calculation the four third order potential derivatives were fit to the experimental mode gammas at X, L and the elastic region. The dipole and angle-bending anharmonic parameters were fixed by theoretical considerations.4

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References