

CALCULATION OF LATTICE DYNAMICAL PROPERTIES FROM ELECTRONIC ENERGIES: APPLICATION TO C, Si AND Ge

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It is shown that lattice dynamical properties of insulators can be calculated directly from the electronic band structure using the "special points" method. The shear moduli and zone boundary transverse acoustic phonon frequencies of C, Si and Ge are calculated with no adjustable parameters, with results in reasonable agreement with experiment.

STRUCTURAL PROPERTIES of crystals, i.e. equilibrium positions of the atoms and their restoring forces, are fundamental to an understanding of chemical bonding in solids. Nevertheless, the relations between electronic and structural properties have been analyzed in depth only in nearly-free-electron metals, ionic crystals, and in certain special cases.¹ In other systems vibrational frequencies have been considered only within the content of parameterized models, e.g. the shell model.¹ Such models can describe very general interatomic forces but are difficult to relate to fundamental electronic properties. In this paper we present a procedure for the calculation of some interesting elastic moduli and phonon frequencies directly from electronic interactions. We apply the method to C, Si and Ge using a simple tight-binding Hamiltonian fitted to electronic data.

Our approach is to calculate the total energy of the crystal as a function of the displacement of atoms from their equilibrium positions. The quadratic terms in the variation determine the harmonic restoring forces, etc. Such an approach has been used successfully for molecules,² however, its utility for crystals has been severely limited because of the difficulty in evaluating the total energy with sufficient accuracy.² Recently, however, it has been shown^{3,4} that the total energy of filled bands can be accurately calculated from the energies at a small number of optimally chosen "special points" (SP's) in the Brillouin Zone (BZ). This greatly reduces the computational effort compared to other means of sampling the BZ. Here we apply the special point technique to the calculation of the total electronic energies of distorted crystals. We show that for distortions of high symmetry, e.g., uniform elastic strain or zone boundary phonons, small sets of SP's are sufficient to calculate the electronic contribution to the harmonic restoring forces.

For the undistorted f.c.c. crystal, we use the sets of irreducible SP's containing respectively 1, 2, and 10 points which have been given previously.^{3,4} To generate the sets of SP's for distorted crystals we follow the

general procedure of reference 4. For example, consider the diamond structure crystal in the presence of a TA phonon at the (001) zone boundary (*X* point of the BZ). The translational symmetry of the distorted crystal is that of a tetragonal Bravais lattice, and there are four atoms per primitive cell as shown in Fig. 1. We find the smallest irreducible set of SP's ($k_x, k_y, k_z a/c$) for the distorted crystal to be (in units of $2\pi/a$, with $a = a_0/\sqrt{2}$ where a_0 is the cubic lattice constant and $c = a_0$): (1/8, 1/8, 0.5a/c), (3/8, 3/8, 0.5a/c), (3/8, 1/8, 0.5a/c) and (1/8, 3/8, 0.5a/c) with equal weighting factors of 1/4. If we regard the diamond structure as an undistorted tetragonal lattice ($u = 0$ in Fig. 1) the latter two points become equivalent and only three points are needed for the evaluation of total energies. To check the convergence of our results we have generated larger sets containing 6 and 20 points for $u = 0$ and 8 and 32 points for $u \neq 0$. For other distortions appropriate sets of SP's have been used.

The remarkably rapid convergence of the numerical integrals obtained using the special points can be demonstrated by the calculations described below for Si, with parameters listed in Table 1, column 3. The total energy of the valence bands of the undistorted f.c.c. crystal is found to be -26.603 eV/atom for the 1 point calculation,³ -26.395 for 2 points, and -26.399 for 10 points.⁴ For comparison the energy calculated viewing the undistorted crystal as tetragonal with 4 atoms per cell yields -26.400 ± 0.002 eV/atom for the sets of 3, 6, and 20 SP's. For a TA (100) distortion shown in Fig. 1 with the displacement $|u| = 0.1a$, the change in the total energies is found to be $\Delta E = 0.0903 \pm 0.0002$ eV/atom for 4, 8, and 32 point calculations. These convergence tests show that with small sets of SP's the distortion energies and hence restoring forces can be easily calculated with an accuracy of a few percent.

In order to describe the electronic bands of C, Si, and Ge, we choose a tight-binding Hamiltonian. It has been shown^{5,6} that the valence bands of these crystals

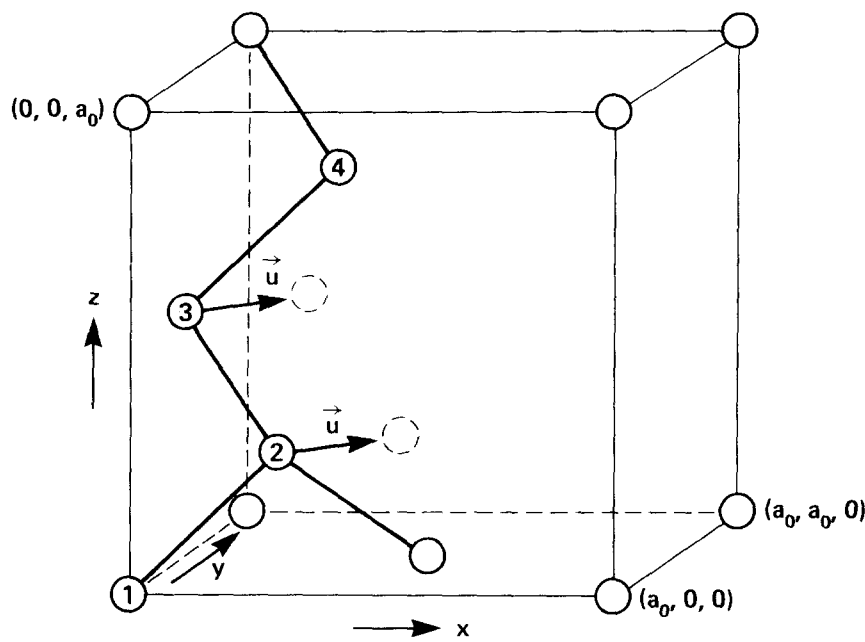


Fig. 1. Displacement pattern of a TA mode at the (100) point (X) for a diamond structure crystal. The periodicity of the distorted crystal may be considered to be simple tetragonal with translation vectors $\mathbf{R}_1 = 1/2(\sqrt{2}, \sqrt{2}, 0)a$, $\mathbf{R}_2 = 1/2(\sqrt{2}, -\sqrt{2}, 0)a$, and $\mathbf{R}_3 = (0, 0, 1)c$, where the a and c parameters are related to the cubic lattice constant a_0 by $c = a_0$, $a = a_0/\sqrt{2}$, and with four atoms per cell as shown. The displacement u is taken parallel to \mathbf{R}_1 in our calculation. For clarity only a few of the atoms in the unit cell are shown.

Table 1. Tight-binding electronic parameters and calculated elastic moduli and zone-boundary phonon frequencies for C, Si and Ge. The experimental values are given in parentheses for comparison. The elastic constant C_{44} is obtained from C_{44}^0 through equation (1) using the experimental values of ζ for Si and Ge (reference 8) and the estimated for C (See reference 8)

	C		Si		Ge
Tight-binding parameters (eV)					
$E_p - E_s$	7.40 ^a	6.70 ^b	7.2 ^a	5.88 ^c	8.41 ^a
$V_{ss\sigma}$	-3.80	-5.55	-2.03	-1.92	-1.70
$V_{sp\sigma}$	4.44	5.91	2.55	1.92	2.30
$V_{pp\sigma}$	4.90	7.78	4.55	1.96	4.07
$V_{pp\pi}$	-1.33	-2.50	-1.09	-0.54	-1.05
Zone boundary frequencies (10^{12} Hz)					
X	20.0	24.5 (24.1 ^d)	6.52	4.85 (4.49 ^e)	3.15 (2.39 ^f)
L	13.3	11.5 (16.6 ^d)	4.72	3.41 (3.43 ^e)	2.44 (1.89 ^f)
Elastic moduli (10^{11} erg/cm ³)					
$C_{11} - C_{12}$	54.8	77.5 (95.1 ^g)	10.81	3.50 (10.21 ^g)	7.85 (8.02 ^g)
C_{44}^0	51.2	74.9	11.58	6.18	9.61
C_{44}	30.9	45.2 (57.6 ^g)	9.43	5.03 (7.96 ^e)	7.83 (6.8 ^g)
R^h	0.81	0.86 (0.68)	0.67	1.15 (0.34)	(0.54)(0.30)

^a From reference 5. ^b See reference 9. ^c From reference 6.

^d WARREN J.L., WENZEL R.G. & YARNELL J.L., *Inelastic Scattering Neutrons*, Vol. 1, p. 361. Proc. Symp. 5th Vienna, Austria 1965 (1966).

^e DOLLING G., *Inelastic Scattering Neutrons Solids Liquids*, p. 37. Proc. Symp. 2nd Chalk River, Can., 1962 (1963).

^f BROCKHOUSE B.N. & DASANNACHARYA B.A., *Solid State Commun.* **1**, 205 (1963).

^g Experimental references given in reference 8.

^h Ratio $R = \{M[\omega_{TA}(X)]^2/2a_0\}/(C_{11} - C_{12})$ discussed in text.

are well described by such a Hamiltonian with s and p atomic basis states with only one-center and two-center nearest-neighbor interactions.⁷ In this case the electronic Hamiltonian is determined by the directions of the first-neighbors relative to the Cartesian frame, the energies E_p and E_s and four first-neighbor interactions $V_{ss\sigma}$, $V_{sp\sigma}$, $V_{pp\sigma}$, and $V_{pp\pi}$.⁷ Within the one- and two-center approximations these parameters depend only upon the nearest-neighbor distance. This simple form for the Hamiltonian is appropriate because it is a prototype Hamiltonian for covalent bonding, and we expect the present conclusions to shed light on the relations of electronic interactions and inter-atomic forces in general covalent systems.

Here we consider only vibrational modes in which the distances between the nearest neighbors do not change. Following the above discussion we assume the tight-binding parameters do not change for such displacements. The change in energy is caused solely by the change in geometry of the atomic environments. With this approximation there are *no free parameters* and all input is from electronic spectra of the perfect crystals. There are three distortions of the diamond structure lattice in which, by symmetry, no bond length are changed: the shear elastic strain for which the elastic constant is $C_{11} - C_{12}$ and the two zone boundary transverse acoustic modes at X and L with frequencies $\omega_{TA}(X)$ and $\omega_{TA}(L)$. We also consider the other shear constant C_{44} , which is not fixed by symmetry since an internal strain is involved.⁸ We define C_{44}^0 to be the shear constant with the constraint that no nearest-neighbor distances change with strain. A correction must be applied to compare with the experimental value of C_{44} , an approximate form⁸ of which is

$$C_{44} = C_{44}^0(1 + \xi)/2, \quad (1)$$

where ξ is the internal strain parameter.⁸

The necessary calculations for $\omega_{TA}(X)$ have been described above. The phonon frequency is given by

$$\Delta E = (1/8)M\omega_{TA}^2(X)u^2, \quad (2)$$

and the resulting frequency is listed in Table 1 for Si as well as for C and Ge. Similar calculations have been carried out to determine $C_{11} - C_{12}$, C_{44}^0 and $\omega_{TA}(L)$. For example, $C_{11} - C_{12}$ is readily determined by using the tetragonal calculation described above with $u = 0$, but changing the c/a ratio from the ideal value of $\sqrt{2}$. The elastic constant is found from

$$\Delta E = (1/48)a_0^3(C_{11} - C_{12})(c/a - \sqrt{2})^2. \quad (3)$$

This shear constant along with C_{44}^0 can also be determined from shear distortions of the tetragonal cell. As an additional check we have calculated two shear constants for a shear normal to the $[111]$ direction and a

uniaxial strain along a $[111]$ axis. The five independent calculations yield consistent results for the two independent shear constants $C_{11} - C_{12}$ and C_{44}^0 within 3%.

The electronic interactions and resulting elastic constants and phonon energies are collected in Table 1 and compared with experimental values. For C and Si we have listed different sets of electronic parameters^{5,6,9} to show the range of results. Table 1 shows that with no adjustable parameters the simple electronic Hamiltonian leads to general overall agreement with experiment. Furthermore the sensitivity is sufficient to use the calculated elastic constants and phonon frequencies to differentiate between different sets of electronic parameters within the simple tight-binding model.

Two features are particularly relevant to our understanding of covalent bonding. First, the shear constant $C_{11} - C_{12}$ has been used by several authors^{8,10} to quantify a scale of covalency and it has been shown that $C_{11} - C_{12}$ varies systematically for the diamond and zincblende structure materials. Here we find that this quantity can be directly determined from an electronic Hamiltonian having a simple chemical bonding interpretation. As shown in Table 1 and verified by systematic variation of the parameters, $C_{11} - C_{12}$ depends primarily upon the σ bonding interactions in agreement with the empirical observations. It is interesting that the two proposed sets of parameters for Si have very different $V_{pp\sigma}$ and $E_p - E_s$. These two sets lead to very similar valence bands, but the parameters of Pandey and Phillips⁶ lead to much lower and narrower conduction bands than the parameters of Chadi and Cohen.⁵ The larger average gap in the latter case is equivalent to the assumption of stronger covalent bonding. We see that it results in higher values for $C_{11} - C_{12}$ which are close to the experimental value. This supports the applicability of suitably chosen simple tight-binding models for these crystals, but investigation with more complicated electronic Hamiltonians will be needed to establish the limits of this approach.

The second feature is the TA frequencies at the zone boundaries, the anomalously low value of which have been the subject of much investigations.^{1,11-14} The most revealing quantity is the ratio $R = \{M[\omega_{TA}(X)]^2/2a_0\}/(C_{11} - C_{12})$. This ratio is 1 in simple bond-bending models^{8,11,12} and the observed deviations from 1 in Si and Ge imply longer range forces. (~ 5 th neighbor¹¹). As shown in Table 1 the calculated values is ~ 1 in diamond in agreement with experiment and is less than 1 in Si and Ge, although not as small as is observed.

We have systematically varied the tight binding parameters and have found that the ratio R depends primarily upon the s - p splitting and the $sp\sigma$ interaction relative to the other σ interactions. Decoupling the s and p states either by decreasing $V_{sp\sigma}$ or by increasing the

splitting $E_p - E_s$ relative to the other bonding interactions leads to a pronounced decrease in this ratio. The effect is evident from comparison to the two calculations for Si. The lowering of the TA frequencies results from the ability of the electronic wave functions to readjust¹⁴ (i.e., rotate and rehybridize) to lower their energy in the presence of a TA distortion. This is a quantum mechanical analog of the readjustment of classical shells or bond

charges¹³ which have previously been used to explain the long-range forces. More detailed investigations of the mechanism for generating these forces and an extension of the calculations to zincblende crystals will be presented elsewhere.¹⁵

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