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Calculation of harmonic and cubic Einstein force constants in diamond-like crystals*

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A theoretical discussion of isotropic and anisotropic single-particle potentials is presented. A model is developed for calculating the constants for diamond-structure carbon, silicon, germanium, and tin. Errors in the isotropic constants are +1%, −34%, −19%, and +35%. For the anisotropic constants errors are +7% and +22% for silicon and germanium. The temperature dependence of the potential constants is discussed through a charge-density theory for stretching force constants in molecules and solids.

I. INTRODUCTION

Valence-force-field constants, which are those familiar to chemists, are the coefficients of a Taylor series wherein the variables are changes in bond lengths and angles. They are obtained by solving the equations of motion according to Wilson's *FG* matrix method.[1] The procedure has been successfully applied to the diamondlike crystals, carbon, silicon, germanium, and tin.[2] The bond-stretching valence-force-field force constants have for these materials been theoretically derived from a charge-density theory.[3,4] In this theory the force constants are dependent on the value of the charge density centered on an atom as evaluated at the nucleus of a neighboring atom. Thermal expansion will stretch the bond and consequently weaken the force constant, which is to be demonstrated in this paper.

Einstein's independent-particle force constants[5] are used in analyzing thermal atomic distributions and play a role in x-ray and neutron-diffraction studies. These force constants occur in Debye-Waller factors,[6] and they have been determined to the harmonic (quadratic) and cubic level for silicon and germanium.[7] Although they were originally believed to be dependent on all first-neighbor and second-neighbor force constants, in the valence-force-field sense,[6] it is found in this paper that for certain modes of vibrations in cubic diamondlike crystals an independent-particle potential may be accurately derived from nearest-neighbor considerations. Because of the dependence of the Einstein force constant on the valence-force-field force constant, the temperature dependence should be similar. This also is to be shown in this paper.

A generalization of the Einstein independent-particle force constant, which was originally, for the purpose of developing a theory of heat capacities in solids, considered to be isotropic, is to include anisotropic higher order terms. This has been necessary to explain (222) reflections of neutrons in silicon and germanium.[7] These reflections would not occur were the atomic distributions isotropic. The neutron structure factor for these materials has a temperature dependence which suggests the anisotropic force constant depends on temperature. Estimates of this constant and its temperature dependence will be made in this paper.

II. VALENCE-FORCE-FIELD AND INDEPENDENT-PARTICLE FORCE CONSTANTS

Let k_R be the valence-force-field bond-stretching harmonic force constant, that is, the bond spring constant. In the diamond lattice a unit cell contains a neighboring pair of atoms. Consider a unit cell $A-B$ with atom A at the coordinate origin and B at equilibrium, a distance R along the [111] direction. On fixing the four neighboring atoms at their equilibrium positions (representing their average locations), and moving A in the [111] direction, the AB bond contributed k_R and each other neighbor contributes $\frac{1}{9}k_R$ to the stretching force constant. The total $\frac{4}{3}k_R$ also holds for displacements of B in the [110] and [100] directions. One might expect the Einstein harmonic force constant is $\frac{4}{3}k_R$, but closer examination shows this is not so. If the unit cell AB is displaced in the [111] direction as a rigid diatomic species, then the restoring force constant is $\frac{2}{3}k_R$, half the previous value. In the [110] and [100] directions it is, respectively, $\frac{4}{3}k_R$ and $2k_R$. Low-energy, and high-displacement acoustic modes contributing heavily to scattering factors will involve superpositions of unit-cell vibrations in all the ⟨111⟩

directions. The effective force constant for each atom is then $\frac{1}{3}k_R$ in each [111] displacement direction. If, then, AB moves as part of a wave in the [111] direction defined above, the restoring force constant on B is a sum of three diatomic contributions. If each of these three diatomic potentials is expanded in a Taylor series in x, y, and z coordinates and only the terms in the symmetry of the crystal are retained, the following formula is obtained:

$$W(R)=\tfrac{1}{2}k_R\,\Delta R^2+\cdots\ , \tag{1a}$$

$$W(R)=\tfrac{1}{6}k_R(x^2+y^2+z^2)-[k_R/(3)^{1/2}R_e](xyz)+\cdots \tag{1b}$$

$$W(R)\equiv\tfrac{1}{2}\alpha(x^2+y^2+z^2)+\beta(xyz)+\cdots\ . \tag{1c}$$

Only terms containing k_R are retained. The contributions of the other valence-force-field constants are small (see Table I) and can be derived by application of the chain rule. Here R_e is the equilibrium nearest-neighbor distance and α and β are the Einstein independent-particle harmonic and cubic force constants. It will soon be seen that while this expansion is not a rigorous derivation of α and β, it gives good estimates of their measured values.

Experimentally, α is determined from the temperature dependence of the intensity of x-ray Bragg reflections.[7,8] In this determination the vibrational frequency spectrum is weighted heavily on the acoustic modes and weakly on the optic modes.[8] For the acoustic modes the two-atom unit cells of the diamond structure move as units to a first approximation, and Eq. (1) is the approximate potential. It should be noted that this potential cannot properly account for lattice dynamics which require third-neighbor interactions,[2] as well as some optical properties. Actual tests of Eq. (1) for α are in Table I. Including the effects of the other bending and stretching harmonic force constants leads to somewhat improved estimates, as is shown in the table. The agreement with experiments supports the moving unit-cell model with only nearest neighbor interactions. Significantly, Eq. (1) gives just as good predictions of the cubic independent-particle force constant β, as determined from the temperature dependence of the anharmonic structure factor for neutrons,

$$F(222)=8ibe^{-M}(2\pi/a)^3(\beta/a^3)hkl(kT)^2\ , \tag{2}$$

where b is nuclear scattering length, M the Debye-Waller factor, a the lattice parameter, hkl the product of Miller indices, and kT the product of Boltzmann's constant with absolute temperature.[7] Equation (2) is derived by taking a classical ensemble average of Eq. (1c).[6]

III. TEMPERATURE DEPENDENCE OF α, β, AND THE $F(222)$ STRUCTURE FACTOR

The Poisson equation for stretching force constants relates them to electronic charge densities of the atoms ρ_a,[3,4]

$$k_R=4\pi Z_b\,\rho_a(R_b)\ , \tag{3}$$

where Z_b is the charge of nucleus b. Generally, ρ_a is approximately proportional to $e^{-\xi R}$:

TABLE I. Predictions of Einstein force constants α and β in Eq. (2) from the valence force field. Theoretical values of k_R are from Ref. 4 and experimental values from Ref. 2.

From	Theoretical k_R	Experimental k_R	Experimental k_R plus others [a]	Experiment
		α (10^{-12} erg/Å^2)		
C	1.24	1.28	1.65	1.635 [b]
Si	0.53	0.49	0.52	0.785 [c]
Ge	0.48	0.43	0.47	0.579 [c]
Sn	0.41	0.32	0.34	0.251 [d]
		$-\beta$ (10^{-12} erg/Å^3)		
C	1.39	1.43	0.49	
Si	0.39	0.36	0.29	0.275 [c]
Ge	0.34	0.31	0.24	0.20 [c]
Sn	0.25	0.20	0.17	

[a] This includes contributions from the other stretching and bending valence-force-field constants as taken from Ref. 2. These include $k_{RR'}$, $k_{\theta\theta}$, $k_{\theta\theta'}$, and $k_{R\theta}$, where θ is the C-C-C angle, and so on for silicon, germanium, and tin.

[b] S. Göttlicher and W. Wölfel, Z. Elektrochem. 63, 891 (1959).

[c] Reference 7 of the text.

[d] D. H. Bilderback and R. Colella, Phys. Rev. B 11, 793 (1975).

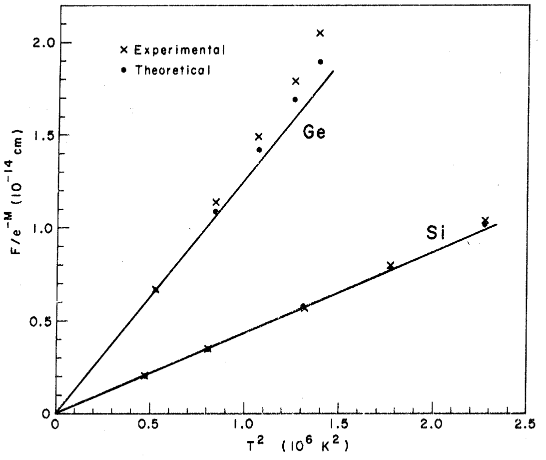

FIG. 1. Experimental and theoretical deviation from the T^2 law for $F(222)$ neutron-diffraction results for Si and Ge. The theoretical points come from Eq. (2) of the text using temperature-dependent formulas Eqs. (6) and (7) and the low-temperature experimental values for α and β. The value for ξ is determined using Eq. (5) and parameters from *Spectroscopic Data Relative to Diatomic Molecules* edited by B. Rosen (Pergamon, Oxford, 1970) for Si and from Ref. 4 of the text for Ge. For Si, $\xi = 3.145$ Å^{-1} and for Ge, $\xi = 5.164$ Å^{-1}.

$$k_R = k_e e^{-\xi(R_e - R_e')} , \tag{4}$$

where

$$\xi = -l_e/k_e - 2/R_e' . \tag{5}$$

Here k_e, l_e, and R_e' are diatomic equilibrium harmonic and cubic force constants and the bond length. Accurate values for k_R can also be calculated from a related molecular-orbital theory.[4]

The temperature dependence of α may be estimated from Eq. (4) for linear thermal expansion according to the formula

$$\alpha(T_2) = \alpha(T_1) e^{-\xi[R_e(T_2) - R_e(T_1)]} , \tag{6}$$

and for β

$$\beta(T_2) = \beta(T_1) e^{-\xi[R_e(T_2) - R_e(T_1)]} [R_e(T_1)/R_e(T_2)] . \tag{7}$$

The neutron scattering results for $F(222)$ in Si and Ge show a deviation from the T^2 dependence given in Eq. (2). When α and β are functions of T in the "quasiharmonic"[6] theory, good fits to experimental data are obtained.[7] On using Eqs. (6) and (7) and expanding $\beta(a_0\alpha)^{-3}$, using the fact[4] that $\xi R_e > 6$, it is seen that $e^M F(222)/T^2$ increases linearly with T. This appears to account in part for the positive curvature in plots of $e^M F(222)$ vs T^2 for Si and Ge.[7] Figure 1 shows the experimental data, the T^2 line, and the points calculated using Eqs. (6) and (7) and experimental values of $\alpha(T_1)$ and $\beta(T_1)$ with $T_1 = 688$ °K for Si and $T_1 = 728$ °K for Ge. The calculated and experimental values are listed in Table II. The fit is improved and the remaining gap between experimental and theoretical points suggests core and bond electronic charge densities may not be constant with temperature. Analysis of x-ray measurements on the (222) reflections in Si and Ge suggests the bond charge density decreases as temperature increases.[7] This is a reasonable state of affairs as the solid expands, but the effects on the neutron structure factor may be somewhat too complicated for the above charge density model which omits contributions, due to charge density relaxations, to α and β.

TABLE II. Calculated and experimental values of the (222) neutron structure factors for silicon and germanium.

		F/e^{-M} (10^{-14} cm)	
	T (°K)	Calc.	Expt.[a]
Si	688	0.204	0.204
	898	0.351	0.354
	1146	0.578	0.562
	1330	0.785	0.796
	1807	1.016	1.040
	1649	1.225	1.296
Ge	728	0.668	0.668
	916	1.09	1.14
	1032	1.42	1.49
	1119	1.69	1.79
	1177	1.89	2.05

[a] Reference 7 of the text.

IV. SUMMARY

A means of calculating harmonic and cubic independent-atom potentials in solids has been presented for diamond structure C, Si, Ge, and Sn. To do this, the harmonic valence-force-field potential is expanded in the symmetry of the crystal. The determination of the harmonic constant in this manner is understandable in terms of the thermal motions of unit cells in the solids. The effects of thermal expansion on the Poisson equation for valence stretching force constants from atomic electronic charge densities allows for an understanding of part of the deviation of the neutron structure factor $F(222)$ from T^2 dependence. The remaining component of the deviation probably comes from the temperature dependence of electronic density in the solids and the resulting influence on α and β.

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