Photoelastic Tensor of Silicon and the Volume Dependence of the Average Gap

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The first accurate measurements of the algebraic values of the photoelastic tensor of silicon are reported. The values, determined acousto-optically, are $p_{1111} = -0.094$, $p_{1122} = +0.017$, and $p_{1212} = -0.051$. The results are in strong disagreement with calculations based on the Phillips–Van Vechten theory of ionicity. It is shown that the widely used assumption of a universal power law describing both the intermaterial and intramaterial variations of the homopolar average energy gap with volume must be reinterpreted or revised.

Several recent theories[1-3] describing the properties of tetrahedrally coordinated solids rely on phenomenological arguments relating band parameters to interatomic spacing. The assumption is frequently made that a universal functional dependence exists which describes variations not only from material to material but also for a given material under pressure.[4,3-5] The photoelastic coefficients of silicon, a prototypical homopolar material, provide an accurate and direct test which demonstrates that the assumed bond length dependence is in fact different for intermaterial and intramaterial variation.

I have chosen to treat in particular here the widely known Phillips–Van Vechten (PVV) theory of ionicity.[1] This theory has been used and is being extended to explain various aspects of solids such as atomic coordination, trends in piezoelectric coefficients,[4] ratios of bond-bending to bond-stretching force constants,[6] nonlinear optical susceptibilities,[7] etc. The theory rests on several critical assumptions. Phillips[8] has argued that the nearly free-electron, isotropic, two-band Penn model[9] for the electronic band structure can be used to describe diamond-, zinc-blende-, and wurtzite-type crystals. The dielectric function for this model in the low-optical-energy limit is given by

$$\epsilon_1(0) = 1 + (4\pi n e^2 \hbar^2 / m E_g^2)(1 - B + \tfrac{1}{3}B^2), \qquad (1)$$

where $B = E_g/4E_F$, E_F is the Fermi energy, and e, n, and m are the free electron charge, number density, and mass, respectively. PVV further assumed that the average energy gap E_g can be symmetrically separated into a homopolar part E_h and a heterpolar part C, such that

$$E_g^2 = E_h^2 + C^2. \qquad (2)$$

Based on the calculations of Cohen and Bergstresser[10] PVV concluded that E_h is a function only of

the interatomic spacing r. Finally, it was postulated that there exists a universal power-law dependence of E_h on r,

$$E_h \propto r^{-s}. \qquad (3)$$

For diamond and silicon, $C \equiv 0$ and $E_g = E_h$. From the assumptions above, then, the index s can be determined by plotting E_g versus r for diamond and silicon. The result is $s = 2.48$. PVV have explicitly assumed that Eq. (3) is valid not only from material to material, but also for a single material when r is scaled incrementally. Van Vechten[1] calculated dn/dP for silicon based on the above assumptions and found excellent agreement with the hydrostatic measurements of Cardona, Paul, and Brooks.[11] The possible error in the data of Cardona, Paul, and Brooks was estimated to be 67%. In this paper I report on accurate acousto-optic measurements of the photoelastic tensor of silicon, which are capable of checking the theory much more precisely. My data are in strong disagreement with those of Cardona, Paul, and Brooks and indicate that the assumed intramaterial variation of E_h is incorrect.

The photoelastic tensor (p) is defined by the relation between particle displacement gradients[12] (e) and the changes induced in the optical dielectric tensor (ϵ),

$$\Delta \epsilon_{ij}^{-1} = \sum_{j,\,l} p_{ijkl} e_{kl}. \qquad (4)$$

For a material having cubic symmetry there are three independent photoelastic coefficients p_{1111}, p_{1122}, and p_{1212}. The linear combination $\bar{p} \equiv p_{1111} + 2p_{1122}$ is the effective coefficient relating the change in the dielectric constant to a hydrostatic strain. From the PVV theory [neglecting changes in B, Eq. (1)] one obtains for silicon (or dia-

mond)

$$\bar{p} = \frac{-1}{\epsilon} \frac{d \ln \epsilon}{d \ln r} = \frac{\epsilon - 1}{\epsilon^2} (3 - 2s). \tag{5}$$

The change in the optical dielectric constant here arises from the strain-induced changes in the electron density (i.e., change in unit cell volume) and in the average gap. (We might note here that a simple derivation of $\bar{p}$ from a Drude expression for the dielectric constant gives the same form when the change in E_g with strain is replaced by the change in molecular polarizability.) A similar expression relates $\bar{p}$ and the strain-induced change in the bonding-antibonding level splitting in Harrison's[3] tight-binding bond-orbital model.

The magnitudes of the photoelastic coefficients were measured by a technique similar to the Dixon-Cohen method.[13] An acoustic pulse 0.5 μsec wide having a carrier frequency of 225 MHz was transmitted into a reference material (fused silica) and thence into a 1-cm cube of silicon. Light from a helium-neon laser having a wavelength of 0.6328 μm was Bragg diffracted by the acoustic pulse in the fused silica into a silicon photodiode detector. Light from a helium-neon laser at 3.39 μm was similarly diffracted in the silicon and detected by a calibrated room-temperature InAs photodiode. The Bragg-diffracted intensity I_1 divided by the intensity of the light transmitted when the acoustic pulse is not in the beam, I, is given by[14]

$$\hat{I} \equiv \frac{I_1}{I} = \sin^2 \left[\frac{\pi^2}{2\lambda_0^2} \left(\frac{L}{H} \right) \frac{p^2 n^6}{\rho v^3} P_{ac} \right]^{1/2}, \tag{6}$$

where λ_0 is the light wavelength in vacuum, n the refractive index, ρ the density, v the acoustic velocity, P_{ac} the total acoustic power, L the length of the transducer in the direction of light propagation, H the height of the transducer normal to the light beam, and p the photoelastic coefficient for the given crystal orientation and acoustic and optical polarizations. The transducer was a 3-mm square of 35°-rotated Y-cut, 25-MHz fundamental, LiNbO$_3$. The aspect ratio L/H is therefore constant as the pulse propagates and spreads. [One must be careful to generate pulses which are spatially longer in both materials than the light beam width (1 mm).] The factor of λ_0^{-2} in Eq. (6) reduces the diffraction efficiency greatly. It was necessary in two cases, and therefore for consistency in all cases, to use boxcar integration to measure peak heights. The intensities of the four pulses corresponding to

the same acoustic pulse propagating from the fused silica into the silicon and then returning were measured. The intensity measurements were "deconvolved" using Eq. (6). The square root of the product of the values in silicon divided by those in fused silica gives[13] the ratio of $n^6 p^2/\rho v^3$ in silicon to the known value[15] in fused silica. Inserting the known values of n, ρ, and v gives finally the value of p.

Two anti-reflection-coated cubes of silicon (high-purity p-type, 54-Ω-cm resistivity) were used, each x-ray oriented to better than half a degree. One cube had all (100) faces; the second had (111) and (11$\bar{2}$) faces. Four redundant measurements were made. In the first cube for longitudinal-mode acoustic pulses propagating in the [001] direction and light propagating along [010], the experiment with light polarized along [001] gives a value for p_{1111}; with light polarized along [100] one obtains p_{1122}. In the second cube for a longitudinal mode propagating along [111] and light propagating along [11$\bar{2}$], one obtains for light polarized along [111], $p_{1111}' \equiv \frac{1}{3}(p_{1111} + 2p_{1122} + 4p_{1212})$; and finally with light polarized normal to [111], $p_{1122}' \equiv \frac{1}{3}(p_{1111} + 2p_{1122} - 2p_{1212})$. By measuring the polarization of the diffracted light for light incident at 45° with respect to the acoustic propagation direction, it was found that $p_{1111}/p_{1122} < 0$ and $p_{1111}'/p_{1122}' < 0$. The absolute signs of the photoelastic coefficients were determined by acoustic photoelastic refraction.[16] The experimental values of p, n, ρ, and v for silicon and fused silica are listed in Table I. Reproducibility of measurements was accurate to 2%. For $\bar{p}$ and p_{1212} agreement between values determined from different orientations was better than 5%. I believe that 5% represents the magnitude of the possible error in the measurements. A transverse acoustic pulse was transmitted along [001] as a check. The value of p_{1212} determined agreed with the previously mentioned measurements within 4%.

Several related measurements in the literature can be compared with the results of this study. The previously mentioned measurements[11] of dn/dP under hydrostatic pressure imply a value of $\bar{p} = -0.150$. Vetter[17] performed a more accurate static measurement from which one obtains $\bar{p} = -0.070$. Pedinoff and Seguin[18] used an acoustic method with no reference material. They had a combined experimental error (measurement error plus possible systematic error) of about 40%. Their values (magnitudes only) were $|p_{1111}| = 0.08$, $|p_{1122}| = 0.01$, and $|p_{1212}| = 0.07$, in fair agreement

TABLE I. Summary of photoelastic coefficients and material parameters of silicon and fused silica.

	$\bar{p}$	p_{1111}	p_{1122}	p_{1212}	n	ρ (g/cm^3)	$v_{\text{long}}^{[001]}$	$v_{\text{long}}^{[111]}$	$v_{\text{trans}}^{[001]}$ (10^5 cm/sec)
Silicon	-0.059 ± 0.003	-0.094 ± 0.005	$+0.017 \pm 0.001$	-0.051 ± 0.002	3.430[b]	2.328[c]	8.433[d]	9.356[d]	5.845[d]
Fused silica		$+0.121$[a]	$+0.271$[a]	-0.075[a]	1.457[a]	2.201	5.965[e]	5.965[e]	3.768[e]

[a] Ref. 15.

[b] C. D. Salzberg and J. J. Villa, J. Opt. Soc. Amer. **47**, 244 (1957).

[c] *Crystal Data Determinative Tables*, edited by J. D. H. Donnay (American Crystallography Association, Oak Ridge, Tenn., 1963).

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with our data. From piezobirefringence measurements one can derive values for $p_{1111} - p_{1122}$ and p_{1212}. Extrapolating the data of Nikitenko and Martynenko[19] to 3.39 μm gives $p_{1111} - p_{1122} = -0.154$ and $p_{1212} = -0.077$. More sophisticated measurements[20] imply $p_{1111} - p_{1122} = -0.118$ and $p_{1212} = -0.048$, in quite good agreement with our data.

The theoretical prediction, Eq. (5), gives a value of $\bar{p} = -0.153$. My experimental value of $\bar{p}$ is -0.059. This would imply a value of $s = 1.88 \pm 0.01$. There clearly is a difference in the functional dependence of E_h on r between going from diamond to silicon and simply straining silicon. Results in other areas (e.g., positron annihilation in alkali metals[21] and phonon frequency variation in semiconductors[22]) display possibly analogous behavior. The difference here could arise in several ways. It could be that a simple power-law fit of $E_h(r)$ to diamond and silicon is incorrect when extended to other materials. Or it could be that Eq. (3) is correct as a parametrization of E_h for different materials at zero pressure, and that the intermaterial and intramaterial variations may just be different. One does not expect *a priori* that it is, in fact, a universal function. On the other hand, it is possible that the intermaterial and intramaterial variations are in general quite similar, as has been assumed; and the difference here may be more a manifestation of the different cores of diamond and silicon. If you squeeze silicon until it has the same spacing as diamond, you do not have diamond! In fact you would most likely have a more polarizable (smaller E_h) material than diamond. Similarly we expect that the variation of E_h with r is smaller between materials having the same cores than with different cores. For isoelectronically related materials we might therefore expect the variation to be quite similar

to the strain dependence of the elemental material.

It should be noted that Eq. (1) is valid only for a one-gap model and for $\hbar\omega \ll E_g$. Because the lowest direct gap in silicon is 3.3 eV and my measurements are made at 0.37 eV, I assume that dispersion in $\bar{p}$ as $\lambda \to \infty$ should be small. Also extrapolation of the measurements of Refs. 17, 19, and 20 indicate negligible dispersion in the photoelastic coefficients below 0.37 eV. (I plan to measure p at 1.08 eV in the near future.)

For completeness I mention here that Van Vechten has also compared the theoretical and experimental values of $d\ln(\epsilon)/d\ln(r)$ for diamond and germanium and found good agreement. For several reasons the comparison made cannot be accepted. First, experimental measurements of $d\ln(\epsilon)/dP$ in diamond vary widely because of experimental difficulties and/or strong impurity effects. The data of Gibbs and Hill,[23] chosen for the comparison, were obtained from capacitance measurements yielding a value of $d\ln(\epsilon)/dP = (-1.07 \pm 0.09) \times 10^{-7}$ cm^2/kg. Ramachandran[24] measured the changes at optical frequencies and found $d\ln(\epsilon)/dP = (-0.56 \pm 0.08) \times 10^{-7}$ cm^2/kg. Measurements of the elastic properties also vary widely. Van Vechten used the bulk modulus determined by Bhagavantam and Bhimasenachar,[25] $k = 5.77 \times 10^{12}$ dyn/cm^2, which is 30% larger than the more recent, ultrasonic datum, $k = 4.42 \times 10^{12}$, of McSkimin and Bond.[26] (Note: Van Vechten inadvertently cited Ref. 26, but used the data of 25.) Using Refs. 23 and 25, a value for $d\ln(\epsilon)/d\ln(r) = +1.85$ was obtained. This implies a value of $s = 2.62$. References 24 and 26 on the other hand give $d\ln(\epsilon)/d\ln(r) = +0.74$ which implies $s = 1.95$ in disagreement with the PVV theory. The comparison of theory and experiment for germanium also is uncertain. The change with strain of the

d-shell correction to the dielectric susceptibility is unknown and represents an added complication and uncertainty in trying to obtain $dE_n/d\ln(r)$. Further the experimental values are again at variance. The data of Cardona, Paul, and Brooks[11] imply a value of $d\ln(\epsilon)/d\ln(r) = +3.16$, whereas the acousto-optic data of Abrams and Pinnow[27] (assuming that p_{1111} and p_{1122}—which have the same sign—are negative) give $d\ln(\epsilon)/d\ln(r) = +11.8$. [Unfortunately, the acousto-optic measurements were made at an acoustic frequency of 20 MHz so that the assumption of Bragg diffraction was incorrect. Without knowing the exact experimental conditions, the size of the error cannot be assessed. The correction would tend to make $d\ln(\epsilon)/d\ln(r)$ somewhat smaller.]

In summary then the value of $\bar{p}$ measured here in silicon is in serious disagreement with the value calculated from the PVV theory and seems to require revision or reinterpretation of the assumptions about the volume dependence of E_h. Further experimental work is needed to clarify the situation in diamond and germanium.

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