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Temperature dependence of the diamagnetic and dielectric susceptibility of silicon*

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We report high-precision measurements of the temperature dependence of the diamagnetic susceptibility, $\chi(T)$, and the temperature derivative of the infrared refractive index dn/dT of Si. A simple Debye-Waller picture accurately predicts the low-temperature behavior of dn/dT. The temperature dependence of dn/dT allows the prediction of the Van Vleck paramagnetic component of the valence-electron susceptibility. The precision of the measurements of $\chi(T)$ and dn/dT is sufficiently high to reveal that our understanding of the temperature dependence of the valence-electron diamagnetic component is incomplete.

I. INTRODUCTION

A chemical-bond description of the electronic properties of solids has recently been utilized to explain trends among families of materials, and may be useful for predicting new materials with unusual properties. This approach yields an overly simplified picture of the electronic structure of solids, but one which is valuable in studying chemical trends and which avoids the computational difficulties of band theory. The chemical-bond theory is most powerful in investigating those properties of solids which are determined predominantly by bonding (local order), as opposed to those determined by the crystal structure (long-range order). In general, properties that result from the average behavior of all the valence electrons in the solid are expected to be determined by short-range order. We can call such properties *chemical-bond properties*.

The first chemical-bond property to be understood and exploited was the electronic contribution to the dielectric susceptibility.[1,2] This property yields information about the strength of the chemical bond simply because stronger bonds are less easily polarized by an electric field. Later, Hudgens, Kastner, and Fritzsche[3] (HKF) showed that a simple chemical-bond model describes the magnetic susceptibility of the A^NB^{8-N} semiconductors (C, Si, Ge, GaAs, and GaP). More recently, Sukhatme and Wolff[4] (SW) and, independently, Chadi, White, and Harrison,[5] showed that the HKF model could be derived using a Hamiltonian similar to those of Hall[6] and Weaire and Thorpe.[7] According to SW, the magnetic susceptibility can be written

$$\chi = \chi_c + \chi_v + \chi_p\,, \tag{1}$$

where χ_c is the diamagnetic susceptibility of the core electrons, and the valence electrons give rise to a diamagnetic term χ_v and a paramagnetic term χ_p.

$$\chi_v = -\frac{Ne^2}{4mc^2}\left(\frac{1}{1+S}\right) \times \sum_{j=1}^{4}\left[\langle r_\perp^2(j)\rangle_{\text{local}} + \langle r_\perp^2(j)\rangle_{\text{overlap}}\right]. \tag{2}$$

Here, $\langle r_\perp^2(j)\rangle_{\text{local}}$ is the matrix element of $(\vec{r}\times\vec{B})^2/B^2$ evaluated for the jth sp^3 orbital on a given site, where $\vec{B}$ is the magnetic field; $\langle r_\perp^2(j)\rangle_{\text{overlap}}$ is the matrix element of $(\vec{r}\times\vec{B})^2/B^2$ between the two orbitals forming the jth bond. N is the number of atoms in the solid. (We will take N to be two times Avogadro's number.) The overlap correction (S) is included explicitly. SW estimate that the $\langle r_\perp^2(j)\rangle_{\text{overlap}}$ term is less than 15% of the $\langle r_\perp^2(j)\rangle_{\text{local}}$ term.

The last contribution in Eq. (1) is the Van Vleck paramagnetism χ_p resulting from virtual magnetic dipole transitions between the valence and conduction bands. SW give

$$\chi_p = \tfrac{1}{2}N(e\hbar/mc)^2[1/(1-S^2)](1/E_g)\,, \tag{3}$$

where $E_g \equiv [2SE_0 + 2|V_2|]/(1-S^2)$ is the energy difference between bonding and antibonding states in the limit that $V_1 = \vec{B} = 0$. Here E_0 is the average energy of an sp^3 orbital, V_2 is the matrix element of the Hamiltonian between the two orbitals forming a bond, and V_1 is the matrix element between two orbitals on the same atom. Equations (1), (2), and (3) represent an expansion in powers of V_1/V_2 in which terms of order $(V_1/V_2)^2$ and higher are omitted.

To compare the SW theory with experiment, one must separate the diamagnetic and paramagnetic contributions to the valence electron susceptibility. This is because for the covalently bonded tetrahedral semiconductors χ_v and χ_p are both large and nearly cancel. Therefore, a theory which adequately predicts the individual terms may yield a total susceptibility in substantial disagreement with experiment. In addition, the individual terms each yield different information about the chemical bonding. χ_v is sensitive to the spatial extent of the valence charge density, whereas χ_p is sensitive to the symmetry of the bonding. Specifically, the factor $\frac{1}{2}$ in Eq. (3) is appropriate only for sp^3 hybridization. (See appendix.)

HKF showed that it is possible to use the weak temperature dependence of the diamagnetism to separate χ_p and χ_v. They assumed that the largest contribution to the temperature dependence arises from the decrease of E_g with increasing T, resulting in larger χ_p. It was expected that the matrix elements of r^2 and of the angular momentum which are involved in χ_v and χ_p, respectively, are less sensitive to T than E_g. This is because these matrix elements measure the spatial extent and symmetry of the wave functions, and wave functions are, in general, less sensitive to perturbations than energies. HKF further assumed that $E_g(T)$ could be extracted from measurements of the temperature dependence of the refractive index, n. In other words, they assumed that the E_g in Eq. (3) is the same as the energy gap in a simplified Penn model for the electronic contribution to the dielectric constant ϵ. For Si, which has no d electrons, this has the form

$$\epsilon = n^2 = 1 + (\hbar\omega_p/E_g)^2\,, \tag{4}$$

where ω_p is the valence-electron plasma frequency, $\omega_p^2 = 4\pi N_v e^2/m$ for valence-electron density N_v. This simplified model for the dielectric constant is obtained using the same assumptions as those leading to the model for χ in Eqs. (2) and (3). Within limits analogous to those leading to Eq. (3), $V_1 = \vec{E} = 0$, where $\vec{E}$ is the electric field; the energy gaps E_g appearing in Eqs. (3) and (4) are the same.

The origin of the temperature dependence of the average gap is itself of some interest. For the most part it arises from the electron-phonon interaction. The temperature variation of E_g has been predicted by Yu and Cardona,[8] (YC) treating the Brooks and Yu theory.[9] A comparison between this prediction and experiment is given in detail in Sec. III.

The results reported by HKF substantially support the assumption that most of the T dependences of χ arise from that of E_g. Indeed, the values of χ_v and χ_p obtained using this assumption for Si are in good agreement with the theoretical calculations of SW. However, the results for diamond, where dE_g/dT is small, could only be explained by assuming that χ_v is also temperature dependent. Since χ_v is proportional to $\langle r^2\rangle$, HKF postulated that $d\ln\chi_v/dT = 2\alpha$, where α is the thermal-expansion coefficient. The precision with which HKF could separate χ_v and χ_p was, however, limited by the precision of published values of dn/dT and thus $\chi_v(T)$ could not be accurately determined. The present measurements were carried out with the aim of improving the precision of the measurements of dn/dT, χ and $d\chi/dT$ for Si, thus determining the temperature dependence of χ_v and χ_p. This allows a stringent test of the simple theories.

II. EXPERIMENTAL DETAILS

The temperature dependence of the refractive index was measured for single-crystal Si (n-type 10^{15} cm^{-3} carriers). The sample (thickness $l = 0.85$ cm) was polished flat and parallel to within a tenth of a wavelength of visible light. Infrared radiation from a He-Ne laser ($\lambda = 3.391$ μm) was passed through the sample and detected with a liquid-nitrogen-cooled InSb detector. The sample was suspended in vacuum on a liquid-nitrogen-cooled cold finger, and the temperature was measured (with an accuracy of ±0.1 K) using a calibrated copper-constantan thermocouple soldered to the sample. Since interference maxima occur wherever $m\lambda = 2nl$, (m is the order of the fringe) dn/dT can be determined by counting fringes:

$$\frac{1}{2\epsilon}\frac{d\epsilon}{dT} = \frac{1}{n}\frac{dn}{dT} = \frac{1}{m}\frac{dm}{dT} - \alpha\,. \tag{5}$$

Using known values[10] of $\alpha(T)$, Eqs. (4) and (5) were used to determine $(\partial E_g/\partial T)_P/E_g$ at temperatures between 77 and 300 K. The temperature derivative E_g can be written

$$\left(\frac{\partial E_g}{\partial T}\right)_P = \left(\frac{\partial E_g}{\partial T}\right)_V - \frac{3\alpha}{\kappa}\left(\frac{\partial E_g}{\partial P}\right)_T\,, \tag{6}$$

where κ is the compressibility, $(\partial E_g/\partial P)_T$ is the pressure derivative of the average gap, and $(\partial E_g/\partial T)_V$ is the electron-phonon interaction. Equation (6) together with Eq. (4), and using $(\partial E_g/\partial P)_T/\kappa = 0.66$,[14] gives

$$\frac{1}{\epsilon - 1}\left(\frac{\partial\epsilon}{\partial T}\right)_P = \left(\frac{\partial\ln\omega_p^2}{\partial T}\right)_P - 2\left(\frac{\partial\ln E_g}{\partial T}\right)_P = -3\alpha - 2\left(\frac{\partial\ln E_g}{\partial T}\right)_P\,, \tag{7}$$

or

$$\frac{1}{E_g}\left(\frac{\partial E_g}{\partial T}\right)_V = 0.5\left\{\alpha - \frac{1}{\epsilon - 1}\left(\frac{\partial\epsilon}{\partial T}\right)_P\right\}, \tag{8}$$

where $\partial\epsilon/\partial T$ is measured at zero pressure. Using the best measurements available for the refractive index[11] ($n = 3.404 \pm 0.004$ at 150 K and $\lambda = 3.4$ μm) and for the density[12] of Si, one finds $\hbar\omega_p = 16.6$ eV and $E_g = 5.1$ eV. Note that this is different from E_g given by Van Vechten[13] for two reasons. First, our E_g is measured at 150 K whereas Van Vechten gives a room-temperature value. Second, Van Vechten uses the full Penn model instead of Eq. (4). The estimated error in $\Delta n/\Delta T$ of the experimental points is 2% for $\Delta T = 3$ K. Previous measurements[14] have precision of

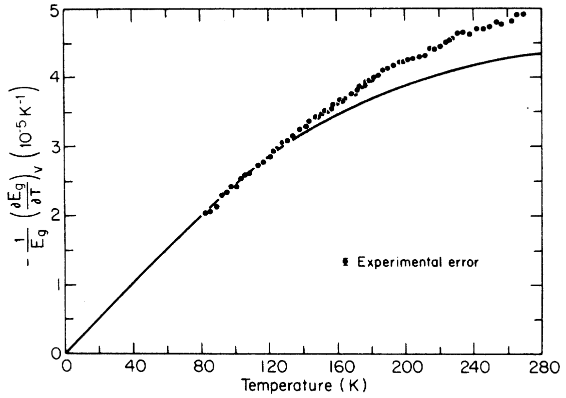

FIG. 1. Logarithmic temperature derivative of E_g at constant volume for Si obtained by using the temperature derivative of the refractive index. Solid curve is predicted by Yu and Cardona using the form of E_g proposed by Heine and Jones. Note the good agreement at low temperature.

only 5 to 10% for $\Delta T \gtrsim 20$ K. Therefore, the data of Fig. 1 represent, by far, the most precise and accurate measurement of the temperature derivative of the refractive index of Si.

The magnetic susceptibility was measured in the temperature range 100 K $\leq T \leq$ 230 K with a Cahn RG[15] electrobalance using the Faraday technique. The total susceptibility χ was determined by calibrating the system with a Ge sample $[\chi = (-1.06 \pm 0.01)\times 10^{-7}\ \mathrm{cm^3/g}]$. The Si sample ($p$-type, 5×10^{15} carriers) was suspended from a fused silica fiber in a liquid-nitrogen-cooled hangdown tube. Thermal coupling was accomplished through conduction in 2 Torr of He gas for some measurements and by radiation cooling for others. For the He-gas system, normal as well as magnetic buoyancy are negligible at this pressure. The effects of thermomolecular flow and convection were eliminated by subtracting force changes observed in zero magnetic field. The temperature of the sample was monitored with a thermocouple placed in close proximity. There was a reproducible temperature gradient between the sample and thermocouple which was calibrated using a sample of MnF_2, an antiferromagnet for which $\chi(T)$ is well known. When measurements were carried out in vacuum, sample temperature was calibrated in the same manner. Furthermore, it was observed that after sufficient time adsorption and desorption effects were negligible. The uncertainty in sample temperature is estimated to be ±0.5 K. The absolute measure of χ is accurate to 0.9%, and the relative error is much smaller, 0.03%. The relative error is three times smaller than the best previous measurement.[16,17] Therefore, the data shown in Fig. 2 are the most precise measurements of the temperature dependence of valence-electron diamagnetism ever reported.

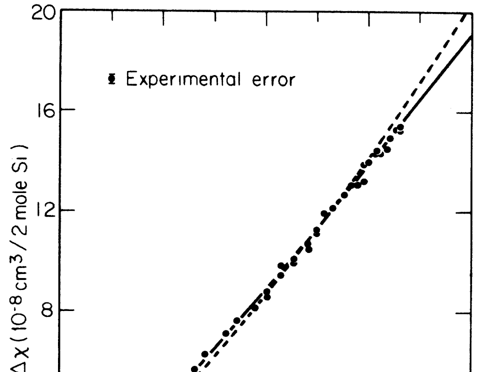

FIG. 2. Variation of magnetic susceptibility of Si with temperature. Solid line is obtained by fitting model described in text to experimental points $[\beta = 7.0,\ \chi_p = 35.6 \times 10^{-6}\ \mathrm{cm^3/(2\ mole\ Si)}]$. Dashed line is prediction of model using theoretical estimate of Sukhatme and Wolff, $\chi_p = 33.2 \times 10^{-6}\ \mathrm{cm^3/(2\ mole\ Si)}$, $(\beta = 2.0)$.

III. DIELECTRIC SUSCEPTIBILITY

Yu and Cardona[8] predicted $(\partial E_g/\partial T)_V/E_g$ using an approximate form of the relationship proposed by Heine and Jones[18] for E_g;

$$E_g \simeq 2[v(111)]^2(a/2\pi)^2\,, \tag{9}$$

where a is the lattice constant in Bohr radii and $v(111)$ is the (111) pseudopotential form factor. Equation (8) is valid in the limit that $v(220) < v(111)$ for homopolar $A^N B^{8-N}$ semiconductors. According to the Brooks-Yu theory all pseudopotential form factors should decrease with increasing T at constant volume. This decrease is described by multiplying by the appropriate Debye-Waller factor, $\exp[-|\vec{g}|^2\langle\vec{u}^2\rangle/6]$. Therefore

$$\frac{1}{E_g}\left(\frac{\partial E_g}{\partial T}\right)_V \cong -\tfrac{1}{3}|\vec{g}(111)|^2\frac{\partial\langle\vec{u}^2\rangle}{\partial T}\,, \tag{10}$$

where $\langle\vec{u}^2\rangle$ is the thermal average of the square of the displacement of an atom from its equilibrium position, and $\vec{g}$ is a reciprocal-lattice vector. Yu and Cardona (YC) evaluated $\langle\vec{u}^2\rangle$ using a Debye model for the phonon spectrum so that the only parameter in the prediction is the Debye temperature, Θ_D, which is taken from heat capacity data. One can show[19] that in the Debye approximation

$$\frac{\partial\langle\vec{u}^2\rangle}{\partial T} = \left(\frac{9\hbar^2}{MkT^2}\right)F\left(\frac{\Theta_D}{T}\right) \tag{11}$$

with

$$F(x)=\frac{1}{x^2}\left(\frac{2}{x}\int_0^x \frac{y\,dy}{e^y-1}-\frac{x}{e^x-1}\right), \qquad (12)$$

where M is the mass of a Si atom.

The solid curve in Fig. 1 is the YC prediction of $(\partial E_g/\partial T)_V/E_g$ with $\Theta_D = 647$ K. In the low T limit, these equations reduce to

$$\frac{1}{E_g}\left(\frac{\partial E_g}{\partial T}\right)_V \simeq -|\vec{g}(111)|^2 \frac{\hbar^2\pi^2}{Mk\Theta_D^3}T. \qquad (13)$$

In this low-temperature regime, the agreement between theory and experiment is surprisingly good. Perhaps the agreement at higher T would be improved by including other pseudopotential form factors which contribute to E_g. More important, however, would be the use of a realistic treatment of the phonon density of states. At ~160 K, where the deviation of theory from experiment becomes apparent, kT is sufficiently large that deviations from the Debye model are important. The room-temperature value of $(\partial E_g/\partial T)_V/E_g$ is close to that[20] of $(\partial E_2/\partial T)_V/E_2$ where E_2 is the largest peak in ϵ_2, the imaginary part of the dielectric function, substantiating the relationship between E_2 and the average gap.[18]

IV. MAGNETIC SUSCEPTIBILITY

The first step in separating the various components in Eq. (1) is the calculation of χ_c. Calculations were carried out for Si^{4+} using a Hartree-Fock-Slater-$X\alpha$ technique. The result is in agreement with earlier calculations,[21] $\chi_c = -4.6\times10^{-6}$ cm^3/(2 mole Si). (All our analysis is done for two moles of Si to facilitate comparison with A^NB^{8-N} compounds.)

HKF assumed that the temperature derivative of χ_v was proportional to α and that $\partial\chi_p/\partial T$ was proportional to $-(\partial E_g/\partial T)_P/E_g$. Then the change of χ between temperature T_0 and some higher temperature T is given approximately by

$$\Delta\chi = \chi(T)-\chi(T_0)$$
$$=\beta\chi_v\int_{T_0}^{T}\alpha(T)dT-\chi_p\int_{T_0}^{T}\frac{1}{E_g}\left(\frac{\partial E_g}{T}\right)_P dT, \qquad (14)$$

where χ_v and χ_p are the average values over the temperature range studied and β is an unknown constant of proportionality $d\ln\chi_v/dT=\beta\alpha$. HKF assumed $\beta=2$. A polynomial was fit to the data of Fig. 1 to make analysis more convenient. It was found that a second-order polynomial fit the data quite accurately in the temperature range of the susceptibility measurements (100–230 K). In this temperature range $\alpha(T)$ increases approximately linearly with T so integrating $\alpha(T)$ is straightforward. Using Eq. (1) we can rewrite Eq. (14) in terms of the two parameters β and χ_p:

$$\Delta\chi=\beta[\chi-\chi_c-\chi_p]\int_{T_0}^{T}\alpha(T)\,dT$$
$$-\chi_p\int_{T_0}^{T}\frac{1}{E_g}\left(\frac{\partial E_g}{\partial T}\right)_P dT, \qquad (15)$$

where the integrals are experimental functions of temperature. χ at 150 K was measured to be $-(6.34\pm0.06)\times10^{-6}$ cm^3/(mole Si), in agreement with the result of HKF.

Several methods of analysis were applied to the data of Fig. 2. First, using the calculation of SW for the average Van Vleck matrix element [the coefficient of $1/E_g$ in Eq. (3)] and $E_g = 5.1$ eV, we compute a theoretical $\chi_p^{\text{th}} = 33.2\times10^{-6}$ cm^3/(2 moles Si). This allowes the determination of β from a least-squares fitting procedure. It was found that $\beta = 2.0\pm0.3$, and the prediction of Eq. (15) for $\Delta\chi(T)$ using this value of β is shown (dashed curve) in Fig. 2. Although the agreement is quite good, there is a small systematic discrepancy between theory and experiment.

A second approach was to allow both χ_p and β to vary. This required a nonlinear regression, and the best fit is given by the solid curve in Fig. 2. For this curve $\beta = 7.0\pm0.5$ and $\chi_p = (35.6\pm0.4)\times10^{-6}$ cm^3/(2 moles Si).[22] As can be seen from the figure, the fit is considerably better for these values of the parameters.

The theory of SW suggests a different analysis of the data. As can be seen from Eq. (2), the temperature dependence of χ_v comes mostly from the temperature dependence of S. This is because $\langle r_\perp^2(j)\rangle_{\text{local}}$ is temperature independent (the orbitals do not vary), and $\langle r_\perp^2(j)\rangle_{\text{overlap}}$ is very small, so its temperature coefficient is negligible. To be consistent, however, one should then consider the temperature dependence of S not only as it effects χ_v, but also χ_p [Eq. (3)]. Differentiating equation (1) and using Eqs. (2) and (3)

$$\frac{d\chi}{dT}=\left[-\frac{1-S}{1+S}(\chi-\chi_c)+\chi_p\right]\left(\frac{S}{1-S}\right)\left(\frac{1}{S}\frac{dS}{dT}\right)-\frac{\chi_p}{E_g}\frac{dE_g}{dT}. \qquad (16)$$

Assuming that S depends only on the bond length b, and using $S = 0.5$ chosen by SW, we have

$$\Delta\chi=\frac{-b}{S}\frac{dS}{db}\left[\tfrac{1}{3}(\chi-\chi_c)+\chi_p\right]\int_{T_0}^{T}\alpha(T)\,dT$$
$$-\chi_p\int_{T_0}^{T}\frac{1}{E_g}\left(\frac{\partial E_g}{\partial T}\right)_P dT. \qquad (17)$$

In this case the nonlinear regression yields $\chi_p = (35.7\pm0.2)\times10^{-6}$ cm^3/(2 mole Si) and

$-(b/S)(dS/db) = 7.4 \pm 0.3$. The fit is indistinguishable from the solid curve in Fig. 2.

V. DISCUSSION

The value of χ_p which best fits the data, $(35.6 \pm 0.2) \times 10^{-6}$ cm^3/(2 mole Si) is close enough to that predicted by SW, 33.2 ± 10^{-6} cm^3/(2 mole Si) that one should consider the agreement excellent. The small difference might arise from differences between the average magnetic and average electric gap. Indeed, it is surprising that one obtains such *good* agreement since the two average gaps are weighted with different matrix elements that connect different valence and conduction states.

Lacking any better model, HKF assumed that χ_v scales with the square of the lattice constant (i.e., $\beta = 2$). This value of β and the value of χ_p predicted by SW, gives a fair estimate of $\Delta\chi$. However, the present experimental data are precise enough to determine that β is actually quite a bit larger than 2. This is surprising since it means that the bond charge seems to be expanding *faster* than the lattice. Si is not a special case in this regard. Recent measurements on alkali halides yield the same result.[23]

Analyzing the data on the basis of the SW theory gives an unexpectedly large value of $-(b/S)(dS/db)$. The fractional change in the overlap is largest when $S = S_0 e^{-b/b_0}$ (i.e., for small overlap) where b_0 is the decay length of the hybrid orbitals. The best fit then yields $b/b_0 = 7.4$, which is surprisingly large. Since $S = 0.5$, one expects a much smaller value. Of course, the $\langle r_\perp^2(j)\rangle_{\text{overlap}}$ term decreases as the lattice expands, so this only makes the situation worse. It is possible that $(1/E_g)(dE_g/dT)$ is different for the magnetic and electric average gaps, but since this electron-phonon interaction depends almost entirely on the properties of the phonons this seems very unlikely. It is also possible that the Van Vleck matrix element varies with with T because of bond-angle fluctuations. However, since large increases with temperature of the diamagnetism have been observed also in alkali halides (for which the Van Vleck term is negligible), it is likely that it is our understanding of χ_v that is deficient. One possibility is that, in addition to the effects of lattice expansion, the electron-phonon interaction affects the wave functions and changes $\langle r^2(j)\rangle_{\text{local}}$ or S. This hypothesis could be checked if one could measure $(\partial\chi/\partial P)_T$ with sufficient precision. Unfortunately, experimental techniques have not yet been devised which will allow these measurements.

The agreement between the simple prediction [Eq. (13)] of $(\partial E_g/\partial T)_V/E_g$ and experiment (Fig. 1) is excellent, and is confirmation of the Brooks-Yu theory. Brooks-Yu suppose that E_g changes with temperature because phonons reduce the long-range correlations in atomic positions. This ties the temperature dependence of E_g to long-range order and suggests that $d\ln E_g/dT$ is not a chemical-bond property, even though E_g itself certainly is. This is clearly seen in Eq. (13) which shows that $d\ln E_g/dT$ depends only on phonon and lattice parameters, whereas E_g itself depends on the electronic structure.

One is then tempted to conclude that $d\ln E_g/dT$ is not a chemical-bond property, but one should examine whether this conclusion is consistent with all available evidence. If loss of long-range order decreases the average gap according to $\exp[-|\vec{g}|^2\langle\vec{u}^2\rangle/6]$, then in amorphous Si where atomic positions are completely uncorrelated one expects a very small value of E_g. However E_g is the *same* to within a few percent in amorphous and crystalline Si.[24] Furthermore, recent measurements[25] show that $d\ln E_g/dT$ is comparable in the amorphous and crystalline phases. These facts suggest that dE_g/dT is in fact a chemical-bond property and that a deeper understanding of the temperature dependence of E_g may be possible. Perhaps a chemical-bond picture can be developed which yields the Brooks-Yu result in the limit of the perfect crystal.

APPENDIX

There is a simple way of predicting the size of the matrix element M in the Van Vleck susceptibility, $\chi_p = M/E_g$, where overlap is neglected. The Van Vleck term arises from the term $-(e/mc)\vec{P}\cdot\vec{A}$ in the Hamiltonian which gives a contribution to the energy in second-order perturbation theory. This contribution is

$$\Delta E = -\frac{e^2B^2}{4m^2c^2}\sum_i \sum_j \frac{\langle i|L_z|j\rangle\langle j|L_z|i\rangle}{E_j - E_i}, \qquad \text{(A1)}$$

where the states $|i\rangle$ are occupied and the states $|j\rangle$ are empty. Most of χ_p, therefore, arises from virtual excitations between filled bonding bands and empty antibonding bands. Replacing the energy denominators by the average gap E_g, and recalling that $\chi = \partial^2E/\partial B^2$, we obtain

$$M = \frac{e^2}{2m^2c^2}\sum_i \sum_j \langle i|L_z|j\rangle\langle j|L_z|i\rangle. \qquad \text{(A2)}$$

We cannot immediately use completeness to reduce this sum to matrix elements of L_z^2 because the states $|j\rangle$ are not a complete set. However, the total of states $|i\rangle$ plus $|j\rangle$ *is* complete. Furthermore, the matrix elements $\langle i|L_z|j\rangle\langle j|L_z|i\rangle$ and $\langle i|L_z|i\rangle\langle i|L_z|i\rangle$ are equal for a given pair of bonds, if we maintain the Weaire-Thorpe[7] criterion that only orbitals on the same site or in the same bond mix. Therefore,

$$M=\frac{e^2}{4m^2c^2}\sum_i \langle i|L_z^2|i\rangle . \qquad \text{(A3)}$$

This is trivial to evaluate. For example, with sp^3 orbitals

$$\langle i|L_z^2|i\rangle=\tfrac{1}{4}\langle S+P_+ +P_- +P_0|L_z^2|S+P_+ +P_- +P_0\rangle , \qquad \text{(A4)}$$

where P_+, P_0, P_- are p states with $L_z = 1, 0,$ and -1, respectively. Therefore, $\langle i|L_z^2|i\rangle=\frac{1}{2}\hbar^2$, and since there are four electrons per atom, for sp^3

$$M=e^2\hbar^2/2mc^2 , \qquad \text{(A5)}$$

as in Eq. (3). For pure p bonding as in amorphous arsenic, one would obtain

$$M=\tfrac{2}{3}(e^2\hbar^2/mc^2) . \qquad \text{(A6)}$$

Similar results can be computed for other hybridizations.

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