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Phonon coupling to core spectra in homopolar semiconductors

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Using the temperature-dependent broadening in silicon soft-x-ray emission, we have made the first measurements of core-hole–phonon coupling in a nonpolar material. This coupling is significantly weaker than in metals and polar insulators. We propose a simple microscopic model appropriate for nonpolar semiconductors which is able to explain the observed weak coupling.

The sudden appearance of the core-hole potential which accompanies an x-ray absorption or emission event produces "shake-up" phonons and plasmons which can alter soft-x-ray emission (SXE) spectra. In this paper we address phonon coupling which produces a broadening of the spectrum that is often described well as Gaussian. There is considerable variation in the coupling strength from one material to another. We shall use the temperature dependence of the broadening to estimate the coupling strength in three classes of materials: metals, polar insulators, and nonpolar insulators. Our temperature-dependent SXE data for silicon are the first measurements of this type in a nonpolar material. We find that the coupling is significantly weaker for this nonpolar material than for either metals or polar materials. As will be shown below, a *microscopic* approach must be used to obtain a reasonable estimate of the coupling strength in nonpolar materials.

Phonons, created in both the absorption and emission process, result in a temperature-dependent broadening of the spectra. For the case of complete relaxation the broadening standard deviation of the phonons (σ_P) is given by[1]

$$\sigma_P^2 = S(\hbar\omega_0)^2 \coth(\hbar\omega_0/2kT) \ . \tag{1}$$

The dimensionless quantity S is the phonon coupling constant and is the average number of phonons of frequency ω_0 created during absorption or emission transitions. In x-ray transitions the excited-state lifetime is often comparable to the phonon period and partial relaxation must be considered. A partial-relaxation theory was developed independently by Almbladh[2] and Mahan[3] and applied to metals. Almbladh has shown that even when partial-relaxation effects are present, if σ_P^2 is plotted against $\coth(\hbar\omega_0/2kT)$ the slope is still equal to $S(\hbar\omega_0)^2$. We have also verified this numerically using Mahan's model. In our analysis we determine the coupling constant by measuring this slope and assuming a single phonon frequency. We assume Gaussian broadening even though for small S this is only approximate.

We have measured the $L_{2,3}$ x-ray emission of undoped crystalline silicon (c-Si) and heavily doped ($n \approx 10^{20}$ cm^{-3}) crystalline silicon (Si:P) at several temperatures. Details of the spectrometer have been described elsewhere.[4] The energy uncertainty was about 0.07 eV and the resolution was 0.1 eV. The samples were unpolished fragments cleaved in air and about 2–3 mm in size. For the high-temperature measurements the samples were mounted in holders made of thin molybdenum sheet. The samples were heated to incandescent temperatures by the electron beam used to excite the x rays (typically 3 keV at 1 mA). For the low-temperature measurements the samples were heat sunk on a cooled sample holder. The low temperature was approximately 250 K. The elevated temperatures of the c-Si sample were measured using an optical pyrometer with an estimated uncertainty of about ±25 K. The evaluated temperature of the Si:P sample was limited to about 870 K to keep the phosphorus from diffusing out.

A simple model was used to fit the data in the valence-band edge and exciton region of the spectrum. The model consisted of a straight line broadened with a Gaussian for the valence-band edge and another Gaussian for the exciton. A spin-orbit core-level splitting of 0.61 eV was used in the fitting function. Figure 1 shows the upper valence band and exciton region of the Si:P emission spectrum. Shown in Fig. 2 is the measured Gaussian broadening (σ^2) plotted as a function of the phonon temperature-dependent factor $\coth(\hbar\omega_0/2kT)$. The measured broadening includes phonon contributions (σ_P) as well as other sources. For the valence band we assume that the temperature dependence is due only to phonons. However, the excitons, in addition to the phonon contribution, also have a nonphonon temperature dependence and are discussed later. Broadening sources which are independent of temperature include finite core lifetimes, instrumental resolution, and in the case of the exciton an unresolved excitonic series. The estimated coupling constants (S) for the valence-band data in Fig. 2 were determined from the slopes using Eq. (1) with an assumed phonon energy of $\hbar\omega_0 = 0.04$ eV. Our choice of ω_0 has been estimated for silicon using the atomic mass and bond-force constant[5] and assuming a breathing mode with only nearest-neighbor interactions. This is approximately the longitudinal-acoustic-phonon frequency at the zone boundary which is reasonable since in the one-dimensional case (with a two-atom basis) that is the breathing mode. Changing $\hbar\omega_0$ by ±0.01 eV changes the resulting coupling constant S by about 30%.

Listed in Table I(a) are the data for the nonpolar materials c-Si, Si:P, and C (diamond). In the case of dia-

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mond, only room-temperature data were available[6] so the resulting value of S is an upper limit. Table I(b) shows similar data for several metals and a polar insulator. Most of these have much larger coupling constants than the nonpolar materials. The Li, Al, and K data are from the SXE work of Tagle, Arakawa, and Callcott;[7] the edge widths (10–90 %) were measured, converted to standard-deviation values, and then the Fermi-Dirac broadening was subtracted. As a measure of the Fermi-Dirac broadening (σ_{FD}) we use the second moment of the derivative of the Fermi-Dirac distribution function $[\sigma_{\mathrm{FD}}=(\pi/\sqrt{3})(kT)]$. The total measured broadening consists of the phonon and Fermi-Dirac contributions and is assumed to be $\sigma^2=\sigma_P^2+\sigma_{\mathrm{FD}}^2$. The Na data are from the inelastic electron scattering results of Slusky *et al.*[8] The KI data are from the temperature-dependent studies of the K $2p_{3/2}$ linewidths of Citrin *et al.*[9]

When the atoms of a metal vibrate, the electron density surrounding the core ion is changing; the binding energy and x-ray transition energies of the core ion are modulated by the phonon vibrations. Phonon couplings in simple metals have been calculated by several authors and in most cases are in reasonable agreement with experiment.[10] The data for the metals in Table I(b) show moderate phonon coupling with S values ranging from about 4 to 15.

The temperature dependence of the core x-ray-photoemission linewidths of potassium halides was studied by Citrin *et al.*[9] They calculated the relaxation energy (ΔE) of neighboring atoms around the core hole using polaron theory. The coupling results from the long-range Coulomb interaction of the core hole with the ionic polarizability of the medium. The coupling constant was obtained by assuming that the relaxation energy appears as S longitudinal-optical phonons of a single frequency (ω_0). Their result is

$$S\hbar\omega_0=\Delta E=e^2\left[\frac{6}{\pi V_m}\right]^{1/3}\left[\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right]. \qquad (2)$$

Here V_m is the primitive cell volume, ϵ_∞ is the high-frequency dielectric constant (electronic polarizability only), and ϵ_0 is the static dielectric constant (electronic and ionic polarizability). Equation (2) predicts $S\approx 40$ for KI. The coupling constant can also be estimated from Eq. (1) using the temperature-dependent x-ray photoemission spectroscopy (XPS) linewidths. Citrin's XPS data for the $2p$ core exciton of KI covering a temperature range of 300–500 K give an S value of about 70. More recently, Mahan[11] has analyzed the Citrin data using a multimode model and obtained closer agreement. Clearly the phonon coupling in polar materials is large.

In the case of nonpolar materials (C and Si) we have found that the phonon coupling is small but nonzero

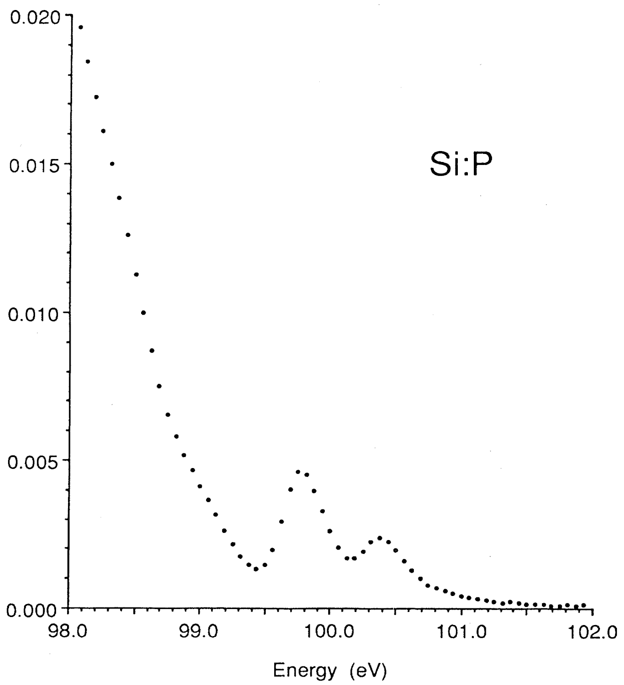

FIG. 1. SXE spectrum of Si:P showing the upper valence band and core exciton. Valence-band area has been normalized to 1. Because of the spin-orbit-split core level there is a slope discontinuity at the band edge (98.8 eV) and the core exciton is seen as two peaks.

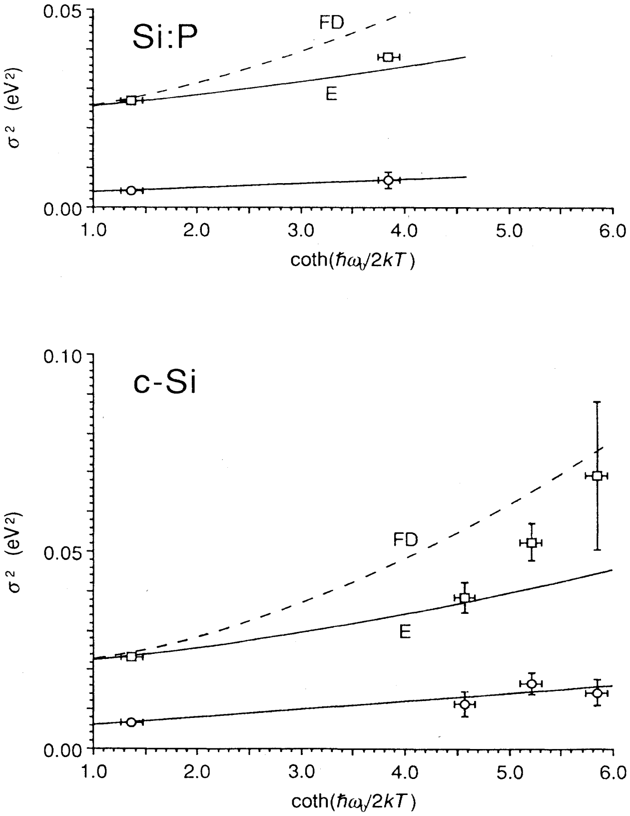

FIG. 2. Temperature-dependent broadening for *c*-Si and Si:P. The phonon coupling constants were determined by a linear fit of the valence-band data (circles) to Eq. (1). The exciton data (squares) are shown with two fitting functions using the calculated exciton broadening (E) and Fermi-Dirac broadening (FD) for the nonphonon temperature dependence.

($S \approx 1$). Although this coupling has been calculated for metals and polar materials, we are not aware of any work on nonpolar materials. Nonpolar coupling is based on the relatively weak interactions between the core hole and the induced dipole moments of surrounding atoms. A simple macroscopic estimate of the relaxation energy based on the dielectric constant and bulk modulus shows that it varies as r^{-5} and most of the coupling comes from the region near the core hole. We therefore must use a microscopic approach and only nearest-neighbor interactions will be considered.

TABLE I. Temperature-dependent phonon broadening data for (a) nonpolar materials and (b) metals and a strongly polar insulator. Data for the *c*-Si and Si:P valence band (VB) indicate a weak phonon coupling; also shown for comparison is the exciton (ex) data. The silicon data are from our SXE measurements and sources for the other data are given in the text.

Sample	T (K)	σ (eV)	$\hbar\omega_0$ (eV)	S
		(a) Nonpolar materials		
C	300	0.096	0.16	0.36
c-Si	250	0.081	0.040	1.3±0.3
(VB)	1043	0.108		
	1193	0.129		
	1343	0.120		
Si:P	250	0.063	0.040	0.7±0.5
(VB)	870	0.083		
c-Si	250	0.153		
(ex)	1043	0.196		
	1193	0.229		
	1343	0.263		
Si:P	250	0.164		
(ex)	870	0.195		
		(b) Metals and polar materials		
Li	80	0.089	0.0205	12.9
	300	0.128		
Na	112	0.017	0.0083	6.9
	300	0.049		
Al	101	0.102	0.0206	3.8
	278	0.104		
	623	0.129		
K	120	0.055	0.0053	14.7
	223	0.069		
	284	0.073		
	317	0.075		
KI	300	0.295	0.0175	71.5
	350	0.310		
	400	0.327		
	450	0.339		
	500	0.356		
	550	0.375		

The core-hole field polarizes and attracts each of the four nearest neighbors with a gradient force given by

$$F_{\mathrm{grad}} = -\frac{\partial}{\partial r}\left[\frac{\alpha E^2}{2}\right] = -\frac{\alpha}{2}\frac{\partial}{\partial r}\left[\frac{e^2}{\epsilon^2 r^4}\right] = \frac{2\alpha e^2}{\epsilon^2 r^5} \ . \qquad (3)$$

In this equation α is the atomic polarizability, E is the field of the core hole, and ϵ is an effective dielectric constant between the core hole and nearest-neighbor atoms. Between the core hole and each neighbor is a bond force which, for small displacements, can be expressed as

$$F_{\mathrm{bond}} = -\frac{\partial}{\partial r}U_{\mathrm{bond}} = -\frac{\partial}{\partial r}\frac{C_0}{2}\left[\frac{r-r_0}{r_0}\right]^2 = \frac{C_0}{r_0^2}(r-r_0) \ . \qquad (4)$$

The equilibrium bond distance is r_0 (2.35 Å), U_{bond} is the bond stress energy, and C_0 is the bond radial force constant which is determined from elastic properties ($C_0 \approx 55$ eV for Si).[5] Equating F_{grad} to F_{bond} and setting $r = r_0$ we find the relative bond strain in the presence of the core hole to be about $0.1/\epsilon^2$. For α we have used a longitudinal bond polarizability obtained by fitting Si phonon data[12] ($\alpha \approx 6$ Å^3). The relaxation energy is the bond stress energy of the four nearest-neighbor bonds for breathing mode phonons and the coupling constant is given by

$$S\hbar\omega_0 = \Delta E = 4\frac{C_0}{2}\left[\frac{0.1}{\epsilon^2}\right]^2 = \frac{1.1}{\epsilon^4} \ . \qquad (5)$$

This weak, short-range interaction involving longitudinal-acoustic phonons is similar to an acoustic polaron.[13] Our measured coupling constant for the *c*-Si valence band is 1.3, which agrees with Eq. (5) if $\epsilon = 2.2$. A reasonable estimate of ϵ is $\epsilon(q)$, where q is the wave vector corresponding to longitudinal-acoustic phonons at the zone boundary ($q \approx 1$ Å^{-1}). Calculations of this quantity range from 2.5–4.5 for silicon.[14] Considering the simplicity of the model these results are not unreasonable. The dielectric constant arises from the polarizability of both the bound valence electrons and free electrons [$\epsilon = 1 + 4\pi(\chi_{\mathrm{bound}} + \chi_{\mathrm{free}})$]. In *c*-Si the concentration of free electrons is mainly from excitations of the incident electron beam and is estimated to be roughly 10^{18} cm^{-3} based on the beam current and carrier lifetimes. Assuming Thomas-Fermi screening by these free electrons[15] ($\epsilon^{\mathrm{TF}} = 1 + 4\pi\chi_{\mathrm{free}} = 1 + k_0^2/q^2$), we obtain $4\pi\chi_{\mathrm{free}} \approx 0.07$ so $4\pi\chi_{\mathrm{bound}}$ must be about 1.13.

The phonon coupling of Si:P is significantly less than that of *c*-Si (see Fig. 2). This can be understood in terms of increased screening in the Si:P sample. The high concentration of free donor electrons in Si:P ($\approx 10^{20}$ cm^{-3}) increases $4\pi\chi_{\mathrm{free}}$ to about 0.35, giving $\epsilon = 2.5$. Equation (5) then gives $S = 0.74$ consistent with the data. Thus using a microscopic description we can understand the observed valence-band coupling constant for *c*-Si and Si:P. The exciton broadening for both *c*-Si and Si:P has a greater temperature dependence than does the valence band and is to be expected. The exciton has an additional nonphonon temperature dependence since the distribution of electron states associated with the exciton includes the bound state as well as electrons thermally excited into the conduction band. The resulting distribution for this bound exciton has a second moment (σ_E) which depends on both temperature and the exciton binding energy. In calculating σ_E the exciton binding energy is assumed to be 0.07 eV, consistent with our earlier work[16] although the result is not very sensitive to the binding energy. The total exciton broadening consists of the phonon and nonphonon contributions ($\sigma^2=\sigma_P^2+\sigma_E^2$) with the phonon contribution being the same as in the valence band. The quantity σ_E is smaller than σ_{FD} for metals. For purposes of comparison, Fig. 2 shows plots of the total broadening calculated using both σ_E and σ_{FD} for the nonphonon temperature dependence; the curves have been adjusted so that they have the same y intercept. The data points generally fall between these two curves.

Based on the equivalent core approximation,[17] Si with a core hole is equivalent to a P atom. The Si—P bond is like a Si—Si (core hole) bond and by the previous arguments should be reduced about 2% from the equilibrium Si—Si bond distance (2.35 Å). An interesting test of this would be to measure the Si—P bond distance in Si:P using extended x-ray-absorption fine-structure spectroscopy.

In conclusion, we have used the temperature dependence of the phonon broadening of x-ray transitions to estimate core-hole phonon coupling constants for a variety of materials. Metals and polar solids have moderate to large coupling constants which can be predicted with models using macroscopic parameters. In contrast, nonpolar solids have weak coupling that can be understood with a simple microscopic model in which the core hole interacts with nearest-neighbor-induced dipole moments. The further reduction in coupling for Si:P can be explained using Thomas-Fermi screening. These results represent the phonon coupling when no other mechanism is present and should be present in all materials.

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