Indirect Energy Gap of ^{13}C Diamond

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(Received 24 May 1990)

Optical-absorption and luminescence measurements on ^{13}C and ^{12}C diamonds establish that the indirect energy gap is 13.6 ± 0.2 meV higher for ^{13}C than for ^{12}C diamond. Zero-parameter calculations, allowing for the changes in electron-phonon coupling and lattice parameter, give an estimated shift of 16.5 ± 2.5 meV.

PACS numbers: 78.20.Dj, 78.55.Hx

In this Letter we report the first measurements of the variation of the electronic energy gap of a semiconductor with its isotropic composition. We show that the indirect electronic energy gap of diamond increases by 13.6 ± 0.2 meV from ^{12}C to ^{13}C. A simple *zero-parameter* calculation shows that the change can be closely accounted for in terms of the isotopically induced changes in the electron-phonon interaction and in the lattice volume.

The ^{13}C diamonds used here were grown from 99% ^{13}C amorphous carbon. The powder was compressed and heated in a vacuum at 1800–2000 °C to remove adsorbed gases. The compressed disk formed the source material in a growth cell using Fe as the solvent catalyst and 1 at.% Zr as a nitrogen getter.[1] Diamonds with diameters of 2 to 3 mm were grown in 18 h at 6 GPa and 1500 °C.

By minimizing the incorporation of nitrogen, the diamonds were optically transparent for photon energies up to the energy gap (which is at 5.47 ± 0.005 eV at 295 K for ^{12}C diamond[2]). Absorption measurements at room temperature and 77 K were made after polishing a pair of parallel optical windows on the samples. Luminescence was generated using 45-keV electron-beam excitations with a beam of typically 10 μA focused to 300 μm diameter and with the samples embedded in indium on a copper cold finger at 77 K. Spectral calibration was checked by superimposing the emission of a Fe-Ne hollow cathode discharge lamp on the measured spectra. The cathodoluminescence spectra have not been corrected for the wavelength-dependent response of the optical system.

Natural diamond is 98.9% ^{12}C and 1.1% ^{13}C. The optical features associated with its indirect energy gap are well known.[2,3] The valence-band maxima are at $k=0$ and are split by a spin-orbit interaction of ≈ 6 meV. The minima in the conduction band lie at wave vectors $k=k_{\min}=0.76 \pm 0.02$ of the $\langle 001 \rangle$ zone boundary. When an electronic transition occurs between the valence- and conduction-band extrema in optical-absorption and luminescence processes, the wave vector is conserved by the emission or absorption of phonons. The peaks labeled *A*, *B*, and *C* in Fig. 1 are due, respectively, to the recombination of a free exciton with the emission of transverse-acoustic, transverse-optic, and longitudinal-optic phonons of wave vector $\pm k_{\min}$ and quanta in ^{12}C diamond of[3]

$$\hbar\omega_{\mathrm{TA}}=87 \pm 2, \quad \hbar\omega_{\mathrm{TO}}=141 \pm 2, \qquad\qquad (1)$$
$$\hbar\omega_{\mathrm{LO}}=163 \pm 1 \text{ meV}.$$

Features B_2 and B_3 are further free-exciton processes involving a TO phonon of $\pm k_{\min}$ plus, respectively, one and two $k=0$ optic phonons. Additionally, luminescence is observed from the decay of excitons bound to effective-mass-like boron acceptors.[4] The natural diamond has an uncompensated boron concentration, determined from Hall-effect measurements,[4] of 5×10^{16} cm^{-3}. The boron concentration in the part of the ^{13}C diamond examined is estimated to be about 3×10^{16} cm^{-3} from the ratio of the intensities of the free- and bound-exciton peaks; this impurity was present as accidental contamination from the growth environment. These impurity concentrations are too small to perturb the crystals' band states. The bound-exciton spectrum is shown in more

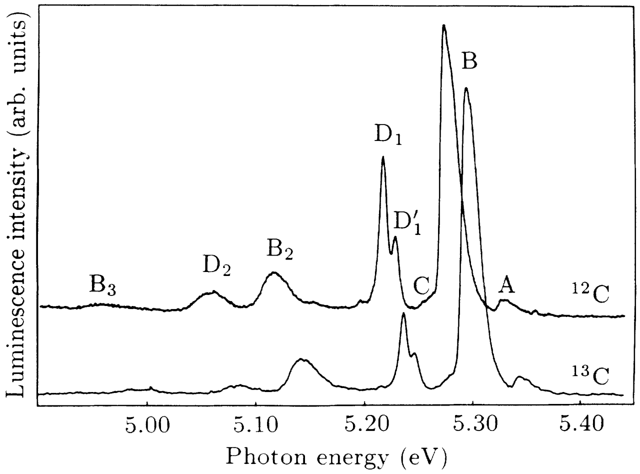

FIG. 1. Spectra measured at 77 K of the phonon-assisted free-exciton cathodoluminescence features (*A*, *B*, and *C*) and the phonon-assisted bound-exciton features (*D*) from a natural semiconducting ^{12}C diamond and a ^{13}C synthetic diamond.

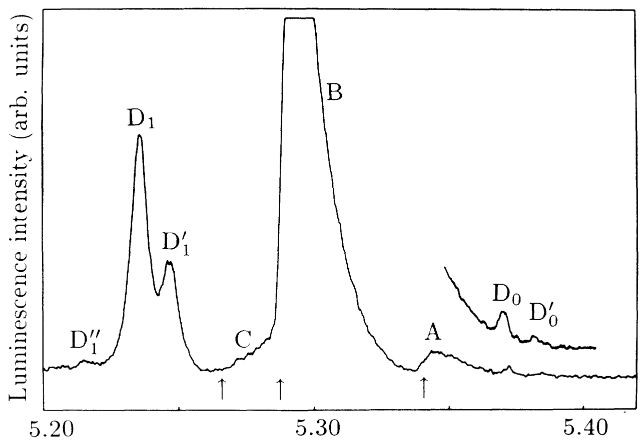

FIG. 2. Detailed spectra measured at 77 K of zero-phonon cathodoluminescence from bound excitons (D_0 and D_0') and phonon-assisted features (D_1, D_1', and D_1'') in ^{13}C diamond. The arrows mark the predicted thresholds of the free-exciton features A, B, and C, as derived in the text.

detail for the ^{13}C diamond in Fig. 2. Two zero-phonon components D_0 and D_0' occur at energies[3]

$$E(D_0)=E_{gx}-E_{4x},\quad E(D_0')=E_{gx}'-E_{4x}', \tag{2}$$

where E_{gx} and E_{gx}' are the energies of excitons associated with the upper and lower valence bands, and E_{4x} and E_{4x}' are the binding energies of the upper and lower valence-band excitons to the neutral acceptors. The peaks D_1 and D_1' are TO phonon replicas of D_0 and D_0', and D_1'' is the LO phonon replica of D_0. Consequently, D_1 and D_1' occur at an energy $\hbar\omega_{\rm TO}$ below D_0 and D_0', and D_1'' is at $\hbar\omega_{\rm LO}$ below D_0. The natural diamond has an uncompensated boron concentration, determined from Hall-effect measurements,[4] of 5×10^{16} cm^{-3}. The boron concentration in the part of the ^{13}C diamond examined is estimated to be about 3×10^{16} cm^{-3} from the ratio of the intensities of the free- and bound-exciton peaks. These concentrations are too small to perturb the crystals' band states.

Near-band-gap luminescence from ^{13}C diamond occurs at higher energies than the corresponding features in ^{12}C diamond (Fig. 1). Table I lists the energies of the bound-exciton features in ^{13}C diamond and compares them with our data for ^{12}C, which agree with those of Ref. 3. From Table I, the zero-phonon exciton lines D_0 and D_0' are 14 ± 0.7 meV higher for ^{13}C than for ^{12}C diamond. The phonon energies $\hbar\omega_{\rm TO}$ and $\hbar\omega_{\rm LO}$, derived from the energies of the zero-phonon lines and the one-phonon peaks D_1, D_1', and D_1'', are lower by a factor of 0.96, equal within experimental error to the factor $(\frac{12}{13})^{1/2}=0.961$ expected to first order when the lattice is changed from ^{12}C to ^{13}C.

The free-exciton peaks A, B, and C are broadened by strain in the crystal, by thermal effects, and by the split valence-band structure. The low-energy thresholds are at[3]

$$E_{\rm th}(A)=E_{gx}-\hbar\omega_{\rm TA},\quad E_{\rm th}(B)=E_{gx}-\hbar\omega_{\rm TO},$$
$$E_{\rm th}(C)=E_{gx}-\hbar\omega_{\rm LO}. \tag{3}$$

The vertical arrows in Fig. 2 show the predicted positions of these thresholds in ^{13}C using the phonon energies for ^{13}C listed in Table I, and with

$$^{13}E_{gx}={}^{12}E_{gx}+[{}^{13}E(D_0)-{}^{12}E(D_0)],$$

where the superscripts denote the isotope. The use of E_{gx} assumes that the binding energy E_{4x} of an exciton is the same in ^{13}C diamond as in ^{12}C diamond; this is justified by the exciton having very similar states whether it is bound or free, so that the bound and free states will be equally affected by the isotope change. The predicted thresholds shown in Fig. 2 appear to be consistent with the experimental data.

Figure 3 shows the absorption edge of the ^{13}C diamond measured at room temperature and at 77 K. Three thresholds are visible in the room-temperature absorption spectrum. Thresholds i and ii correspond to the creation of an exciton with the *absorption* of a TO phonon or a TA phonon, respectively, and iii corresponds to the creation of an exciton with the *emission* of a TA pho-

TABLE I. Energies and energy separations in meV of bound-exciton features in ^{12}C and ^{13}C diamond. The nomenclature is discussed in the text.

Feature	^{12}C	^{13}C	Difference
D_0'	5368 ± 0.5	5382 ± 0.5	14 ± 0.7
D_0	5356 ± 0.5	5370 ± 0.5	14 ± 0.7
D_1'	5227.0 ± 0.3	5246.5 ± 0.3	
D_1	5214.8 ± 0.3	5234.6 ± 0.3	
D_1''	5193 ± 0.5	5215 ± 0.5	
Phonon derived from	^{12}C	^{13}C	Ratio
$\hbar\omega_{\rm TO}$ $E(D_0)-E(D_1)$	141.2 ± 0.6	135.4 ± 0.6	0.959 ± 0.006
$\hbar\omega_{\rm TO}$ $E(D_0')-E(D_1')$	141.0 ± 0.6	135.5 ± 0.6	0.961 ± 0.006
$\hbar\omega_{\rm LO}$ $E(D_0)-E(D_1'')$	163 ± 0.7	155 ± 0.7	0.951 ± 0.006

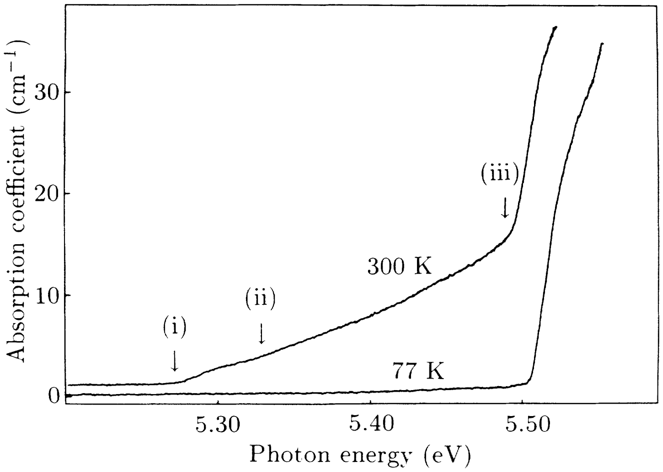

FIG. 3. Absorption spectra of ^{13}C diamond measured at 300 and 77 K. Processes with thresholds i and ii involve the destruction of TO and TA phonons, and threshold iii involves the creation of a TA phonon.

non.[2] At 77 K the probability of the phonon-absorption processes is negligible, and the optical absorption begins at threshold iii; there is also a shift[2] of the energy gap by $+10 \pm 2$ meV as the temperature is lowered from 300 to 77 K. Comparing the spectra of Fig. 3 with those for a natural semiconducting diamond, the absorption feature iii is 10.2 ± 0.1 meV higher in energy in ^{13}C. Threshold iii occurs at an energy $E_{\text{th}}(\text{iii}) = E_{gx} + \hbar\omega_{\text{TA}}$. From (1), $\hbar\omega_{\text{TA}}$ is expected to be 3.4 ± 0.08 meV smaller in ^{13}C than in ^{12}C diamond. Consequently, the absorption data give E_{gx} 13.6 ± 0.13 meV larger in ^{13}C. The weighted mean of the absorption and luminescence data is that E_{gx} is 13.6 ± 0.2 meV higher in ^{13}C than in ^{12}C diamond.

We show now that the isotopic dependence of E_{gx} arises mainly from electron-phonon coupling, with a smaller but significant contribution from the dependence of the atomic spacing on the isotope. A simple *zero-parameter* estimate of the dominant electron-phonon term can be made from the known temperature dependence of the energy gap of ^{12}C diamond. Optical measurements of the temperature dependence of E_{gx} in ^{12}C have been reported[2] for the range 77-663 K (Fig. 4). At these temperatures there is essentially no change in the thermal distribution of the electrons since the energy gap is ≈ 5.5 eV. It has been shown[5] empirically that the temperature dependence of the energy gap of a semiconductor is proportional to the Bose-Einstein statistical factor of an average phonon. We generalize this to write the energy gap as

$$E_{gx}(T) = E' + \int d\omega f(\omega)\{n(\omega,T) + \tfrac{1}{2}\} - a(c_{11} + 2c_{12})\Delta V(T)/3V. \tag{4}$$

Here $n(\omega,T)$ is the Bose-Einstein occupation number, and $f(\omega)d\omega$ is the difference in the electron-phonon coupling for the conduction-band minima and the valence-band maximum for those modes in the frequency range ω to $\omega + d\omega$, the energy gap at 0 K being $E' + \frac{1}{2} \times \int d\omega f(\omega)$. The final term in (4) allows for the temperature-dependent lattice expansion, $\Delta V(T)/V$ being the fractional volume expansion[6] to temperature T; c_{11} and c_{12} are elastic constants,[7] and a is the change in energy per unit compressional hydrostatic stress, measured[8] as $a = 5 \pm 1$ meV GPa^{-1}. The volume expansion accounts for only about 6% of the temperature dependence of E_{gx} (Fig. 4). Most of the measured temperature dependence arises from the term $\int d\omega f(\omega) n(\omega,T)$. The functional form of $f(\omega)$ is not known. However, we find that a precise fit (Fig. 4) can be made to the temperature dependence of E_{gx} using $f(\omega) = c\omega g(\omega)$, where $g(\omega)$ is the density of phonon states[9] for ^{12}C diamond, and the constant c of proportionality is given by the fit to $E_{gx}(T)$. Some justification for the use of the Bose-Einstein term is found in pseudopotential theory[10] where temperature dependence is introduced through structure factors which contain Debye-Waller terms. When the Debye-Waller factors are expanded as power series in the atomic displacements the dominant terms are proportional to the mean-square displacements $\langle u^2 \rangle$ of each atom. For a harmonic oscillator of angular frequency ω, mass m, and in its nth quantum state, $\langle u^2 \rangle = \hbar(n + \frac{1}{2})/$

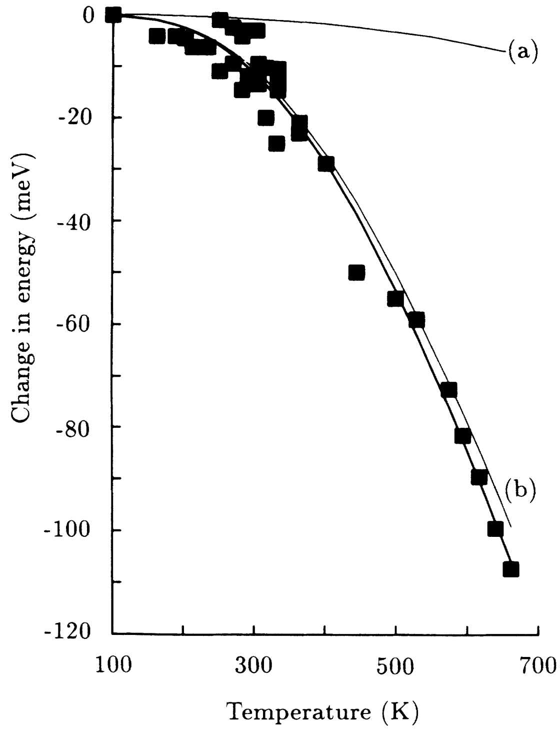

FIG. 4. Squares: Experimental data of Ref. 2 for the temperature dependence of the indirect energy gap of diamond. The calculated shift (thick line) is the sum of contributions from the lattice expansion (curve a) and the electron coupling (curve b), using $f(\omega) = c\omega g(\omega)$.

$m\omega$, producing the temperature dependence as in (4). At low temperature $\langle u^2\rangle = \hbar/2m\omega$, giving an isotope dependence because $\langle {}^{13}u^2\rangle/\langle {}^{12}u^2\rangle = (12/13)^{1/2}$. Consequently, at 0 K, changing the isotope gives a contribution to ${}^{13}E_{gx} - {}^{12}E_{gx}$ of

$$\Delta_1 = \tfrac{1}{2}[(\tfrac{12}{13})^{1/2}-1]\int d\omega f(\omega)$$
$$= 13.5 \pm 2\ \text{meV}. \qquad (5)$$

Although the best fit to the data in Fig. 4 is obtained when $f(\omega) = c\omega g(\omega)$, adequate fits are obtained for $f(\omega) = c'\omega^{0.5} g(\omega)$ to $f(\omega) = c''\omega^{1.6} g(\omega)$, producing most of the uncertainty quoted in (5). The 20% uncertainty in a contributes a further 0.1 meV to the uncertainty in (5).

A second contribution Δ_2 to the isotopic dependence of E_{gx} comes from the volume change produced by changing the isotope. The equilibrium volume of a crystal is obtained when its free energy is minimized, and at 0 K the free energy contains the zero-point energies of all the modes of vibration. In diamond the frequencies of vibration decrease with increasing volume. If the molar volume of a purely harmonic crystal is V_0, its zero-point energy at a volume $V_0 + \Delta V$ would be $\frac{1}{2}\sum \hbar\omega_i(1-\gamma_i \times \Delta V/V_0)$, where γ_i is the Grüneisen parameter of the ith mode. The volume will increase until the reduction in zero-point energy is balanced by the increase in elastic energy, $\frac{1}{6}(c_{11}+2c_{12})(\Delta V^2/V_0)$. This balance occurs at $\Delta V = [3/2(c_{11}+2c_{12})]\sum \hbar\omega_i\gamma_i$. The difference in molar volume of ^{13}C and ^{12}C is therefore

$${}^{13}V - {}^{12}V = \frac{3}{2(c_{11}+2c_{12})}\sum_i \hbar\omega_i\gamma_i[(\tfrac{12}{13})^{1/2}-1], \qquad (6)$$

where the frequencies are for ^{12}C, and the sum is over $3N$ modes of vibration, N being the Avogadro number, and density of phonon states being known.[9] Values of the Grüneisen parameter[11] span the range $\gamma = 1.15$–1.6, so that the fractional volume change is

$$({}^{13}V - {}^{12}V)/{}^{12}V = -(1.45 \pm 0.15)\times 10^{-3}.$$

We have previously estimated the volume change in similar diamonds using the change (by $-50\ \text{cm}^{-1}$) in the Raman frequency[12] as

$$({}^{13}V - {}^{12}V)/{}^{12}V = -(1.0 \pm 0.07)\times 10^{-3}.$$

Using both these estimates we obtain a shift to the energy gap of

$$\Delta_2 = a(c_{11}+2c_{12})({}^{13}V - {}^{12}V)/3\,{}^{12}V = 3 \pm 1.3\ \text{meV}.$$

Although there is a large uncertainty here, this term is small compared with Δ_1.

For completeness we note that for a mode with a typical Grüneisen parameter of 1.3, the volume change from ^{12}C to ^{13}C modifies the ratio of the frequencies to ${}^{13}\omega/{}^{12}\omega = 0.963$, equal to the first-order effect $(\frac{12}{13})^{1/2} = 0.961$ within experimental error.

We have shown that the indirect energy gap of diamond changes by 13.6 ± 0.2 meV when the isotope composition changes from ^{12}C to ^{13}C. Most of this shift is caused by the isotopic dependence of the electron-phonon coupling, giving a shift estimated from the temperature dependence of the energy gap as $\Delta_1 = 13.5 \pm 2$ meV. An additional smaller contribution, estimated to be $\Delta_2 = 3 \pm 1.3$ meV, comes from the difference in molar volume of ^{12}C and ^{13}C diamond. The total shift estimated with no adjustable parameters of 16.5 ± 2.5 meV is closely comparable to the measurement.

We thank the United Kingdom Science and Engineering Research Council for the provision of a CASE studentship to S.C.L., and Gene Baraff and Jörg Weber for helpful comments.

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