PHYSICAL REVIEW B VOLUME 44, NUMBER 13 1 OCTOBER 1991-I

Rapid Communications

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *should be no longer than 4 printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

Isotopic dependence of the lattice constant of diamond

H. Holloway, K. C. Hass, and M. A. Tamor
Ford Motor Company, Research Staff, SRL/MD3028, P.O. Box 2053, Dearborn, Michigan 48120-2053

T. R. Anthony and W. F. Banholzer
General Electric Company, Corporate Research and Development, Building K1, Room SA59, Schenectady, New York 12301

(Received 8 May 1991)

We report measurements of lattice constants of single-crystal synthetic diamonds that cover the range of isotopic compositions from almost-pure ^{12}C to almost-pure ^{13}C. These provide a demonstration of an effect of isotopic composition on the lattice constant of this material. The results are consistent with a linear dependence $a_0(C,25\,^\circ C,x) = 3.567\,15 - 0.000\,53x$ Å, where x is the atom fraction of ^{13}C. This corresponds to a fractional change between the end compositions of $\Delta a_0/a_0 = -1.5\times10^{-4}$, which is less than the smallest value in a range of theoretical estimates that have been published previously. The synthetic diamonds yielded (400) Bragg peaks with widths in the range 12–17 arc sec that are not perceptibly dependent on the isotopic composition.

Several recent studies of synthetic diamond have focused on the changes that occur with change in isotopic composition. The effects seen have included a striking, and potentially useful, increase in the thermal conductivity in isotopically nearly pure ^{12}C diamond.[1] Recent reviews and discussions of these effects have been given by Banholzer and co-workers.[2,3] Among the expected effects is a decrease in lattice constant as the ^{13}C content is increased from the 1.1% found in natural diamond. To date there has been no experimental verification of this prediction,[4] although isotopic effects have been observed with the lattice constants of other materials.[5–7] Collins *et al.*[8,9] have provided three different indirect estimates of the atomic volume change between ^{12}C and ^{13}C diamond. These correspond to fractional changes in lattice constant that range from $\Delta a_0/a_0 = -2.1\times10^{-4}$ in an earlier paper[8] to the most recent value[9] $\Delta a_0/a_0 = -(4.8\pm0.5)\times10^{-4}$. Thus, there is an evident need for a direct experimental determination of the true magnitude of this effect.

In the present Rapid Communication we report lattice-constant measurements of natural abundance and isotopically enriched diamond that are precise enough to show the isotope effect and define its magnitude. Since the weight to be attached to our findings depends upon the validity of our procedures, we will describe them in some detail, together with checks that were made using subsidiary measurements in which the lattice constants of Si and Ge were compared.

Lattice-constant measurements were made with a double-crystal diffractometer (Blake Industries) using a technique in which the specimen is rotated to Bragg reflect the x-ray beam, first to one side and then to the other (i.e., in the "plus" and "minus" settings). The change in incident angle between these settings gives twice the Bragg angle. The incident x-ray beam was provided by a channel-cut monochromator [Si(220)] using an arrangement similar to that described by Bartels,[10] except that the angle between the pair of channel-cut crystals was fixed to give a single wavelength (approximately Cu $K\alpha_1$), rather than being adjustable for a choice of spectral lines. This arrangement passes a wavelength range that is significantly reduced from the inherent width of the x-ray line, so that measurements may be made without significant dispersive broadening of the Bragg peaks. Measurements of the incident angles for maximum diffracted intensity and thereby of Bragg angle were made using a shaft encoder calibrated to 10^{-4} deg ($\sim\frac{1}{3}$ arc sec) and the measured Bragg angles were reproducible to a few times this precision. (Attainment of this precision does depend on the inherently narrow Bragg peaks of the highly perfect crystals that are available with many materials that have the diamond or zinc-blende structures. Peak broadening from significant decreases in perfection would decrease the precision.) Analyses of the major errors (from the limited precision of Bragg angle measurement, from specimen misalignment, especially tilt, and from temperature gradients in the diffractometer) suggest probable uncertainties that approach 10^{-5} in our values of the lattice constant of crystals with dimensions near 1 cm and may be somewhat larger for smaller specimens whose tilts cannot be adjusted so precisely.[11]

Our values for lattice constant are based upon the standard[12–14]

$$a_0(\mathrm{Si},22.5\,^\circ C) = 5.431\,019\,6(11)\ \text{Å},$$

which corresponds to the currently accepted value for the

peak wavelength[12,13]

$$\lambda(\text{Cu } K\alpha_1) = 1.540\,594\,5(11)\ \text{Å},$$

where the parentheses enclose the uncertainty (one σ) in the last digits. Where we cite earlier measurements of lattice constants we have corrected, as necessary, to this current value for $\lambda(\text{Cu } K\alpha_1)$. Measurements were made at ambient temperatures in the range 22–26 °C. The corrections needed to convert to 25 °C were small and were made using values of the thermal-expansion coefficient near 300 K:[15]

$$\alpha(\text{diamond}) = 1.0\times10^{-6}\ \text{K}^{-1},$$

$$\alpha(\text{Si}) = 2.56\times10^{-6}\ \text{K}^{-1},$$

$$\alpha(\text{Ge}) = 5.9\times10^{-6}\ \text{K}^{-1}.$$

Combined with the standard value for Si, this gives

$$a_0(\text{Si},25\,^\circ\text{C}) = 5.431\,054(1)\ \text{Å},$$

in good agreement with an earlier value for 25 °C of 5.431 056(1) by Hom, Kiszenick, and Post.[16]

Since our channel-cut monochromator is only approximately centered on the Cu $K\alpha_1$ line, its output was calibrated using the (333) reflection from a dislocation-free (111)-oriented silicon crystal plate (Eagle-Picher). (Here and elsewhere, all measurements have been corrected for refraction.[17]) This gave the result that our nominal Cu $K\alpha_1$ radiation was actually centered at $\lambda = 1.540\,578\,5(50)$ Å (with a conservative error estimate) when the monochromator was at 25 °C. This corresponds to a misalignment of the channel-cut crystals of approximately 2 arc sec. Thus, the peak of the monochromator output was displaced by $(1.0\pm0.3)\times10^{-5}$ of the wavelength of the spectral line, corresponding to about $\frac{1}{40}$ of the inherent linewidth at half maximum. When using this result with different temperatures, we have allowed for the change in output wavelength with change in temperature due to thermal expansion of the monochromator.

To test the precision of our technique, the measurements of diamond were preceded by supplemental measurements on Si and Ge specimens. For the Si measurements we used (400) reflections from (100)-oriented device-quality wafers supplied by Exsil and by Monsanto. The relative results for the lattice constants are

$$a_0(\text{Si},25\,^\circ\text{C}) = \begin{cases} 5.431\,054\ \text{Å}: & \text{Eagle-Picher (taken as standard)}, \\ 5.431\,08\ \text{Å}: & \text{Exsil}, \\ 5.431\,07\ \text{Å}: & \text{Monsanto}. \end{cases}$$

Here the standard value has been assigned to the (111)-oriented Eagle-Picher specimen, since the increase in Bragg angle of the (333) reflection over that of the (400) reflection makes it more suitable for precise measurements. The other values are relative to this. Note that the maximum range is about 5×10^{-6} of a_0, in agreement with the error estimate given earlier.

For the Ge measurements we used specimens of low-dislocation-density ($< 1500\ \text{cm}^{-2}$) Ge from Eagle-Picher to measure the (400) reflections from a (100)-oriented crystal and the (333) and (444) reflections from a (111)-oriented crystal. These gave lattice constants that were quite consistent with each other, i.e.,

$$a_0(\text{Ge},25\,^\circ\text{C}) = \begin{cases} 5.657\,82\ \text{Å}: & \text{from (400)}, \\ 5.657\,84\ \text{Å}: & \text{from (333)}, \\ 5.657\,87\ \text{Å}: & \text{from (444)}. \end{cases}$$

For comparison of these results with previous measurements it is convenient to consider the ratio of the lattice constant of Ge to that of Si at 25 °C. Here we have available an especially precise direct comparison by Baker and Hart[18] plus earlier individual measurements of Si and Ge by Hom, Kiszenick, and Post.[16] Our results and the earlier work give

$$a_0(\text{Ge},25\,^\circ\text{C})/a_0(\text{Si},25\,^\circ\text{C}) = \begin{cases} 1.041\,754: & \text{from Ge(400)}, \\ 1.041\,757: & \text{from Ge(333)}, \\ 1.041\,762: & \text{from Ge(444)}, \\ 1.041\,767: & \text{Baker and Hart}, \\ 1.041\,776: & \text{Hom, Kiszenick, and Post}. \end{cases}$$

These preliminary results with large (> 1 cm) Si and Ge plates confirm our expectation of lattice-constant measurements with a precision somewhat better than 1×10^{-5}. For the lattice-constant measurements of diamonds with dimensions of a few millimeters, where the tilt adjustment is less precise, we will increase this uncertainty by about 50% to give somewhat conservative error bars of $\pm0.000\,05$ Å.

We examined five synthetic diamonds that had been made at General Electric Company by a technique that is described in Ref. 3. These had compositions that spanned almost the complete range from ^{12}C to ^{13}C and they were of two types. First, there were two plates with (100) orientation and facet dimensions $3.0\times1.5\ \text{mm}^2$ that had been removed from their seed crystal. These had atom fractions of ^{13}C, x, equal to 0.011 (natural abundance) and 0.001 (i.e., almost-pure ^{12}C). Second, there were as-grown specimens [with approximately 2-mm (100) facets] to each of which was still attached a small seed crystal. These covered the ^{13}C enriched range with $x = 0.38$, 0.68, and 0.99. The uncertainties in x are at most 0.01 for the three ^{13}C enriched specimens and much less for the first group. As will become evident, the effects of these uncertainties in composition are quite negligible by comparison with those arising from the measurements of lattice constant.

Examination of x-ray rocking curves for (400) reflections showed that all five specimens were of high crystal perfection, yielding peak widths at half maximum of 12–17 arc sec. There was no perceptible dependence of the peak width on isotopic composition. While the observed widths are larger than the theoretical values (which would be limited to about 4 arc sec by the divergence of our monochromator), they do approach those of good semiconductor crystals and they are well suited to precise lattice-constant measurements. [For comparison

we examined a (111)-oriented platelet of natural diamond (Drukker type 2A), which gave (111) peak widths of 240–260 arc sec.] The two specimens that had been separated from their seeds always yielded narrow rocking curves, although the one with natural abundance sometimes gave a split peak that we attribute to a low-angle grain boundary with tilt of about 0.01°. (For measurements of lattice constant we adjusted the specimen position to avoid the region of this boundary.) In contrast, the group of specimens to which seeds were still attached required some adjustment to give narrow rocking curves, rather than broad and multiple peaks. We attribute this to the difficulty inherent in manipulating a small crystal so as to avoid x-ray illumination of a much less perfect region adjacent to the seed. However, the narrow Bragg peak illustrated in Fig. 1 was obtained from a specimen with the seed still attached and it is quite representative of the narrow curves that were attainable with all five specimens. This observed independence of the Bragg-peak width on isotopic composition eliminates the possibility that the previously reported isotopic dependence of the thermal conductivity[1] is due to a large change in crystal perfection. Thus, the correct explanation for the variation in thermal conductivity is more likely to be associated with the fundamental properties of the isotopically disordered lattice.

The observed dependence of the lattice constant on ^{13}C content is shown in Fig. 2. There is a significant variation that is linear within the precision of the measurement. A least-squares fit to the data gives

$$a_0(\mathrm{C},25\,^\circ\mathrm{C},x)=3.56715-0.00053x\ \text{Å},$$

corresponding to a fractional change between the end compositions of

$$\Delta a_0/a_0=-1.5\times10^{-4}.$$

This value is of the same order of magnitude as the three estimates of Collins *et al.*,[8,9] although these previous indirect estimates are too large by factors between 1.4 and 3.2.

One of the previous estimates,[8] $\Delta a_0/a_0=-(3.3\pm0.2)\times10^{-4}$, is based on the small discrepancy (1.34 cm^{-1}) between the observed shift (50 cm^{-1}) in the diamond Raman frequency from 1.1% to 99% ^{13}C and the expected shift based on the average ionic mass. That this estimate is in error by more than a factor of 2 is not surprising in view of the caveats expressed in Ref. 8 concerning the isotopic compositions and the neglect of factors other than a volume change that might contribute to the difference in Raman frequencies (e.g., isotope scattering). The other two estimates[8,9] are based on the London theory of the variation in crystal volume with isotopic substitution.[6,19] In the zero-temperature limit, which is appropriate here because of the large Debye temperature of diamond ($\Theta_D=2200$ K), this theory gives a fractional change in lattice constant of

$$\frac{\Delta a_0}{a_0}=-\frac{2}{3}\frac{\Delta M}{M}\frac{1}{Ba_0^3}\sum_i\gamma_iE_i\,, \tag{1}$$

where $\Delta M/M$ is the fractional change in mass, B is the bulk modulus, and E_i and γ_i are the energy and Grüneisen parameter associated with the ith phonon mode, respectively. Using Eq. (1), and assuming a constant Grüneisen parameter of $\gamma=1.1$ and a Debye frequency spectrum, Collins *et al.*[8] obtained the closest of their three estimates, $\Delta a_0/a_0=-2.1\times10^{-4}$. This number was later refined[9] to $\Delta a_0/a_0=-(4.9\pm0.5)\times10^{4}$, apparently using the same theory, although it is unclear how the later value follows from the range of γ values that are cited (1.15–1.6).

The order-of-magnitude agreement between the theoretical estimates and the present experimental value of $\Delta a_0/a_0$ suggests that the London theory does describe the essential physics of the lattice-constant change in diamond. The residual disagreement most likely arises from the crude approximations made in implementing this theory; e.g., the true frequency spectrum of diamond is far from Debye-like and Grüneisen parameters for individual modes differ by as much as a factor of 5.[20]

The lattice constant that we obtain for the natural abundance

$$a_0(\mathrm{C},25\,^\circ\mathrm{C},x=0.011)=3.56714(5)\ \text{Å}$$

is slightly larger than the value, $a_0=3.56706(1)$ Å, obtained previously by Hom, Kiszenick, and Post[16] from a natural diamond. The difference appears to be somewhat larger than the range of our experimental uncertainty, but we do not have an explanation for it. [Previous authors

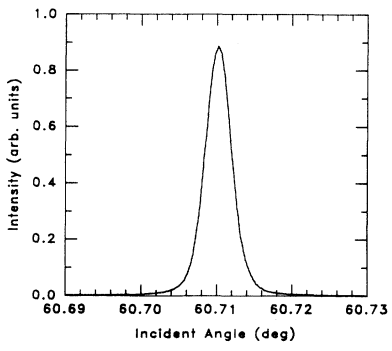

FIG. 1. X-ray rocking curve for the (400) reflection from a synthetic diamond with 38% ^{13}C. The width at half maximum is 0.0040° = 14.5 arc sec. This curve is representative of those that were obtained over the whole range of isotopic compositions.

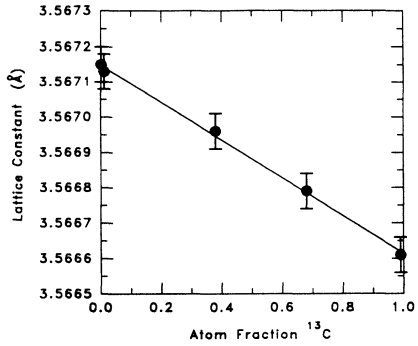

FIG. 2. Isotopic dependence of the lattice constant of diamond at 25 °C. The line is a least-squares fit to the data.

have reported increases in the lattice constant of natural diamond with increase in nitrogen content,[21-24] but our nitrogen impurity levels are orders of magnitude less (<1 ppm) than would be required to give a significant increase in the lattice constant.] It is of interest that the atomic density of ^{13}C diamond, at 1.7632×10^{23} cm^{-3}, is about 0.04% larger than that of natural diamond thereby giving it, by a small margin, the largest atomic density of any known solid.

In summary, we have made measurements that show the variation of the lattice constant of diamond with isotopic composition. The extent of this variation is significantly smaller than the smallest in a range of published theoretical estimates. The synthetic diamonds that we studied were of high crystal perfection for this material, as judged by the narrowness of the measured Bragg peaks. The lack of any significant variation in peak width with isotopic composition suggests that the observed composition dependence of the thermal conductivity is unlikely to arise from a variation in crystal quality.

We thank Jim Fleischer, Dick Chrenko, Eoin O'Tighnearnaigh, and Suresh Vagarali for their assistance in obtaining the crystals.

[1]T. R. Anthony, W. F. Banholzer, J. F. Fleischer, L. Wei, P. K. Kuo, R. L. Thomas, and R. W. Prior, Phys. Rev. B **42**, 1104 (1990).

[2]W. F. Banholzer, T. R. Anthony, and R. Gilmore, in *Proceedings of the Second International Conference on New Diamond Science and Technology, 1990,* edited by R. F. Messier, J. T. Glass, J. Butler, and R. Roy (Materials Research Society, Pittsburgh, 1991).

[3]W. F. Banholzer, in *Proceedings of the International Conference of Optical Science Engineering, The Hague, 1991,* edited by S. Singer (SPIE, Bellingham, WA, in press).

[4]Banholzer, Anthony, and Gilmore (Ref. 2) report measurements of the lattice constants of diamond with various isotopic compositions, but the precision was not adequate to demonstrate the effect.

[5]Early references to LiH-LiD and ^{6}LiF-^{7}LiF are cited by R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1963), Vol. 1, Chap. III.

[6]A. A. Berezin and A. M. Ibrahim [Mater. Chem. Phys. **19**, 407 (1988)] give references to LiH-LiD, ^{6}Li-^{7}Li (as the metal, the hydride, and the fluoride), and ^{24}Mg-^{26}Mg, ^{40}Ca-^{48}Ca, and ^{58}Ni-^{64}Ni (as the oxides). This paper also contains a brief account of the London theory.

[7]The isotope effect in single-crystal Ge has been demonstrated by R. C. Buschert, A. E. Merlini, S. Pace, S. Rodriguez, and M. H. Grimsditch, Phys. Rev. B **38**, 5219 (1988).

[8]A. T. Collins, G. Davies, H. Kanda, and G. S. Woods, J. Phys. C **21**, 1363 (1988).

[9]A. T. Collins, S. C. Lawson, G. Davies, and H. Kanda, Phys. Rev. Lett. **65**, 891 (1990).

[10]W. J. Bartels, J. Vac. Sci. Technol. B **1**, 338 (1983).

[11]The specimens were adjusted so that their surfaces just touched a pointer whose tip was both on the axis of rotation and centered in the beam from the monochromator. This procedure gives negligible error due to displacement of the specimen from the rotation axis. (Note that because we measure the incident angle for the Bragg condition, rather than the angular position of the diffracted beam, the results are insensitive to displacement of the specimen surface from the axis of rotation, provided that the lattice planes have negligible curvature.) The tilts of the specimens with respect to the rotation axis were adjusted by maximizing the peak intensity when the specimens were illuminated by a beam with height about 1 cm or as large as permitted by the specimen size.

[12]E. R. Cohen and B. N. Taylor, Phys. Today **43** (8), BG9 (1990).

[13]E. R. Cohen and B. N. Taylor, CODATA Bulletin 63 (Pergamon, Elmsford, NY, 1986).

[14]P. Becker, P. Seyfried, and H. Seigert, Z. Phys. B **48**, 17 (1982).

[15]*Physics of Group IV Elements and III-V Compounds,* edited by O. Madelung, Landolt-Börnstein, New Series Group III, Vol. 17a, Pt. B (Springer-Verlag, Berlin, 1982).

[16]T. Hom, W. Kiszenick, and B. Post, J. Appl. Cryst. **8**, 457 (1975).

[17]A discussion of and formulas for the refraction correction are given by R. W. James, *The Optical Principles of the Diffraction of X-rays* (Cornell Univ., Ithaca, 1965), Chap. II, pp. 53–55. These standard results are based upon the extent to which the center of the symmetric Darwin diffraction peak of a perfect crystal is displaced from the Bragg angle. In the presence of absorption this peak shrinks asymmetrically to give the Darwin-Prins curve, whose maximum intensity occurs at a smaller angle than the Darwin curve, thereby slightly reducing the refraction correction. For a more precise calculation of the refraction corrections, we convoluted the calculated Darwin-Prins curves with the calculated output from our channel-cut monochromator to obtain directly the difference between the position of the measured peak and the Bragg angle. The resulting refraction correction is negligibly different from James' result with the diamond and Si reflections used here, but it is about 10% smaller for the Ge reflections. To facilitate analysis of our results, the Darwin-Prins corrections that we have used are given below and, for comparison, the corrections calculated using James' formulas are appended in parentheses.

diamond(400): $-0.00148°$ ($-0.00148°$),

Si(400): $-0.00090°$ ($-0.00091°$),

Si(333): $-0.00085°$ ($-0.00086°$),

Ge(400): $-0.00172°$ ($-0.00189°$),

Ge(333): $-0.00152°$ ($-0.00172°$),

Ge(444): $-0.00247°$ ($-0.00275°$).

[18]J. F. C. Baker and M. Hart, Acta Crystallogr. Sect. A **31**, 364 (1975).

[19]H. London, Z. Phys. Chem. **16**, 302 (1958).

[20]B. Parsons, Proc. R. Soc. London, Ser. A **352**, 297 (1977).

[21]W. Kaiser and W. L. Bond, Phys. Rev. **115**, 857 (1959).

[22]V. I. Lisoivan and R. R. Dikovskaya, Instrum. Exp. Tech. (USSR) **4**, 992 (1969).

[23]V. I. Lisoivan and E. V. Sobolev, Dokl. Akad. Nauk SSSR **214**, 1311 (1974) [Sov. Phys. Dokl. **19**, 56 (1974)].

[24]V. I. Lisoivan and V. A. Nadolinnyi, Dokl. Akad. Nauk SSSR **274**, 72 (1984) [Sov. Phys. Dokl. **29**, 1 (1984)].