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Equations of state of ^{12}C and ^{13}C diamond

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X-ray powder-diffraction measurements performed at the ESRF between 10^{-4} and 22 GPa have been used to infer the equations of state (EOS) of both ^{12}C and ^{13}C diamonds. The experiments were carried out with a diamond-anvil cell and care was taken to obtain the most hydrostatic pressure conditions using nitrogen, argon, or ethanol:methanol:water mixtures as pressure transmitting media. The cell parameter determinations were precise enough to distinguish the small volume differences between the two isotopic end members. Fits of the data to Birch-Murnaghan EOS yield an isothermal bulk modulus of ^{12}C diamond $[K_{0T}=446(4)$ GPa for K'_{0T} fixed to 4], in excellent agreement with the values inferred from ultrasonic and Brillouin scattering measurements. The EOS of ^{13}C is very close to that of ^{12}C diamond $[K_{0T}=438(8)$ GPa for $K'_{0T}=4]$. This result is at variance with previous acoustic measurements which suggested that the bulk modulus of ^{13}C diamond is 17% higher than that of ^{12}C diamond. [S0163-1829(99)03545-6]

I. INTRODUCTION

A precise knowledge of the equation of state (EOS) of diamond is fundamental in both physics and Earth sciences. Diamond is an archetypal simple covalent material. The way it responds to high-static pressures provides important insights on the repulsive part of the covalent bond-interaction potential.[1] Natural diamonds are also unique samples coming from the deep Earth (from depths down to 700 km, i.e., pressures in excess of 25 GPa).[2] Minerals elastically constrained are often observed in diamonds. Elastic stresses develop in response to the relative compressibility and thermal expansivity of the diamond and the host mineral, and provide direct informations on the depth at which diamonds have grown.

There exist few direct measurements of the room-temperature EOS of diamond using x-ray diffraction[3,4] and the EOS was retrieved from a limited number of experimental points. Acoustic (ultrasonic and Brillouin) techniques give strong constraints on the values of the adiabatic bulk modulus.[5] Apart from these measurements there are also many theoretical calculations of the EOS of diamond which need to be tested against extensive and reliable experimental values.[1,6–8]

It has been proposed from acoustic and x-ray-diffraction measurements that the EOS of diamond is sensitive to the ^{12}C-^{13}C isotopic substitution.[3,9,10] It has been reported that some elastic moduli of pure ^{13}C diamond are larger than those of ^{12}C diamond. For instance, it has been suggested that the c_{12} elastic modulus doubles in the range 0–99% ^{13}C substitution implying a 17% increase in the bulk modulus.[9] However, this result is still controversial since the opposite behavior between the two diamond species has been proposed from Raman spectroscopy measurements.[11] The issue of this controversy is essential since a difference in the EOS of the compounds would provide important information on the behavior of the quantum isotope effect at high pressures. Moreover, a significant difference in the EOS of both isotopic end members may change the isotopic fractionation factor of diamond at high pressures and thus modify the current interpretation of the ^{13}C/^{12}C composition of natural diamonds which is made on the assumption of a null pressure effect on the isotope quantum effect.

Therefore the purpose of the present work is to provide the most accurate measurements of the EOS of both ^{12}C and ^{13}C diamonds under hydrostatic pressure conditions using high-pressure powder x-ray-diffraction techniques.

II. EXPERIMENTAL PROCEDURE

A. Diamond samples

For ^{12}C diamond, a powder of synthetic diamond with a mean grain size of 2–4 μm was used. The ^{13}C diamond powder has been synthesized in a multianvil press (localized in Clermont-Ferrand, France, UMR 6524 CNRS, Magmas et Volcans) from 99% ^{13}C graphite powder. Synthesis conditions were 10 GPa and 1800 K. These starting products were characterized by Raman spectroscopy and powder x-ray diffraction. The cell parameters and the frequencies of the Raman-active modes are in agreement with previous determinations[11,12] within accuracy of the measurements (see Sec. II C).

B. High-pressure techniques

High pressures were generated with a membrane-type diamond-anvil cell (MDAC).[13,14] The sample chamber consists of a stainless steel gasket, preindented to a thickness of 50 μm and drilled with a 150-μm-diameter hole, squeezed between two diamonds with 300-μm culets. Diamond powders were compressed with two types of pressure transmitting media. Fully hydrostatic compression was achieved up

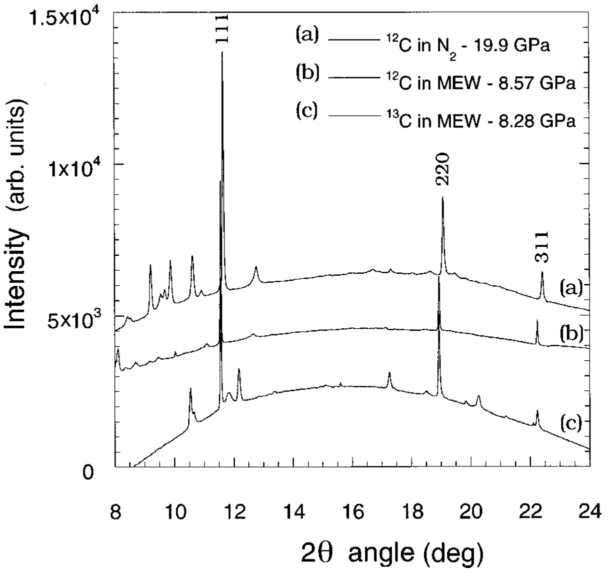

FIG. 1. Typical high-pressure x-ray powder-diffraction patterns of ^{12}C and ^{13}C obtained after integration of two-dimensional image plates. The (111), (220), and (311) reflections are observed. The additional peaks are either related to the pressure transmitting media (N$_2$) or to trace of the Pt capsule used for ^{13}C diamond synthesis.

to 13 GPa by using a 16:4:1 methanol-ethanol-water (MEW) mixture. Compression experiments were also achieved up to 22 GPa using cryogenically loaded Ar or N$_2$. A few spherical ruby chips (1–3 μm in diameter) were placed around the sample for pressure measurements using the classical ruby fluorescence technique.[15]

C. X-ray diffraction

Angle-dispersive x-ray-diffraction spectra were recorded at high pressures on the ID9 beamline of the European Synchrotron Radiation Facility (ESRF). A bright monochromatic x-ray beam ($\lambda = 0.45252$ Å) was collimated on the sample through the diamonds. The x-ray spot size at the sample was $20\times 20\,\mu$m. Diffraction spectra were acquired with an imaging plate located at 450 mm from the sample, with exposure times of 2 mn (Fig. 1). The two-dimensional diffraction images were integrated with the FIT2D software.[16] Lebail profile refinements of the diffraction data (Fig. 1) were carried out with the program package GSAS (Ref. 17) and provide cell parameters of both isotopic species of diamonds with a precision of $1-3\times 10^{-4}$ Å. Our cell parameter determination for ^{12}C diamond at ambient conditions $[a_0 = 3.5678(2)]$ is offset by about $+7\times 10^{-4}$ Å when compared with more accurate determinations[12] $[a_0 = 3.567\,15(5)]$ due to uncertainties in the wavelength calibration. This offset is constant and is the same for both isotopic species and at all pressures. The precision in the cell parameter determination leads to a precision of $3\times 10^{-3}-1\times 10^{-2}$ Å^3 in the volume determination.

III. RESULTS

The data for ^{12}C diamond are reported in Table I. Two compression experiments were performed. The first one was carried out from room pressure up to 16 GPa in a MEW pressure transmitting medium. This liquid medium freezes at 13 GPa and the onset of freezing is clearly observed by a significant broadening of the ruby fluorescence band indicating nonhydrostatic conditions. Thus only the 23 measurements performed up to 13 GPa under hydrostatic conditions were used for the determination of the EOS parameters. The second experiment, from 3 GPa up to 22 GPa, was performed with N$_2$ as pressure-transmitting medium. More than 20 measurements were made in this pressure range (Table I). The width of the ruby fluorescence lines were similar to those observed in the liquid MEW medium indicating nearly hydrostatic conditions. The (111), (210), and (311) diffraction peaks of cubic diamond (space group $Fd3m$) were observed (Fig. 1) and allowed a very precise determination of the cell volume at all pressures. No significant difference is observed between the two compression curves in their common pressure range, i.e., from room pressure up to 13 GPa.

The resulting $V(P)$ data (Fig. 2) were fitted to a Birch-Murnaghan equation of state:

$$P = \tfrac{3}{2}K_{0T}\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right] \times\left\{1 + \tfrac{3}{4}(K'_{0T} - 4)\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]\right\}, \qquad (1)$$

where P is the pressure, V_0 the cell volume at room pressure and temperature, V the cell volume at pressure P and room temperature, K_{0T} the isothermal bulk modulus at room pressure and temperature, and K'_{0T} its pressure derivative $K'_{0T} = (\partial K_{0T}/\partial P)_T$. Different data subsets have been fitted to Eq. (1): the subset including only the data points obtained in the MEW medium, the subset including only the data obtained with N$_2$ as pressure transmitting medium, and finally the whole set of data. The $V(P)$ data were fitted either to extract V_0, K_{0T}, and K'_{0T} or to extract V_0 and K_{0T} assuming $K'_{0T} = 4$ (see Table II), taking into account the uncertainties in both pressures and cell volumes. Uncertainties on the inverted parameters were evaluated *a posteriori* from the resolution matrix. Whatever the data subset used, the quality of the fit is very similar and leads to consistent values of K_{0T} and K'_{0T}. Moreover, the parameters of the EOS obtained in a limited pressure range in the MEW medium ($10^{-4}-13$ GPa) are in excellent agreement with those derived from a larger pressure-range data set ($10^{-4}-22$ GPa).

The data for ^{13}C diamond are reported in Table I. Two compression experiments were performed: the first one from room pressure up to 11 GPa in a MEW pressure transmitting medium and the second one from 3 GPa up to 17 GPa using Ar as pressure-transmitting medium. The (111), (210), and (311) refections of cubic ^{13}C diamond were observed. At variance with the ^{12}C diamond samples, a less homogeneous grain size of the ^{13}C diamond led to bridging of the sample grains between the diamond anvils and to an unsatisfactory spot statistics at high pressures. As a consequence, we performed the same data analysis as for ^{12}C diamond taking into account only the data points obtained below 10 GPa in the MEW medium and 13 GPa in the Ar experiment. It can be noticed that the two compression curves do not cross in the investigated pressure range. The inferred values of K_{0T} for

TABLE I. Experimental pressure-volume data used for the determination for the EOS of ^{12}C and ^{13}C diamond. MEW data obtained using a 16:4:1 methanol/ethanol/water mixure as pressure transmitting medium. N_2 and Ar data obtained with N_2 or Ar as pressure transmitting media.

^{12}C diamond				^{13}C diamond			
N_2		MEW		MEW		Ar	
P (GPa)	V (Å^3)	P (GPa)	V (Å^3)	P (GPa)	V (Å^3)	P (GPa)	V (Å^3)
0.0001	45.417(7)	0.89(4)	45.323(7)	0.0001	45.384(7)	4.45(22)	44.939(3)
1.19(6)	45.287(11)	2.24(11)	45.175(11)	0.29(1)	45.354(11)	7.98(40)	44.610(7)
1.69(8)	45.236(11)	2.63(13)	45.132(11)	0.68(3)	45.317(11)	8.86(44)	44.531(7)
2.31(11)	45.170(11)	0.46(2)	45.3743(7)	1.11(5)	45.254(7)	9.77(49)	44.433(7)
2.94(15)	45.122(11)	0.95(5)	45.317(7)	1.71(9)	45.211(11)	11.20(56)	44.313(3)
3.59(18)	45.057(11)	1.60(8)	45.250(3)	2.22(11)	45.155(11)	12.80(64)	44.106(3)
4.42(22)	44.973(11)	2.12(11)	45.194(11)	2.68(13)	45.106(3)		
5.28(26)	44.898(3)	2.77(14)	45.135(3)	3.34(17)	45.053(3)		
6.30(31)	44.795(3)	3.44(17)	45.068(3)	3.93(19)	44.977(3)		
7.14(35)	44.708(7)	4.11(20)	45.003(11)	4.47(22)	44.936(7)		
8.09(40)	44.628(11)	5.09(25)	44.911(3)	5.47(27)	44.826(7)		
9.45(47)	44.512(7)	5.70(28)	44.864(7)	6.05(30)	44.789(7)		
9.97(49)	44.465(7)	6.54(33)	44.771(11)	6.86(34)	44.695(7)		
10.81(54)	44.381(7)	6.85(34)	44.754(3)	7.82(39)	44.609(7)		
11.97(60)	44.269(7)	7.46(37)	44.692(3)	8.28(41)	44.587(7)		
12.58(63)	44.213(11)	8.21(41)	44.621(3)				
13.62(68)	44.12587)	8.57(43)	44.589(11)				
14.59(73)	44.040(7)	9.49(47)	44.498(7)				
15.49(77)	43.967(7)	9.87(49)	44.476(3)				
16.63(83)	43.873(11)	10.78(54)	44.391(3)				
17.98(90)	43.764(7)	11.64(58)	44.314(3)				
19.05(95)	43.662(7)	12.51(62)	44.224(3)				
19.91(99)	43.585(7)	13.37(67)	44.157(3)				
21.11(1.10)	43.487(7)						

the different data subsets lie between 438 and 443 GPa (Table III). These values are 1–2% smaller than those of ^{12}C diamond, but this difference remains within the uncertainties in EOS parameter determination.

The difference in the cell parameter at ambient conditions for the two diamond types is $^{12}a - {}^{13}a = 7\times10^{-4}$ Å, which is in good agreement with previous determinations which gave 5×10^{-4} Å.[12]

IV. DISCUSSION

The present values for K_{0T} [446(4) GPa for $K'_{0T}=4$] for ^{12}C diamond agree well with the adiabatic values K_{0S} derived from ultrasonic and Brillouin scattering measurements. The adiabatic values must be corrected to get K_{0T} through the relation[18]

$$K_S = K_T(1+\alpha\gamma T). \tag{2}$$

However, for diamond the difference at room temperature between K_{0S} and K_{0T} is very small (0.1%) since $\alpha=3\times10^{-6}\,\mathrm{K}^{-1}$ (Ref. 19) and $\gamma=1$. McSkimin and Andreatch[20] obtained $K_{0S}=442$ GPa and $K'_{0S}=4$ from the determination of the pressure dependence of the elastic constants. Grimsditch and Ramdas,[5] Vogelgesang *et al.*,[21] and Zouboulis *et al.*[22] reported values of K_{0S} between 442 and 445 GPa while Hurley *et al.*[9] obtained 448 GPa.

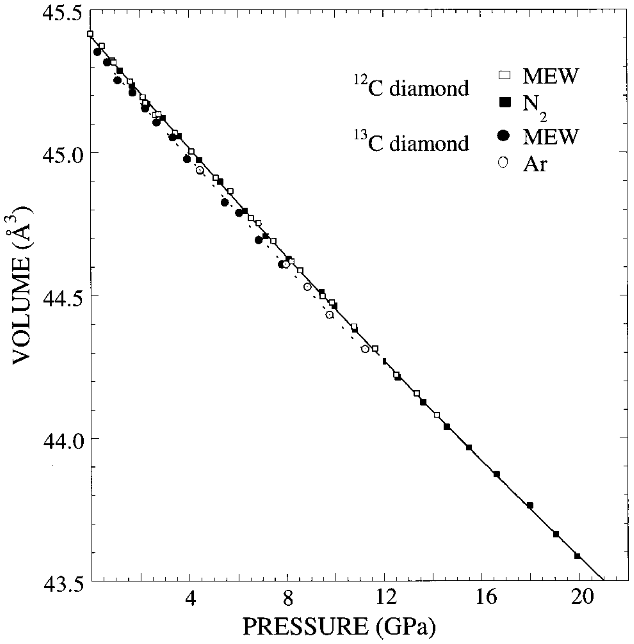

FIG. 2. Cell volume vs pressure curves for ^{12}C and ^{13}C diamond.

TABLE II. Bulk modulus (K_0) and pressure derivative (K'_0) for ^{12}C diamond obtained by fitting the $V(P)$ data to a Birch-Murnaghan equation of state. MEW data from data points obtained using a 16:4:1 methanol/ethanol/water mixture as pressure transmitting medium in the pressure range 10^{-4} 13 GPa. N_2 data from data obtained with N_2 as pressure transmitting medium in the pressure range 10^{-4} 22 GPa. Whole data parameters obtained from the whole (MEW+N_2) data set. Numbers in indicate the standard deviations of the fit.

	MEW data		N data		Whole data set	
V_0 (Å^3)	45.416(4)	45.414(4)	45.414(6)	45.413(5)	45.415(3)	45.413(3)
K_{0T} (GPa)	436(7)	445(7)	444(13)	447(6)	440(9)	446(4)
K'_0	6.5(2.9)	4 (fixed)	4.5(1.9)	4 (fixed)	5.3(1.6)	4 (fixed)

The comparison with existing static data is more difficult since only a few measurements have been carried out so far. Aleksandrov *et al.*[4] have measured the EOS of ^{12}C diamond up to 40 GPa on single crystals using He as a pressure transmitting medium. They quote that their $V(P)$ data match Eq. (1) with $K_{0T}=442\,\text{GPa}$ and $K'_{0T}=4.0(7)$, the values reported by McSkimin and Andreatch.[20] However, it seems that these authors have not directly inferred K_{0T} and K'_{0T} from their own dataset. Moreover, the molar volumes were determined from only one diffraction peak and the number of experimental points was twice less than in the present report over a larger pressure range. More recently, Fujihisa *et al.*[3] have carried out angle dispersive x-ray powder-diffraction experiments. They have measured the cell volumes at 8 pressures between room pressure and 35 GPa and report $K_{0T}=440$ (4) GPa for $K'_{0T}=4$. They also mention that the cell volumes measured above 10 GPa (5 among the eight experimental points) are not reliable since the pressure in the diamond cell was nonhydrostatic above this pressure.

Our results for the bulk modulus of ^{12}C diamond are thus in very good agreement with previous values especially those derived from acoustic and Brillouin measurements. They show also that reliable parameters of the EOS of a very incompressible compound can be obtained from high quality powder-diffraction measurements performed under hydrostatic conditions in a pressure range of less than 20 GPa.

The present study also shows that the EOS of both ^{12}C and ^{13}C diamonds are similar. Previous studies on the elastic constants and bulk moduli of both types of diamond have led to controversial results. Hurley *et al.*[9] have measured the c_{11} and c_{44} elastic moduli of ^{12}C and ^{13}C diamonds using ultrasonic techniques. They showed that c_{11} is not affected by the ^{13}C substitution while c_{44} decreases by 2%. They also obtained information on the effect of isotopic substitution on the effective elastic moduli,

$$c_{\text{eff}}=\frac{c_{11}+2c_{12}+4c_{44}}{3}.$$

This later modulus is 6% higher in ^{13}C diamond when compared with nearly pure ^{12}C diamond (1299.1 and 1233.8 GPa). Such data imply that c_{12} is nearly doubled in ^{13}C diamond. The adiabatic bulk modulus K_{0S} calculated from

$$K_{0s}=\frac{c_{11}+2c_{12}}{3}$$

would therefore be 448 GPa for ^{12}C diamond and 520 GPa for ^{13}C diamond, i.e., a 17% difference. These results have been questionned by Ramdas *et al.*[10] who used Brillouin spectroscopy to investigate the elastic properties of diamond. They found that c_{11} is higher by 0.5% in ^{13}C diamond. They did not measure c_{44} but showed that c_{eff} is only marginally affected by isotopic substitution, being 0.5% lower in ^{13}C diamond compared with ^{12}C diamond (1212.7 vs 1218.7 GPa). Therefore their data do not indicate a large difference between the adiabatic bulk moduli of the two isotopic species of diamond. This conclusion has also been reached more recently by Vogelgesang *et al.*[21]

Fujihisa *et al.*[3] have measured the cell volumes of ^{13}C at 8 pressures between room pressure and 35 GPa and inferred $K_{0T}=454(4)$ GPa for $K'_{0T}=4$. However, like their study of ^{12}C, the nonhydrostatic pressure conditions prevailing above 10 GPa and the limited number of experimental points make this K_{0T} value poorly constrained.

Our volume determination is precise enough to see a difference of 17% in the bulk moduli between both diamonds. A simple calculation using Eq. (1) shows that the $V(P)$ curves should cross between 1 and 2 GPa if one takes $K_{0T}=442$ GPa and $K'_{0T}=4$ for ^{12}C diamond and $K'_{0T}=520$ GPa and $K'_{0T}=4$ for ^{13}C diamond, which is not observed.

TABLE III. Bulk modulus (K_0) and pressure derivative (K'_0) for ^{13}C diamond obtained by fitting the $V(P)$ data to a Birch-Murnaghan equation of state. MEW data from data points obtained using a 16:4:1 methanol/ethanol/water mixture as pressure transmitting medium in the pressure range 10^{-4}–13 GPa. Whole data parameters obtained from the whole (MEW+Ar) data set. Numbers in brackets indicate the standard deviations of the fit.

	MEW data		Whole data set	
V_0 (Å^3)	45.381(7)	45.381(7)	45.378(7)	45.383(6)
K_{0T} (GPa)	441(11)	440(11)	443(15)	438(8)
K'_0	3.8(2.0)	4 (fixed)	1.9(2.1)	4 (fixed)

The measured bulk modulus of ^{13}C may be 1% smaller than the one of ^{12}C diamond, consistent with the Raman measurements of Muinov *et al.*[11] which show that the frequency ratio ($^{12}\nu/^{13}\nu$) of the Raman-active mode decreases with increasing pressure, but in disagreement with the Brillouin measurements of Vogelgesang *et al.*[21] The slight difference in the bulk moduli may thus be the signature of a small pressure dependence of the quantum isotope effect.

The discrepancy with the results of Hurley *et al.*[9] cannot be accounted simply. Several explanations can be proposed. One could invoke experimental problems in their measurements or in those of Ramdas *et al.*[10] At the moment there is no reason to advocate such problems. If the change in bulk moduli is effective, then the only difference with our study lies in the frequency range of the measurements, i.e., static vs ultrasonic for Hurley *et al.*[9] The rationale for such a behavior remains an open question.

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