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Nuclear-resonance-photon-scattering study of the effective temperatures of diamond and of highly oriented pyrolytic graphite

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Nuclear-resonance scattering of bremsstrahlung, employing nuclear self-absorption from the 3089-keV and the 3684-keV levels in ^{13}C, has been used to determine the effective temperatures $T_{\parallel}$ and $T_{\perp}$ of highly oriented pyrolytic graphite (HOPG) at 10, 295, 495, and 683 K in directions parallel and perpendicular to the hexagonal layers. The effective temperature of isotopic diamond (^{13}C) at 295 K was also measured. The bremsstrahlung source was generated using the 4.1-MeV electron accelerator of the University of Stuttgart. In HOPG, the nuclear self-absorption ratios for the parallel and perpendicular directions were quite different, revealing a significant anisotropy in the values of $T_{\perp}$ and $T_{\parallel}$. Comparison between the observed values and those deduced from the vibrational density of states of HOPG agree, within error in $T_{\perp}$, but the measured $T_{\parallel}$ is higher by about 20%. In diamond, the measured effective temperature is higher by 32% than the calculated value. The results are discussed in view of the calculated phonon spectra of HOPG and of diamond.

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I. INTRODUCTION

One of the long-standing problems is the large discrepancy between the measured and calculated effective temperatures of the C atoms in graphite.[1–4] Graphite is known to be highly anisotropic and to have a hexagonal structure in which the bonding between the carbon atoms in the hexagonal planes is covalent (trigonal sp^2 bonds) and much stronger than the weak van der Waals binding between the hexagonal planes. The anisotropy in graphite is also reflected in the high c/a ratio where $a = 0.1415$ nm, the distance between the C atoms within the basal plane, and $c = 0.335$ nm is the distance along the perpendicular direction, i.e., between neighboring planes. Diamond has a fcc crystallographic structure, where each C atom is isotropically bound (sp^3 bonds) to four C atoms positioned at distances of 0.154 nm.

An important problem concerning the study of the two systems is the measurement of the *effective temperatures* of the C atoms. The notion of the effective temperature was first introduced by Lamb;[5] it is related to the *total* kinetic energy of the C atom in the sense that it includes the part due to its internal zero-point vibrational motion. Because of its high anisotropy, graphite may be characterized by two effective temperatures: $T_{\parallel}$ (related to the covalent binding parallel to the graphite planes) and $T_{\perp}$ along the perpendicular direction. Because of the stronger binding, $T_{\parallel}$ is expected to be much higher than $T_{\perp}$; both can be measured using a sample of highly oriented pyrolytic graphite (HOPG) and applying the nuclear-resonance-photon-scattering (NRPS) technique[6,7] in a self-absorption mode. Diamond is isotropic and hence has a single effective temperature.

The NRPS method monitors the Doppler broadening of nuclear levels caused by the *total linear momentum component* of the scattering carbon atom (including that of its zero-point motion) along the direction of the photon beam. Here, we deal specifically with the resonance photon scattering from the 3089- and 3684-keV levels[8,9] in ^{13}C (whose abundance is 1.11% in natural carbon). The Doppler width is given by $\Delta = E(2kT_s/Mc^2)^{1/2}$ where E is the excitation energy, M is the nuclear mass, k is the Boltzmann constant, and T_s is the effective temperature of the scattering atom which is related to its *total* kinetic energy. In HOPG, for each nuclear level, two Doppler broadenings, $\Delta_{\parallel}$ and $\Delta_{\perp}$, may be defined, corresponding to effective temperatures $T_{\parallel}$ and $T_{\perp}$ in directions parallel and perpendicular to the hexagonal layers.

In the NRPS method, described in Fig. 1, a bremsstrahlung beam [Fig. 1(a)] is employed; it is first passed through a ^{13}C nuclear absorber which generates absorption dips [Fig. 1(b)] corresponding to the Doppler-broadened shapes of the nuclear levels at 3089 and 3684 keV. This modified beam is then scattered from the sample. The scattered intensity is proportional to the overlap integral between the Doppler-broadened shapes of the nuclear absorption dip and the nuclear level. This is shown as the shaded area in Fig. 1(c) for the case in which the modified beam is parallel to the graphite planes (represented by $T_{\parallel}$). This shaded area is

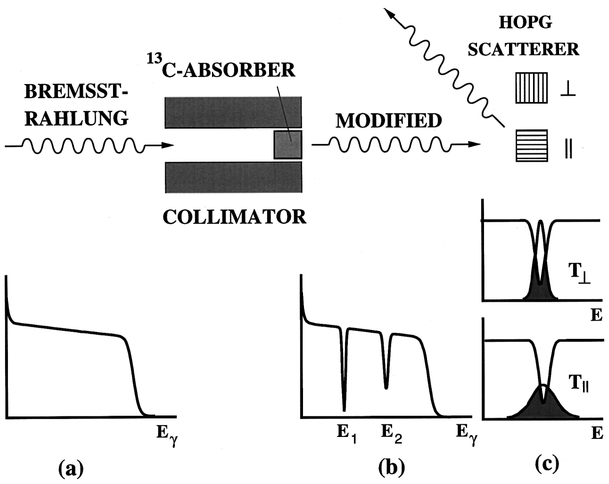

FIG. 1. The upper part of the figure from the left describes a bremsstrahlung beam passing through a collimator to a nuclear absorber which creates the Doppler-broadened dips corresponding to the two nuclear levels in ^{13}C. The modified bremsstrahlung spectrum then strikes the cubic HOPG sample oriented with its hexagonal planes parallel to the photon beam. The perpendicular orientation of the HOPG is also displayed at the top right corner. The lower diagrams represent from left to right (a) schematic drawing of the energy spectrum of the bremsstrahlung, (b) its modified shape caused by nuclear absorption, and (c) the shaded areas represent the overlap integral between the Doppler-broadened shapes of one of the dips in the modified spectrum and that of the corresponding nuclear level. The other shaded area above (c) shows the other overlap integral with the beam perpendicular to the hexagonal planes of the HOPG yielding a smaller scattered intensity.

larger than that of the perpendicular orientation shown at the top of Fig. 1(c) and is represented by $T_\perp$. Thus, by using a nuclear absorber, as shown in Fig. 1, we created a situation in which the scattered intensity is proportional to the Doppler broadening of the nuclear level of the scatterer which in turn is related to its effective temperature.

In this connection, it may be mentioned that the effective temperature T_s is related to the phonon spectrum $g(\nu)$ of the atomic lattice through the Lamb equation:[5]

$$T_s=\frac{\int_0^{\nu_m} g(\nu)h\nu\alpha\, d\nu}{k\int_0^{\nu_m} g(\nu)d\nu}, \tag{1}$$

with $\alpha=[(e^{h\nu/kT}-1)^{-1}+\frac{1}{2}]$, and ν_m is the maximum cutoff frequency of the lattice. Using Eq. (1) the values of $T_\parallel$ and $T_\perp$ were calculated by integration over the vibrational frequency distribution $g_i(\nu)$ in HOPG with $i=\parallel,\perp$ reported by Young and Koppel.[10]

The NRPS technique can be applied only in cases in which the Doppler width Δ is much larger than Γ, the natural width of the nuclear level. This condition is fulfilled in the present work as may be seen in Table I which lists the parameters of the nuclear levels of ^{13}C used for calculating the scattering intensities and shows that Δ is about 20 times larger than Γ. The large values of the Doppler widths are caused by the very high zero-point vibrational motion of the C atoms in graphite where the average effective temperature at 0 K is around 700 K.

TABLE I. Parameters of the ^{13}C nuclear levels used in calculating the resonantly scattered photon intensities and the self-absorption ratios. J_0 and J refer to the spin of the ground state and of the excited states of ^{13}C, respectively. The statistical factor $g=(2J+1)/(2J_0+1)$. The Doppler widths $\Delta_\parallel$, $\Delta_\perp$ are those of HOPG and are calculated at 295 K using $T_\parallel=951$ K, $T_\perp=583$ K.

Level	3089 keV	3684 keV
Γ (eV)	0.500 ± 0.025[a]	0.403 ± 0.030
Γ/Γ_0	1	1
J	1/2	3/2
J_0	1/2	1/2
g	1	2
$\Delta_\parallel$ (eV)	11.36	13.55
$\Delta_\perp$ (eV)	8.91	10.63

[a] This is a weighted average taken from Ref. 9 and that from a recent measurement based on the level widths of ^{27}Al.

This nuclear technique was used recently for studying the effective temperature of ^{13}C atoms in amorphous carbon[4] (AC). The same technique was first applied to study the anisotropic binding of the boron atoms in pyrolytic BN which has a hexagonal structure very similar to that of pyrolytic graphite. In that earlier study,[6] the resonance scattering from nuclear levels in ^{11}B was measured using 9-MeV bremsstrahlung. The same method was also used for studying the anisotropic binding of the K atoms in the graphite intercalated compound C_8K where 8.5-MeV bremsstrahlung was used[7] and the resonance scattering from nuclear levels in ^{39}K was measured.

The present work was motivated by some experimental results of $T_\parallel$ and $T_\perp$ of HOPG and of graphite carried out using the neutron Compton scattering (NCS) method.[1–3] Table II summarizes those results together with the calculated values.[10–13] It may be seen that most measured values of $T_\perp$ at 295 K are around 550 K which agree with the calculated value deduced from the vibrational density of states (VDOS) of HOPG as will be discussed later in Sec. IV. However, the situation of $T_\parallel$ is different because the average of the measured values at 295 K, being around 1000 K, is ~20% higher than that deduced from the theoretical VDOS of graphite.[10–13] For diamond, a much larger discrepancy, 32%, was observed[11,14,15] between the measured and calculated values. It is thus of great interest to determine T_s of diamond, and $T_\parallel$, $T_\perp$ using an entirely different technique, namely, the NRPS method which employs nuclear resonance scattering of 4.1-MeV bremsstrahlung, to find to what extent the above discrepancy between the measured and predicted values persists. More details concerning the NRPS method may be found in Ref. 4.

II. EXPERIMENTAL METHOD

The bremsstrahlung source is obtained when a 4.1-MeV, ~200-μA beam of electrons (generated by the 100% duty cycle Dynamitron accelerator of the University of Stuttgart) strikes a 4-mm-thick water-cooled gold radiator. The photon

TABLE II. Measured and calculated effective temperatures of ^{12}C: $T_\parallel$, $T_\perp$ (in HOPG) and T_s (in diamond and nonoriented graphite) at 295 K. The first error in the present results is due to statistics only; the errors in parentheses are due to uncertainties in the level widths Γ. NCS refers to the neutron Compton scattering method.

	NCS[1] (K)	NCS[2] (K)	NCS[3] (K)	Present	Calculated Ref. 10 (K)	Calculated Refs. 12, 14 (K)	Calculated Refs. 13, 15 (K)	Calculated Ref. 11 (K)
				HOPG				
T_s	883±63	834±63	838±23	863±38(95)	715	759[a]	711[a]	660[b],710[b]
$T_\perp$	550±30	552±30	550[c]	607±37(83)	548	550[c]	550[c]	
$T_\parallel$	1050±80	975±80	982[c]	990±55(135)	798	865[a]	793[a]	
				Diamond				
T_s			934±25	967±30(133)		718	725	721

[a] Deduced from T_s after adopting $T_\perp = 550$ K (at 295 K) and using the relation: $T_\parallel = (3T_s - T_\perp)/2$.

[b] Deduced from the VDOS of amorphous carbon and glassy carbon (Ref. 11), and they are different from that of HOPG (Ref. 10). Those calculated values of T_s are different from 743 K quoted erroneously in Ref. 4.

[c] This is an adopted value and is being used for deducing $T_\parallel$.

beam was passed through a 3-mm lead hardener and then to a 1-m-long lead collimator containing a 1.0-cm through hole before hitting the nuclear absorber and then the sample. For detecting the scattered radiation, two hyperpure germanium (HPGe) detectors were used. In the various runs, the detectors were placed at scattering angles in the range 125°–135°. The efficiencies of the various detectors were between 30% and 100% (relative to a standard 7.5×7.5-cm^2 NaI/Tl detector). In front of the detectors, lead sheets with thicknesses between 15 and 30 mm were used as beam hardeners to reduce the huge number of scattered low-energy photons. Other details of the experimental system, the electronics, and data acquisition method are described elsewhere.[16]

The electron beam, the bremsstrahlung, the collimators, and the absorbers were very carefully aligned so that the bremsstrahlung beam could pass in its entirety through the absorber before striking the sample. This was necessary because any fraction of the primary beam which could reach the sample without passing through the absorber could severely distort the self-absorption measurement.

A. The HOPG sample

The sample consisted of five separate HOPG plates, packed together using a very thin plastic foil to form a cubic shape (29 mm on each side) with a total weight of 55 g; it contained a total of 610 mg of ^{13}C. The mosaic spread of the HOPG was determined by neutron diffraction and was found to have a full width at half maximum of $\delta = 10°$. The scattering intensities were measured at 10, 295, 495, 683 K, using a nuclear self-absorber in the path of the photon beam. At 10 K, the HOPG was placed inside a cryostat whose axis coincided with the geometrical axis of the cubic sample and could be rotated so that the *c* axis could be either parallel or normal to the photon beam. For high-temperature scattering intensity measurements, the HOPG sample was placed between two copper plates connected by four thick copper rods to achieve good thermal contact. Electrical heating of the copper base of the HOPG sample was used. Because of the poor heat conductance of HOPG, the temperature gradient between the top and bottom part of the HOPG was very large, amounting to 80 and 186 K at 495 and 683 K, respectively. The actual thermodynamic temperature of the HOPG was taken to be the average of the two readings. The geometry of the system was such that the path of the photon beam was free of the copper rods of the heating system. In order to reduce the background radiation scattered from the walls of the cryostat, it was necessary to provide the outer sleeve of the cryostat and its inner radiation shield with four windows, 40 mm×40 mm each. The windows of the inner radiation shield were covered by an aluminum-coated Mylar (0.02 mm thick), while a Kapton foil (0.13 mm thick) was glued on the windows of the external radiation shield of the cryostat. This arrangement ensured that the photon beam could pass through the sample without hitting any of the higher-*Z* structural materials of the cryostat such as aluminum or stainless steel.

B. The ^{13}C-diamond sample

Since the abundance of ^{13}C in natural diamond is only 1.11%, it was necessary to use an isotopic diamond sample in order to get a significant resonance scattering signal within a relatively short time. The sample (consisting of four pieces of isotopic diamond) weighed 222.5 mg and contained a total of 132.2 mg ^{13}C; it was wrapped using 155.4-mg Al foil. The diamond runs were taken only at room temperature.

C. Self-absorption measurements

For self-absorption measurements, the beam was passed through a 2.295-g/cm^2 absorber of isotopic amorphous carbon (98% ^{13}C) inserted inside a copper cylinder of 11.5 mm inner diameter before hitting the sample. The scattered radiation from the two perpendicular geometries of the HOPG was measured using the two HPGe detectors mentioned above. The comparative nonresonant absorber consisted of an equivalent weight of powdered natural graphite containing 98.89% ^{12}C and 1.11% ^{13}C. The data related to the absorbers and scatterers are listed in Table III. Here we briefly mention that the nuclear absorption ratio is defined as $R = (N_0 - N_n)/N_0$ where N_0 and N_n represent the scattered in-

TABLE III. Input data used for calculating the scattered intensities and nuclear self-absorption ratios. HOPG and diamond scatterers were used. The nuclear absorbers were liquid (Liq) ^{13}CO and amorphous carbon (AC). T_s is the effective temperature of the ^{13}C isotope in the absorbers and scatterers. Asterisks refer to values calculated in Ref. 4, where the numbers in parentheses refer to the thermodynamic temperature at which the value of T_s is given. The data in the first four rows are those of the absorbers while the last two rows are those of the scatterers.

	Weight (g)	Thickness (g/cm^2)	T_s (K)	^{13}C (%)	^{12}C (%)
Liq ^{13}CO		3.431	346* (78)	99	1
Liq CO (natural)		3.384	346* (78)	1.11	98.89
AC (^{13}C)		2.295	822[a] (295)	98	2
AC (natural)		2.152	822[a] (295)	1.11	98.89
Diamond	0.225	0.879		59.4	40.6
HOPG	55	6.5		1.11	98.89

[a] Measured effective temperatures of ^{13}C atoms in AC taken from Ref. 4.

tensities obtained by passing the beam through a nonresonant (natural carbon) and a resonant (^{13}C AC) absorber respectively, before hitting the sample.

For HOPG another set of self-absorption measurements was carried out in which a liquid ^{13}CO nuclear absorber was used where the effective temperature of the ^{13}C in liquid ^{13}CO was calculated as described in detail elsewhere.[4] This method of deducing the effective temperature of ^{13}C in liquid ^{13}CO is reliable as it was tested experimentally in a similar case[17] of liquid N_2. In yet another measurement related to HOPG, the scattered intensity was measured without inserting any absorber in the path of the beam. The results were compared with those measured with a ^{13}CO resonant absorber. The results of the self-absorption together with deduced values of $T_{\parallel}$ and $T_{\perp}$ from all the above measurements are listed in Table IV from which the spread of values may be seen. The errors are mainly statistical errors. The values obtained from the 3684-keV level are generally higher than those obtained from the 3089-keV level. The difference is attributed to the selected values of the level widths. Since we had no reason to prefer one group of values over the other, we took an average over all values, weighted by the statistical error.

The self-absorption measurements in the case of the diamond sample were carried out only at room temperature. The scattered radiation was measured after interchanging back and forth the 2.295-g/cm^2 ^{13}C AC resonant absorber with the comparative nonresonant absorber of natural graphite. The results are listed in Table IV.

III. RESULTS AND DISCUSSION

A. Calculation of scattered intensities

A typical scattered radiation spectrum from the HOPG sample using a liquid ^{13}CO nuclear absorber (3.431 g/cm^2 thick) and a HPGe detector (with an efficiency of 99% relative to that of a NaI detector of dimensions 7.5 cm$\times$7.5 cm) is given in Fig. 2(a); it shows the scattered γ lines corresponding to nuclear-resonance scattering from the two levels in ^{13}C with the HOPG sample oriented with its hexagonal planes parallel to the beam. To illustrate the dependence of the scattered intensity on the orientation of the HOPG with respect to the beam, we show in Fig. 2(b) a difference spectrum between the parallel and perpendicular orientations of the HOPG relative to the photon beam. This difference corresponds to an anisotropy of $I_{\parallel}/I_{\perp}\sim 1.08$ at 295 K.

The calculation of scattered intensities and self-absorption ratios from samples of finite thickness and well-defined geometry follows exactly the same procedure as that described in a previous paper.[4] Here we only mention that the use of the nuclear absorber in the present technique is important and enables us to get a dependence of the scattering intensity on the effective temperature of the scatterer. This in turn means that a measurement of the self-absorption ratio provides a value of the effective temperature of the scatterer. To illustrate this procedure we give in Fig. 3 the calculated results of the nuclear self-absorption ratios versus the effective temperature, for the 3089-keV level in ^{13}C, obtained using

TABLE IV. Measured self-absorption ratios of HOPG and diamond averaged over the two HPGe detectors. Deduced effective temperatures are enclosed in parentheses. The scatterer-absorber combinations are indicated. CO denotes liquid CO where the column with an asterisk refers to a self-absorption measurement where no nonresonant absorber was used (see text). In the diamond case only AC absorber was used.

	Self-absorption ratio and deduced effective temperature			
	HOPG-CO	HOPG-CO*	HOPG-AC	Diamond-AC
3089-keV ∥	0.393±0.008 (888±51)	0.463±0.012* (925±96)*	0.500±0.013 (857±97)	0.485±0.004 (939±33)
3089-keV ⊥	0.447±0.012 (587±46)	0.528±0.014* (525±72)*	0.545±0.010 (554±55)	
3684 keV ∥	0.369±0.011 (1050±97)	0.427±0.016* (1135±175)*	0.472±0.018 (968±157)	0.474±0.005 (914±47)
3684-keV ⊥	0.420±0.018 (708±73)	0.495±0.018* (625±100)*	0.516±0.015 (613±104)	

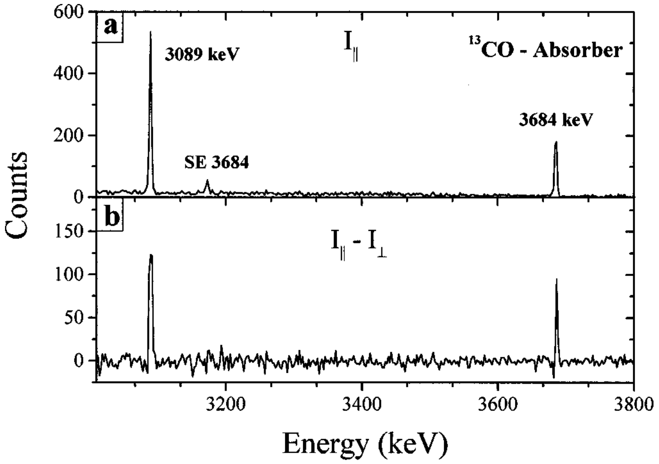

FIG. 2. (a) Typical scattered radiation spectrum from the 6.5-g/cm^2 HOPG sample using a liquid ^{13}CO nuclear absorber (3.341 g/cm^2) and a HPGe detector (99% efficiency) measured with the bremsstrahlung beam parallel to the graphite planes of the sample. SE refers to the single escape peak. (b) The difference spectrum between the parallel and perpendicular orientations of the HOPG relative to the photon beam.

the HOPG sample and absorbers which were actually employed in the present work; the input data are listed in Table III. These calculated curves were used for deducing the effective temperatures $T_\parallel$ and $T_\perp$ of HOPG. Similar curves were calculated for the 3684-keV level and for the isotopic diamond scatterer with the ^{13}C AC absorber; these curves were used for deducing the corresponding effective temperatures of the scatterers.

It is important to emphasize that the $T_\parallel$ and $T_\perp$ results, obtained in the present work at 295 K, are those of the ^{13}C isotope and are weighted averages over eight separate determinations. This is because two different nuclear absorbers (AC and liquid CO) were used, two HPGe detectors and two nuclear levels. Table V lists the deduced averaged values of the effective temperatures, all obtained for the ^{13}C atoms in HOPG and diamond. An important factor which increases the error in the measured results is the uncertainty in the level widths. This has a direct and major effect on the resulting values of T_s, $T_\parallel$ and $T_\perp$ giving rise to an error of up to ~14% and is shown separately in Table V.

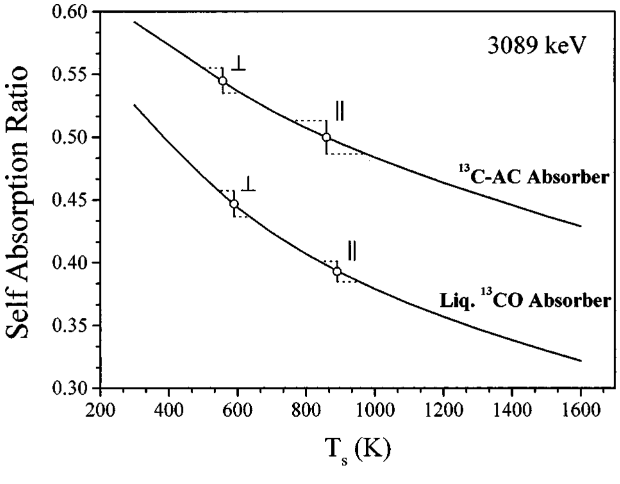

FIG. 3. Calculated nuclear self-absorption of the 3089-keV level as a function of the ^{13}C effective temperature T_s. The thicknesses and ^{13}C abundances of the HOPG scatterer, of the resonant and nonresonant AC and CO absorbers, are listed in Table III, along with the effective temperature of the resonant absorbers. The experimental data points together with the errors are weighted averages of the results from the two detectors.

TABLE V. Measured weighted averages of effective temperatures of the ^{13}C atoms in HOPG and diamond at 295 K. The values may be converted to those for natural graphite by multiplying by the mass factor $(13/12)^{1/2}$. The first error in the deduced effective temperatures is due to statistics only. Errors in parentheses refer to those obtained from the uncertainty in the level widths Γ.

	Effective temperatures HOPG-^{13}C	Diamond-^{13}C
$T_\parallel$ (K)	951±53 (130)	
$T_\perp$ (K)	583±36 (80)	
T_s (K)	829±37 (91)	929±29 (125)

In order to compare the present ^{13}C values with those of the NCS technique obtained by neutron scattering from *natural* samples containing 98.9% ^{12}C, 1.11% ^{13}C, the measured effective temperatures were multiplied by the mass correction factor $(\frac{13}{12})^{1/2}$. For HOPG, another correction was first applied to account for the low quality of our sample having a mosaic spread of the graphite crystallites (with a half-width at half maximum of $\delta = 5°$). The raw measured values $T_\perp^*$ and $T_\parallel^*$ are related to the corrected values $T_\perp$ and $T_\parallel$ by

$$T_\perp^* = T_\perp \langle \cos^2\theta \rangle + T_\parallel \langle \sin^2\theta \rangle, \tag{2}$$

$$T_s = (2T_\parallel^* + T_\perp^*)/3, \quad \text{and} \quad T_\parallel = (3T_s - T_\perp)/2, \tag{3}$$

where

$$\langle \sin^2\theta \rangle = \int_0^{\pi/2} \sin^3\theta \, \exp\{-[(\theta/\delta)^2 \ln 2]\} d\theta \times \int_0^{\pi/2} \sin\,\theta \, \exp\{-[(\theta/\delta)^2 \ln 2]\} d\theta \tag{4}$$

is a weighted average over all crystallite directions θ constituting the HOPG sample. It may be noted that this correction has the effect of increasing the measured $T_\parallel^*$ by 0.6% and decreasing $T_\perp^*$ by 1.9%.

Table II compares our corrected results of $T_\parallel$, $T_\perp$, and T_s (of diamond) with the NCS results and with those obtained using the calculated VDOS of HOPG (Refs. 10, 12, and 13) and diamond.[11,14,15] In general, a good agreement is found between the present results and that of the NCS method. Our large quoted error of ~14% (enclosed in parentheses in Table II) is caused mainly by a ~7% uncertainty in the level widths; the statistical error is much smaller and is also indicated. The present measured $T_\perp$ seem to be higher than the NCS results but within the experimental uncertainties. This is remarkable in view of the fact that the NRPS method is essentially model independent while the NCS technique assumes the validity of the impulse approximation and depends on the final state effects of the scattered neutron from the atoms of the sample. In the NRPS technique, two main assumptions were made. The first is that of free recoil which is well justified because the recoil energies of ^{13}C are 390 and 560 eV, corresponding to the excitation of the 3089- and 3684-keV levels. Those energies are far higher than the atomic binding energies of the carbon atoms in the graphite lattice. The second assumption is that of harmonic approximation expected to be valid at 295 K for graphite which is a strongly bound system since the main contributor to $T_\parallel$ and $T_\perp$ is the high-energy phonons [see Eq. (1)]. At 295 K, this part of the phonon spectrum contributes to $T_\parallel$ and $T_\perp$ through its zero-point energy only. Another point of interest is the momentum transfer which for the present photon scattering experiment is of the order of 3000 A^{-1} while for the NCS technique it is $\sim$150 A^{-1}.

In this connection it should be noted that apart from Ref. 10, all calculations reported the VDOS of nonoriented graphite from which the value of T_s was obtained using Eq. (1). To deduce $T_\parallel$ we adopted $T_\perp = 550$ K at 295 K and used the relation $T_\parallel = (3T_s - T_\perp)/2$. This procedure is justified because the predicted value, $T_\perp = 550$ K, obtained from Ref. 10 agreed nicely with the NCS measurements of Refs. 1 and 2. Table II shows that the deviation between the measured and the calculated values of $T_\parallel$ remains unchanged compared to the NCS results and is still of the order of 20%. This large deviation cannot be due to multiple photon scattering effects in the bulky HOPG sample or in the nuclear absorbers. Such an effect could, in principle, increase the measured value of T_s; it was calculated and found to be less than 1%.

The present value $T_s = (863 \pm 95)$ K at 295 K for ^{12}C in HOPG (Table II) is very close to that of amorphous carbon,[4] $T_s = (856 \pm 128)$ K, deduced from a measured value (822 ± 123) K for ^{13}C. The last two measured values for T_s are higher by 26% than the average of the calculated values: $T_s = 710$ and 660 K obtained using the VDOS of Ref. 11 for amorphous carbon and glassy carbon (Table II). It should be remarked that this calculated value was erroneously quoted in Ref. 4 to be equal to 743 K.

The measured effective temperature T_s of diamond (Table II) is also higher than the calculated values (based on the VDOS) by ~32% and agrees nicely with the NCS result. In this case, multiple scattering effects of photons are expected to be entirely negligible because of the tiny mass (0.225 g) of the sample.

B. Temperature variation of the scattered intensities in HOPG

It may be speculated that the large discrepancies between the measured and calculated effective temperatures in HOPG are caused by *anharmonic* effects. To test this possibility we measured the scattering intensities as a function of temperature to find out to what extent the data will conform to those expected from the calculated phonon spectra of Ref. 10. In this measurement we used exactly the same nuclear absorber as that of the self-absorption measurements described above. The data were taken at 10, 295, (495 ± 40), and (683 ± 93) K for both the parallel and perpendicular orientations of the HOPG sample with respect to the photon beam. The 10-K measurement was carried out using a Displex cryostat. In the high-temperature measurements, the HOPG sample was placed between two copper plates and electrical heating was used. More experimental details concerning this measurement were given in Sec. II A above. The scattering intensity measurements taken with a nuclear absorber in the path of the incident photon beam were normalized to 295 K. These ratios are displayed in Fig. 4 together with the calculated values. Table VI shows the same data along with the measured and calculated effective temperatures using the VDOS of Ref. 10.

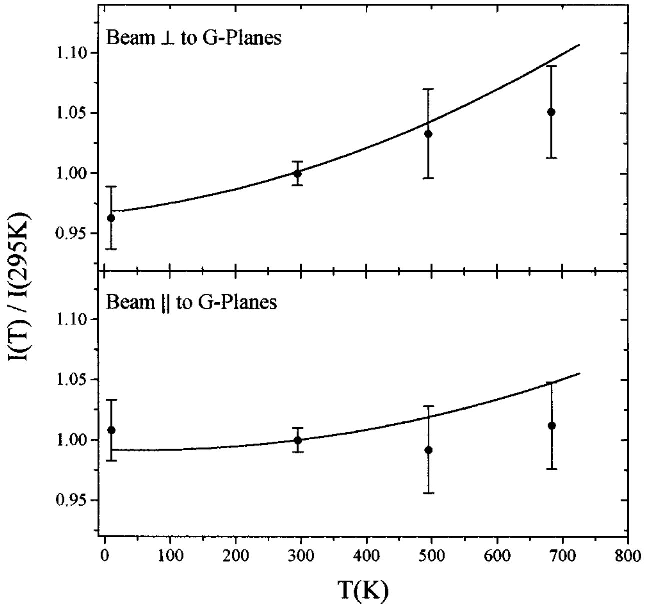

FIG. 4. Measured and calculated (solid lines) scattering intensities $I_\parallel$ and $I_\perp$ from the HOPG sample (relative to 295 K) as a function of T. The ^{13}C AC nuclear absorber was used. The solid lines were calculated using values of $T_\parallel$ and $T_\perp$ deduced from the VDOS of HOPG given in Ref. 10. The input data for the calculations are given in Tables I and III.

The measured scattering intensities were also used for deducing $T_\parallel$ and $T_\perp$ versus T; the results are given in Table VI. These values contains a correction which accounts for the mosaic spread of the HOPG sample used in the present work. It may be noted that the calculated relative increase in $T_\perp$ between 295 and 683 K is about 29% and is more than a factor of 6 larger than the relative increase in $T_\parallel$. This may

TABLE VI. Measured intensities (relative to 295 K) and the corresponding deduced effective temperatures of the ^{12}C atoms in HOPG. The experimental results are weighted averages over the two resonant levels and the two detectors. The calculated effective temperatures using Eq. (1) and $g(\nu)$ of Ref. 10 are also indicated.

T (K)	Relative intensity	Experiment (K)	Calculated Ref. 10 (K)
10; ∥	1.008±0.025	1034±144	770
295; ∥	1.000±0.014	990± 55	798
495; ∥	0.992±0.036	951±187	871
683; ∥	1.012±0.036	1002±182	980
10; ⊥	0.963±0.261	513±113	479
295; ⊥	1.000±0.015	607± 37	548
495; ⊥	1.033±0.037	728±169	671
683; ⊥	1.051±0.038	781±173	818

be intuitively understood by noting that the effective temperature is determined largely by the high-energy vibrational frequencies [Eq. (1)] which for $T_\parallel$ have a peak around 1860 K (as may be seen in Ref. 10) while the two high-energy peaks of $T_\perp$ occur at 650 and 1250 K and hence are more likely to be excited at $T=493$ and 683 K at which the measurements were made.

The measured T variations of $T_\perp$ and $T_\parallel$ contain large uncertainties. Nevertheless, it may be seen that the measured $T_\perp$ increases steadily with T and is almost reproduced by the calculated values. However, the relative increase of $T_\parallel$ with T is much weaker than the calculated one. This behavior of $T_\parallel$ is in line with that expected from a higher effective temperature (than the calculated one) which is supposed to be much less influenced by an increase in T. This result is remarkable as it may be viewed as an independent evidence for the validity of the measured high value of $T_\parallel$ observed here. The measured variations of both $T_\perp$ and $T_\parallel$ with T seem to rule out the influence of anharmonic effects.

IV. CONCLUSIONS

In conclusion, the present results of the effective temperatures in diamond and $T_\parallel$, $T_\perp$ in HOPG using the NRPS method agree with those measured using the NCS technique. The measured results of $T_\perp$ agree with those obtained using the VDOS of HOPG, however, the measured $T_\parallel$ of HOPG and that of diamond seem to deviate considerably (around 20% and 32%, respectively) from the calculated values obtained using the VDOS in both systems. In addition, the results of the experimental T variation of $T_\parallel$ and $T_\perp$ strongly support the measured high value of $T_\parallel$. The present results are also in line with those of amorphous carbon reported recently[4] which also revealed a large deviation between the measured and calculated values. This deviation between the measured and calculated $T_\parallel$ in HOPG and in the T_s of diamond remains an open question. The large error in the present results is mainly contributed by the uncertainties in the level width of the two nuclear levels in ^{13}C. It would be of great interest to remeasure those widths in order to markedly reduce the overall error in the present measurements.

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