

Orientation of molecularly intercalated N_2 in $C_{24}K$

R. Moreh

*Nuclear Research Center, Negev, Beer-Sheva, Israel
and Ben-Gurion University of the Negev, Beer-Sheva, Israel*

S. Melloul

Nuclear Research Center, Negev, Beer-Sheva, Israel

H. Zabel

Experimental Physics IV, Ruhr Universitat Bochum, Germany

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The nuclear-resonance photon-scattering technique was used to study the tilt angle of physisorbed N_2 with respect to the graphene planes of $C_{24}K$ prepared from highly oriented pyrolytic graphite. This was done by measuring the ratio of the resonantly scattered intensities from the 6324-keV level in ^{15}N with the photon beam parallel and perpendicular to the graphene planes. In the temperature range $T=10-190$ K where nitrogen is molecularly intercalated into the $C_{24}K$, a huge anisotropy, a factor ≈ 2.5 , was observed in the scattering cross sections. This is interpreted in terms of the orientation of the molecular axes of the N_2 molecules as being very nearly parallel to the graphene planes. Above 200 K, the amount of molecularly intercalated N_2 was negligible.

I. INTRODUCTION

Binary second-stage graphite intercalation compounds (GIC's) of the form $C_{24}M$ ($M=K, Rb,$ and Cs) are known^{1,2} to molecularly intercalate large amounts of nonpolar molecules such as N_2 , H_2 , and D_2 . Here we employ the term "molecularly intercalate" rather than "physisorb" because of the very large uptake of the gas compared with the physisorption process and also because of the very long time needed for the gas to get into the vacancies between the graphite planes. It was noted that this process increases the interlayer distance occupied by the alkali molecules,¹ thus allowing the "guest" molecules to reside in alkali planes and in the vacancies between the K atoms. It should be remarked, however, that the above nonpolar molecules do not intercalate into the first-stage GIC's such as C_8K because the vacancies in the K planes are too small to accommodate these molecules. This follows from the fact that in the C_8M compounds, the alkali metals are 1.5 times more-densely packed in the K planes than in the $C_{24}M$ compounds, thus resulting in smaller vacancies.

One problem which arises when dealing with the $C_{24}K + N_2$ system is the orientation of the molecularly intercalated N_2 with respect to the graphite planes. It was noted³ that such information can be easily obtained by employing the nuclear-resonance photon-scattering (NRPS) method, which is very sensitive to the spatial orientation of the N_2 molecular axis. In this method the nitrogen should be in the form of ^{15}N in which a nuclear level at 6324 keV can be resonantly excited by photons from the $Cr(n, \gamma)$ reaction. The same technique was used previously^{3,4} to measure the tilt angle of adsorbed molecules such as N_2 and N_2O with respect to the graphite

planes as a function of temperature. It was also used to study the orientation of nitrate molecules^{5,6} in GICs formed from highly oriented pyrolytic graphite (HOPG)+ HNO_3 .

The basic idea of the NRPS technique has been described in detail elsewhere.^{3,7} Here we only mention that in this technique one monitors the Doppler broadening of the nuclear level in ^{15}N caused by the internal zero-point vibrational motion of the N_2 molecule. The Doppler broadening is maximum along the line joining the two atoms of N_2 and minimum in the perpendicular direction. Since the scattering cross section in this resonance process is proportional to the Doppler broadening of the nuclear level, the scattering cross section in the present case may be used to measure the tilt angle of the molecular axis of the N_2 molecule with respect to the graphite planes.

II. EXPERIMENTAL METHOD

A. Photon beam

Experimentally, the photon beam was generated from the (n, γ) reaction on three chromium disks (each 8 cm diameter and 1 cm thick) placed near the core of the IRR2 reactor. The resulting photon beam was collimated and neutron-filtered using 40 cm of borated paraffin. The intensity of the 6324-keV γ line arising from the $^{52}Cr(n, \gamma)$ reaction is $\approx 10^4$ photons/cm² s on the scatterer. The scattered radiation from the $C_{24}K + ^{15}N_2$ target was detected using two hyperpure germanium (HPGe) detectors of volumes 150 and 120 cm³ placed symmetrically at 15 cm and at an angle 130° on both sides of the target. The background-radiation spectrum was obtained by using an identical target chamber containing the same

amount of graphite but with no N₂ in it. The target preparation is explained below; more details concerning the experimental system was published elsewhere.⁸

B. Sample preparation

The target (Fig. 1) consisted of 380 mg of isotopically enriched N₂ gas (99% ¹⁵N) and a C₂₄K sample (weighing 4.2 g), both enclosed inside a 1-mm-thick aluminum cylinder [14 mm i.d. (inside diameter), 7 cm high]. The aluminum can was connected via a conical press fit⁹ to a large-diameter stainless-steel cylinder (48 mm i.d. and 10 mm high) which served as a reservoir of the free N₂, kept close to the sample, but outside the path of the photon beam.

The second-stage GIC, C₂₄K, was prepared from two rectangular HOPG plates by employing the two-zone furnace method¹⁰ where the HOPG temperature was 400 °C and that of the K metal was 250 °C. The resulting dimensions of the target were 30×15×13 mm³ with the *c* axis perpendicular to the 30×15 mm² plane. Because the thickness of the two sides of the C₂₄K sample were nearly the same (namely, 13 and 15 mm), the atomic attenuation of the 6324-keV photons was practically the same for the two positions of the target in which the photon beam was parallel and perpendicular to the graphene planes.

The isotopic ¹⁵N₂ gas was admitted to the sample chamber by keeping the aluminum can (containing the GIC) at liquid-nitrogen temperature and inserting the ¹⁵N₂ gas through a high-pressure valve fitted on top of the cell. The amount of the N₂ gas in the sample chamber was determined by weighing, before and after inserting the gas. The gas-pressure buildup inside the target chamber at 297 K was around 320 psi. The elevated pressure at the target position at 200 > *T* > 80 K ensured relatively quick intercalation of N₂ into the C₂₄K sample.

The target was placed in such a way that only the

lower part containing the C₂₄K was hit by the photon beam (Fig. 1). This ensured that the stainless-steel container was outside the photon-beam path; thus the scattering signal came mainly from the N₂ molecularly intercalated into the GIC and the relative “background” contribution of the “free” N₂ present in the sample chamber was reduced. At *T* < 77 K, the “free” N₂ contribution is negligible because N₂ turns into a liquid and then to a solid condensing at the bottom of the aluminum container and hence is also outside the path of the photon beam. Another reason for avoiding stainless steel in the path of the photon beam is because iron (⁵⁶Fe) is known¹¹ to be a resonant scatterer of the 8512-keV γ line emitted by the Cr(*n*, γ) reaction and could increase the background enormously.

Pure aluminum was used as a structural material not only because it has a low *Z* resulting in low background but also because it is not a resonant scatterer of any of the γ lines of the Cr(*n*, γ) reaction. Apart from iron, copper was also found to be a resonant scatterer; it scatters the 8484-keV γ line of the Cr(*n*, γ) reaction¹² strongly.

It may be noted that the “free” N₂ gas cannot be oriented and thus its contribution to the scattering intensities causes a reduction of the measured ratio *R* of the scattering intensities from the two sample positions with respect to the beam. Thus *R* should be corrected to account for the “free” gas contribution.

The adsorption cell was placed inside a cryostat which varied the sample temperature between 297 and 10 K. Thermal contact between the C₂₄K sample and the walls of the Al cylinder was maintained using thin Al foil which also avoided the movement of the sample relative to the Al cylinder. The cryostat was rotated around an axis coinciding with that of the cylindrical cell from one position where the photon beam was parallel to the graphite planes of the sample to a perpendicular one.

III. THEORETICAL BACKGROUND

The nuclear photon-scattering cross section is determined primarily from a knowledge of the effective temperature *T_e* of the ¹⁵N atom in the molecularly intercalated state considered in the present work. The scattering cross section σ_e may then be determined by using a calculated curve of σ_e versus *T* (e.g., Fig. 1 of Ref. 13, which also discusses the details of the calculations). In order to write the expression of *T_e* for the present case, we briefly review the calculation for two simpler cases discussed in a previous work. We first consider the expression of *T_e* for pure N₂ gas.^{3,8}

$$3kT_e = 3kT/2 + kT + k\alpha_0/2, \quad (1)$$

where $3kT_e$ is the total effective kinetic energy of the two atoms in the diatomic N₂ molecule. The first two terms on the right-hand side of Eq. (1) correspond to the kinetic energy of translation and rotation of the N₂ molecule as a whole, while the last term is the average kinetic energy of vibration of the diatomic N₂ oscillator, where

$$\alpha_0 = (h\nu_0/k) \{ [\exp(h\nu_0/kT) - 1]^{-1} + \frac{1}{2} \}. \quad (2)$$

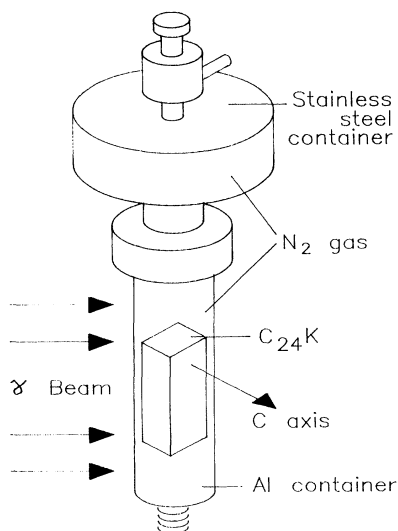


FIG. 1. Target chamber containing the C₂₄K sample + N₂ gas. The path of the γ beam is indicated.

The factor $\frac{1}{2}$ in the last term of Eq. (1) arises from the fact that only the kinetic part of the vibrational energy $\alpha_0 k$ contributes to the Doppler broadening of the nuclear level and hence to T_e .

In a previous paper³ the value of T_e for a N_2 molecule adsorbed on graphite and tilted at an angle ϑ with respect to the surface has been evaluated. In this later case (which is similar to that of the present case) we distinguished between two effective temperatures of the N atom, T_a and T_c being the effective temperatures for incident photons parallel and perpendicular to the graphite planes. The results were³

$$T_a = (\alpha_0 \cos^2 \vartheta + \alpha_2 \sin^2 \vartheta + \alpha_3 + 2\alpha_4) / 4, \quad (3)$$

$$T_c = (\alpha_0 \sin^2 \vartheta + \alpha_1 + \alpha_2 \cos^2 \vartheta) / 2, \quad (4)$$

where α_0 related to the internal vibrational energy of the N_2 molecule was defined above; α_i ($i=1,2$) defined in a similar manner to α_0 of Eq. (2) are related to the out-of-plane vibration and libration of the entire molecule (with ν_1 and ν_2 the corresponding frequencies), while α_i ($i=3,4$) refer to the in-plane vibration and libration of the entire molecule (with ν_3 and ν_4 the corresponding frequencies). The factors $\cos^2 \vartheta$ and $\sin^2 \vartheta$ in Eqs. (3) and (4) arise from projecting part of the kinetic energy and hence the value of T_e of a N_2 molecule (tilted at an angle ϑ) on the graphite plane and on the c axis, respectively. To simplify matters, we assume $\nu_1 = \nu_2$ and $\nu_3 = \nu_4$; thus the out-of-plane motion and the in-plane motion of the N_2 molecules are described by the single frequencies ν_1 and ν_3 , respectively. The value of ν_1 was determined by comparing the measured variation of the scattering cross section versus T (from a sample containing N_2 adsorbed on Grafoil³) with the calculated cross sections. In a similar manner the value of ν_3 was determined by comparing the measured variation of the scattering cross section versus T (from a pure N_2 sample) with calculated cross sections. The deduced values expressed in units of temperature are

$$h\nu_1/k = 250 \text{ K}, \quad h\nu_3/k = 58.3 \text{ K}.$$

In the present work we adopt the above simple model and the deduced values of ν_i for calculating the expected anisotropy in the scattering cross section for a N_2 molecule intercalated between two graphite planes. However, since the out-of-plane force constant between the molecularly intercalated N_2 (in $C_{24}K$) and the two graphite surfaces is roughly expected to be double that of the physisorbed N_2 , ν_1 should therefore be replaced by $2^{1/2}\nu_1$. The in-plane frequency ν_3 is also expected to increase due to the relatively strong interaction between the K^+ ions and the N_2 molecules as compared with the N_2 - N_2 interaction occurring in the N_2 -Grafoil system. To account for this effect, we may replace ν_3 by $2^{1/2}\nu_3$. By substituting these values of ν_i in Eqs. (3) and (4), the resulting values of T_a and T_c (at $T=12$ K) of the ^{15}N atom of N_2 molecules molecularly intercalated in $C_{24}K$ and lying flat on the surface, $\vartheta=0^\circ$, are

$$T_a = 44.2 \text{ K}, \quad T_c = 176.5 \text{ K}.$$

In this calculation, the $C_{24}K$ is assumed to be formed

from HOPG, i.e., fully oriented graphite. These T_a and T_c values should, however, be corrected to account for the mosaic spread of about 12° of the graphene crystallites of the $C_{24}K$ sample. The corrected values are

$$T_a^* = 434.2 \text{ K}, \quad T_c^* = 192.5 \text{ K},$$

which by using Fig. 1 of Ref. 13 may be seen to correspond to scattering cross sections of

$$\sigma_a = 1.27b, \quad \sigma_c = 0.54b,$$

yielding a cross-section ratio $R = 2.34$ at 12 K, and hence are highly anisotropic. The lower solid line of Fig. 2 shows the calculated values of R versus T obtained using the above procedure; it shows a fairly good agreement with the experimental points (see Sec. IV).

An alternative estimate of ν_1 and ν_3 may be obtained by using the results of a study of the phonon spectrum of the N_2 -graphite system.^{14,15} In those studies a decoupling of the in-plane and out-of-plane vibrational modes was assumed and hence effective temperatures parallel and perpendicular to the graphite planes can be deduced from the reported phonon spectra by using the relations

$$kT_a = \frac{\int_0^{\nu_{mc}} g_{\parallel}(\nu) h\nu \alpha d\nu}{\int_0^{\nu_{ma}} g_{\parallel}(\nu) d\nu}; \quad kT_c = \frac{\int_0^{\nu_{mc}} g_{\perp}(\nu) h\nu \alpha d\nu}{\int_0^{\nu_{mc}} g_{\perp}(\nu) d\nu}, \quad (5)$$

where

$$\alpha = [\exp(h\nu/kT) - 1]^{-1} + \frac{1}{2} \quad (6)$$

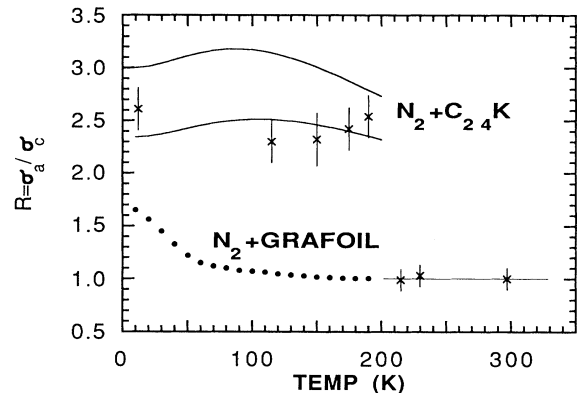


FIG. 2. Measured scattered intensity ratio $R = \sigma_a / \sigma_c$ vs T from the $C_{24}K + N_2$ target where σ_a and σ_c correspond to cross sections where the photon beam is parallel and perpendicular to the graphene planes, respectively. In the range $T \geq 200$ K, the scattered signal is contributed by the "free" N_2 gas present in the dead volume of the sample chamber; hence, $R = 1$ (see text), while at $T < 200$ K, the value of R refers to the scattered signal from the molecularly intercalated N_2 inside the $C_{24}K$ sample (after subtracting the effect of the free nonintercalated gas). The solid lines are calculated for N_2 molecules lying flat at the graphite surface using effective temperatures obtained from two different estimates (see text). The corresponding data for the $N_2 +$ Grafoil system between 10 and 170 K were deduced from Ref. 3.

and $g_i(\nu)$ ($i = \parallel, \perp$) are the phonon density of states^{14,15} of the in-plane and out-of-plane modes of vibration of the N₂ molecules, with ν_{ma} and ν_{mc} the corresponding maximum frequencies.

The resulting values of T_a and T_c correspond to physisorbed N₂ and should be corrected for the different environment of the N₂ molecules in the molecularly intercalated state. The correction is done in a similar manner to that discussed above, yielding

$$T_a^* = 427 \text{ K}, \quad T_c^* = 83 \text{ K},$$

which, at $T = 12 \text{ K}$, lead to the cross sections (see Fig. 1 of Ref. 13)

$$\sigma_a = 1.242b, \quad \sigma_c = 0.414b,$$

yielding a ratio $R = 3.0$. The upper solid curve of Fig. 2 shows the calculated ratios $R = \sigma_a / \sigma_c$ as a function of temperature obtained using the last procedure and assuming a tilt angle $\vartheta = 0^\circ$. It should be emphasized that although the above two estimates seem to be crude, involving many assumptions, the calculated anisotropy R , using the former estimate (lower solid line), is close to the measured values (Fig. 2). The sensitivity of R to variations in ν_1 and ν_3 may be seen by noting that the effect of increasing ν_1 to $2^{1/2}\nu_1$ in the first estimate reduces the calculated R by about 14%, while in the second calculation, the reduction is only 5%. However, a similar increase in ν_3 , i.e., increasing it to $2^{1/2}\nu_3$, changes R by less than 2% in both calculations and hence has almost no effect on the calculated anisotropy. This is because $\nu_0 \gg \nu_1 \gg \nu_3$, which means that the internal frequency of the N₂ molecule is the dominant frequency governing the magnitude of the anisotropy of the system.

IV. RESULTS AND DISCUSSION

A. The molecular-intercalation process

The progress of molecular intercalation was monitored by measuring both the scattered signal from the target (Fig. 1) and the ratio R (of scattered intensities with the photon beam parallel and perpendicular to the graphene plane of the C₂₄K + N₂ sample) at $T \approx 170 \text{ K}$. The onset of molecular intercalation is characterized by an increase in both R and the scattered intensity from ¹⁵N with time. This behavior could only occur when more N₂ gas enters the sample; otherwise, the scattered signal from a constant amount of N₂ should stay the same with time. The molecular-intercalation process was found to be very slow, requiring about a week, at 170 K, for the molecularly intercalated amount of N₂ to reach saturation. Furthermore, the molecular intercalation of N₂ into the C₂₄K sample was also studied as a function of temperature; no N₂ was found to intercalate between 297 and 200 K (where the initial gas pressure was 320 psi). Only below 200 K was the onset of molecular intercalation observed, where the highest rate was found at $T \approx 170 \text{ K}$. Thus, the kinetics of the intercalation of N₂ inside the large sample of C₂₄K (initially prepared using HOPG) is much different from that reported by Watanabe *et al.*¹

who used a powdered sample of C₂₄K. The molecular intercalation also revealed a “hysteresis” effect in the sense that the molecularly intercalated gas took a relatively long time of the order of several hours to “leave” the C₂₄K sample when the temperature was increased from 10 K and above 200 K.

B. Intensity ratios

Figure 3 shows the scattered spectra from ¹⁵N in the C₂₄K + N₂ sample at 12 K at the two geometries of the sample with respect to the photon beam. Note the huge anisotropy of the scattered intensities where a large ratio $R = \sigma_a / \sigma_c \sim 2.6$ is obtained. Large ratios were also observed at all temperatures below 200 K, as shown in Fig. 2. It should be noted that this is the highest anisotropy ever observed in the resonance scattering of γ rays in the MeV range from any system; it illustrates the sensitivity of the present method for monitoring molecular orientation. It is very important to emphasize that in Fig. 2 we distinguish between two temperature regions: At $T \geq 200 \text{ K}$, the scattered signal arises only from the “free” N₂ gas present in the “dead” volume of the sample chamber intercepted by the photon beam, which, obviously, has random orientation and hence a value $R = 1$, while at $T < 200 \text{ K}$, the value of R refers only to the molecularly intercalated N₂ gas inside the C₂₄K sample; it is obtained from the measured scattering intensity by subtracting the contribution of the free nonintercalated gas present in the sample container. This was estimated from a knowledge of the total volume of the sample container, the “dead” volume of the container intercepted by the photon beam, and the known variation with T of the scattered intensities from pure N₂ and from N₂ adsorbed on Grafoil.³

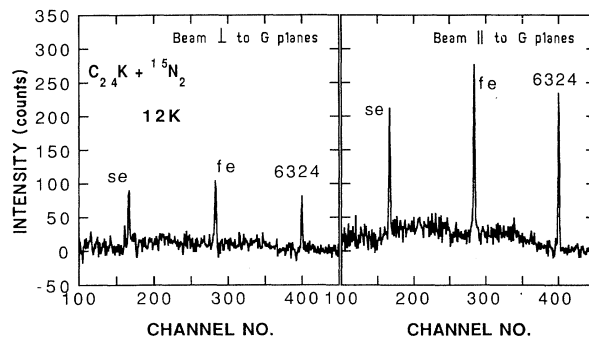


FIG. 3. Portions of the spectra of the scattered radiation (after background subtraction) from ¹⁵N₂ molecularly intercalated in a C₂₄K sample and obtained using a 150-cm³ HPGe detector with the photon beam parallel and perpendicular to the graphene planes. The spectra were taken at 12 K. The three peaks correspond to the photo, first (FE) and second (SE) escape peaks of the resonantly scattered 6324-keV γ line. The running time at 12 K was 11 h at each position.

C. Tilt angle of N₂ molecules

An idea for the expected tilt angle of the N₂ molecules may be obtained by reviewing the main results of a previous study of the tilt of N₂ molecules *physisorbed* on Grafoil.³ This is summarized in Fig. 2 which displays the values of R obtained from the results of Ref. 3. Figure 2 also shows the calculated values of R of the C₂₄K + N₂ system for an assumed tilt of $\vartheta = 0^\circ$ (solid lines) obtained using the two estimates described in Sec. III. The data point at 115 K is in fact an average over measurements carried out at 100 and 130 K. Almost all ratios are found to lie close to the lower calculated line. The agreement between the measured and the lower predicted line is remarkable in view of all assumptions and uncertainties involved in the calculations. It should be emphasized that no free parameters were used and the only frequencies used were derived from a previous work on the physisorption of N₂ of Grafoil, as discussed in Sec. III above. It is also of interest to note the departure of the measured values of R from the predicted upper line obtained using the effective temperatures derived from the theoretical work of Refs. 14 and 15. The reason for the deviation between the two predicted solid lines is not understood.

The above agreement seems to indicate that the out-of-plane tilt angle is close to zero and is almost independent on temperature up to 190 K; it also shows that the N₂ can "enter" the C₂₄K sample only with its molecular axis lying parallel to the graphite planes and only at $T < 200$ K.

An estimate of the upper limit for the tilt angle may be obtained by noting that the calculated R values using a tilt angle $\vartheta = 15^\circ$ was 20% lower than that at $\vartheta = 0^\circ$. Such values would be out of the range of all the data points measured in the present work. We may thus consider $\vartheta = 15^\circ$ as an upper limit for the tilt angle of the N₂ molecules in the above temperature range.

It is of interest to compare¹ the dimensions of the N₂ molecule with the space available between the graphene planes. The large and small van der Waals diameters of N₂ are around 3.0 and 4.0 Å, which are to be compared with 2.05 Å which is the thickness of the interlayer vacancy occupied by the K layer. Thus because of the limited spacing available for accommodating the N₂ molecules in the K plane, one would expect the N₂ molecules to intercalate into the C₂₄K only with their molecular axes parallel to the graphene planes. One would also expect this process to be associated with an expansion of the interlayer spacing and hence a swelling of the lattice constant of the C₂₄K GIC. This expectation is in line with the fact that the molecular intercalation of H₂ and D₂ in C₂₄K was reported¹ to cause an expansion of the lattice constant c_0 from 8.67 to 8.96 Å. More recently, a detailed measurement of the lattice constant was measured as a function of the H₂ and D₂ concentration at 80 K by Doll, Eklund, and Senatore¹⁶ using neutron diffraction and was found to increase with concentration, reaching the same value mentioned above at saturation. It is thus of interest to measure the lattice constant as a function of temperature and of concentration of N₂ for the present system also.

It should be remarked that an early attempt to measure the tilt angle of D₂ molecularly intercalated in a C₂₄K sample was made by Watanabe *et al.*¹ by measuring the intensity of (00 l) reflections using n diffraction, and comparing the results with structure factor calculations; however, no clear conclusion could be reached with that method.

D. Comparison with the N₂ + Grafoil system

It is of interest to compare this behavior of the N₂ molecules (see Fig. 2) with the case of physisorbed N₂ on Grafoil taken from Ref. 3. It was noted³ that under the quadrupole forces of the graphite surface, at $T \leq 30$ K, the N₂ molecules are adsorbed with their molecular axes nearly parallel to the graphite planes. Thus, the N₂ molecules intercalated between two graphite planes in the C₂₄K sample are expected to behave in a similar manner at low T —namely, to lie parallel to the surface. This behavior is reflected in the high anisotropic value of R . It is also of interest to note the limited spacing between the graphite planes which practically forces the N₂ molecules to lie parallel to the surface at low T . Thus, assuming the tilt angle to be close to $\vartheta = 0^\circ$ at 12 K, one should also expect the tilt to be about the same at $T < 200$ K because of the large measured value of R for the present system. In fact, one may estimate the tilt angle at high T from the fact that R drops to 2.4. Assuming the distance between the graphite surfaces to stay the same with increasing value of T , it is estimated that $10 < T < 200$ K, the tilt angle is $\vartheta \leq 15^\circ$. It is of interest to compare the last conclusions based partially on the N₂-Grafoil results³ at low T with those predicted using the simple model discussed in Sec. III.

In this respect the behavior of the N₂ + Grafoil system resembles that of the C₂₄K + N₂ system. Here, however, the large anisotropy persists up to 200 K, while for the N₂-Grafoil system, it drops gradually, with T reaching $R = 1.0$ at 160 K. The main difference in the behavior of the two systems is that in the present case, the N₂ molecules are practically "trapped" in the K planes, presumably at a zero tilt angle (with respect to the graphite planes) and up to 200 K. Above 200 K, the value of R drops *steeply* to $R = 1$, whereby the N₂ molecules "leave" the K planes and hence lose their orientation. This behavior is to be contrasted with the N₂-Grafoil system where the thermal energy increases the librational amplitude of the nitrogen molecules and hence their average tilt angle, causing to drop *gradually* with T from a value of 1.7 at 10 K, reaching $R = 1.0$ (random orientation) at $T \geq 160$ K. The reason for the much lower anisotropy measured in the N₂-Grafoil system at 10 K stems from the structure difference between grafoil and HOPG. In Grafoil, around 44% of the graphite crystallites are randomly oriented and the remaining crystallites have a mosaic spread with a full-width-at-half-maximum (FWHM) angle of 30°. In HOPG (which was used for preparing the C₂₄K sample), the mosaic spread (after K intercalation) has a FWHM angle of 12°, with no randomly oriented crystallites.

V. CONCLUSIONS

We have shown that the NRPS technique can be used for the determination of the orientation of gas molecules molecularly intercalated into GIC's. We have also shown that the N₂ molecules molecularly intercalate into the C₂₄K GIC (at $T < 200$ K) with their axes practically parallel to the graphene planes. Because of the relatively large amount of intercalated N₂ gas in the GIC, the determination of the orientation angle in the present system is much easier and less time consuming as compared with the case of physisorbed gases on graphite. It was also shown that by measuring the variation of the scat-

tered intensity from the sample with time, this technique may also be employed for an *in situ* investigation of the progress and the kinetics of the molecular-intercalation process.

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