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Oriented N_2 molecules intercalated in $C_{24}Rb$

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The intercalation of N_2 molecules in $C_{24}Rb$ (prepared from highly oriented pyrolytic graphite) was studied using the nuclear-resonance photon scattering (NRPS) technique. It was found that nitrogen is intercalated in a molecular form with its molecular symmetry axis parallel to the graphene planes of the $C_{24}Rb$ and that this process occurs even at 296 K; the physintercalated amount of gas increases with increasing external pressure of the gas. The present work may also be viewed as a relatively simple method for preparing samples of molecular N_2 at $T \leq 296$ K aligned with their molecular axes parallel to the graphene planes.

I. INTRODUCTION

In a recent paper[1] we have studied the tilt angle of physisorbed molecular N_2 in $C_{24}K$, using the nuclear resonance photon scattering (NRPS) technique.[2–6] The $C_{24}K$ sample was prepared from highly oriented pyrolytic graphite (HOPG). The tilt angle was determined by measuring the ratio of scattered intensities from the 6324-keV level in ^{15}N with the photon beam parallel and perpendicular to the graphene planes of the $C_{24}K$ sample. A strong anisotropy of a factor ≈ 2.6 in the scattered intensities showed beyond any doubt that the N_2 molecules are oriented nearly parallel to the graphene planes. It was also shown that no N_2 was intercalated in the $C_{24}K$ sample above 200 K, in agreement with the observation of Watanabe *et al.*[7] In addition, the intercalation process of N_2 inside the HOPG-based $C_{24}K$ sample was found to be very slow (taking about two weeks), due to the limitation of the diffusion process, to start only below 200 K, and to have a maximum rate at around 170 K. In the present work, we used the same method to study the N_2 intercalation in $C_{24}Rb$ prepared also from HOPG. A remarkably different feature was observed as the N_2 molecules were found to physintercalate into $C_{24}Rb$ even at a temperature as high as 296 K. Here also the symmetry axes of the molecules are parallel to the graphene planes. This may therefore be viewed as a relatively simple method for preparing aligned samples of molecular N_2 at $T \leq 296$ K.

The basic idea of the NRPS technique, which is described in detail elsewhere,[2–5] relies on monitoring the Doppler broadening of the 6324-keV nuclear level in ^{15}N caused by the internal zero-point vibrational motion of the N_2 molecule. At low temperatures, this zero-point motion is dominant compared to the thermal motion. It is also directional, having maximum magnitude along the direction of the N_2 molecular axis and minimum in the perpendicular direction. This in turn causes the Doppler width of the nuclear level to have a maximum value along the N_2 molecular axis and minimum in the perpendicular direction. In this resonance process, the photon-scattering cross section is proportional to the Doppler broadening of the nuclear level[3,4] and was utilized for the determination of the tilt angle of the molecular axis with respect to the graphite planes.[1,6]

II. EXPERIMENTAL METHOD

A. γ-ray measurements

Experimentally, the photon beam, the sample container, and the variable temperature cryostat were essen-

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tially the same as that explained in Ref. 1. The scattered radiation from the $C_{24}Rb+{}^{15}N_2$ sample was detected using two hyperpure germanium (HPGe) detectors of volumes 150 and 120 cm^3 placed at 15 cm and at 130° on both sides of the target. More experimental details were published elsewhere.[1–3]

B. Sample preparation and neutron diffraction measurements

Two sets of measurements were carried out using two different amounts of N_2 in the $C_{24}Rb$ sample: 232 and 121 mg of isotopically enriched N_2 gas (99% ^{15}N). The amount of N_2 in the cell was determined by weighing the cell before and after gas insertion. In both cases a $25\times11\times5$ mm^3 $C_{24}Rb$ sample (weighing 3.12 g and prepared from HOPG) was employed and enclosed inside the same target holder described in Ref. 1; the c axis of the HOPG was perpendicular to the 25×11 mm^2 plane. It may be noted that no attempt was made to insert the maximum amount of N_2 into the $C_{24}Rb$ sample. According to Ref. 7, the maximum should be about 250 mg and corresponds to one N_2 per Rb atom. The graphite intercalation compound (GIC) sample $C_{24}Rb$ was prepared[7–9] using two steps: In the first, a given mass of HOPG was transformed into C_8Rb by allowing Rb vapor to react with graphite in a two-bulb tube during one week by keeping the graphite at 250 °C and the Rb at 200 °C. The Rb excess was then eliminated and an additional mass of HOPG (equal to twice the initial mass) was added to the C_8Rb, and the mixture was then kept in a sealed ampoule at 370 °C for two weeks. The sample obtained in this manner is a pure second-stage $C_{24}Rb$, as evidenced by measuring the $(00l)$ neutron diffraction spectrum [Fig. 1(a)] at room temperature (RT). The corresponding identity period was $d_i=0.903\pm0.002$ nm; it compares nicely with the literature values[7,8] and is higher than that of the C_{24} K compound[10] being $d_i=0.874$ nm at RT. From the diffraction spectrum we obtained an upper limit of 3% for the possible occurrence of stage 1 and stage 3 GIC's in the $C_{24}Rb$ sample.

Another measurement was performed at 120 K after introducing a small amount (93 mg) of $^{15}N_2$ gas inside the Al container of the sample. The corresponding $(00l)$ reflections at 120 K [Fig. 1(b)] revealed some other weak lines characterized by $d_i=0.947\pm0.002$ nm. The $^{15}N_2$ gas was introduced inside the cell at RT at a pressure of around 3.5 atm for the 232-mg and around 1.6 atm for the 121-mg amount. The c axis of the HOPG was perpendicular to the 25×11 cm^2 plane. The HOPG used for preparing the sample was of low quality; the mosaic spreads (Fig. 2) of the HOPG, of the $C_{24}Rb$, and of the $C_{24}Rb+N_2$ system as determined from the rocking curves of the (006) reflection (Fig. 2) were $\Delta\phi=8.0°$, 11.0°, and 14.0°, respectively, where $\Delta\phi$ is the full width at half maximum of the angular spread. In those measurements the scattering angle was kept fixed (at an angle $2\theta=31°$), corresponding to the (006) reflection, while the sample was rocked around its axis. The mosaicity measurement of the $C_{24}Rb+N_2$ system was carried out after repeated *slow* cycling between RT and 12 K at a rate of

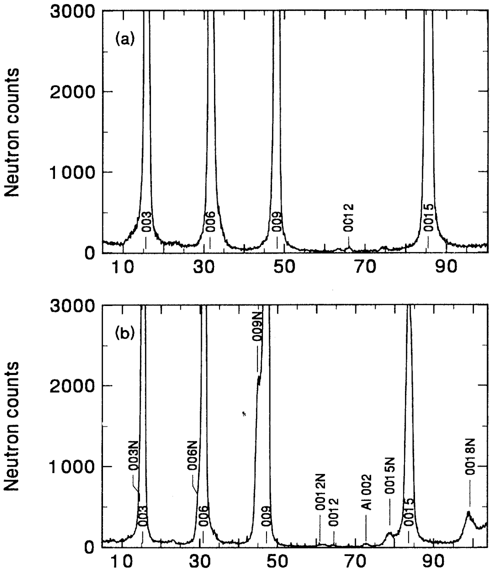

FIG. 1. Neutron diffraction pattern of (a) the $C_{24}Rb$ sample at room temperature using $\lambda=2.453$ Å and yielding $d_i=0.903$ nm. (b) Same sample at 120 K after "inserting" N_2 and using $\lambda=0.240$ nm. The additional weak lines are due to the $C_{24}Rb+N_2$ system. The scattering vector is perpendicular to the $(00l)$ planes. The deduced identity periods are $d_i=0.901$ and 0.947 nm, respectively. Lines denoted by N and Al are contributed by the inserted N_2 and the aluminum container.

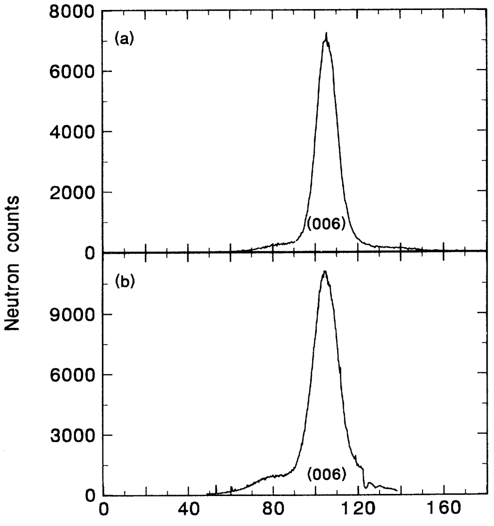

FIG. 2. Rocking curves of the (006) reflections of (a) the $C_{24}Rb$ sample at room temperature using $\lambda=0.245$ nm and $2\Theta=31.7°$. (b) Same sample at 120 K (using $\lambda=0.240$ nm and $2\Theta=31.0°$) after "inserting" N_2. The deduced mosaic spreads are $\Delta\phi=11.0°$ and 14.0°, respectively.

0.5 K/min. The small disruption of the mosaicity of the $C_{24}Rb$ sample under N_2 insertion is in contrast to that of the $C_{24}K+N_2$ system, which revealed a large deterioration of the mosaicity of the $C_{24}K$ sample when cycling between RT and 12 K was carried out.[10] The neutron diffraction measurements were performed at the KANDI-II and KANDI-III diffractometers of the IRR-2 reactor with $\lambda=0.245$ and 0.240 nm, respectively.

III. RESULTS AND DISCUSSION

A. Scattered intensities and nature of the intercalated nitrogen

Figure 3 shows the scattered radiation spectrum from the two perpendicular geometries of the $C_{24}Rb+N_2$ sample with respect to the photon beam. Each spectrum is a sum over measurements taken between 12 and 70 K (for increasing the statistics); it also shows the background spectrum obtained after pumping out the $^{15}N_2$ gas from the $C_{24}Rb$ container. The figure reveals a strong asymmetry of the scattered intensities from the two orientations of the sample.

Here we focus our attention on the measured scattering intensity versus T (Fig. 4) from a nonoriented sample of $(C_{24}Rb+N_2)$, given by the relation $\sigma=(2\sigma_{\parallel}+\sigma_{\perp})/3$, where $\sigma_{\parallel}$ and $\sigma_{\perp}$ are the scattered intensities of the 6324-keV γ line with the photon beam parallel and perpendicular to the graphite planes of the sample. The upper and lower data curves refer to 232 and 121 mg of $^{15}N_2$ in the sample, respectively. Contributions to the scattered intensity come from the intercalated gas inside the $C_{24}Rb$ sample and from the free N_2 gas present in the vicinity of the sample and hit by the γ beam. It is interesting to note that the scattered intensity increases with decreasing T (instead of the expected decrease[6]), reaching a plateau around 130 K and then decreasing with T. Note that the intensities versus T are proportional to the initial amounts of gas in the container. This shows that the amount of gas entering the $C_{24}Rb$ sample is proportional to the external pressure of the gas. The measured increase of intensity at $T<296$ K can only be caused by an increase of the amount of adsorbed N_2 in $C_{24}Rb$ with decreasing T. This process continues until $T\sim 130$ K, where practically all the initial amount of N_2 in the container enters the $C_{24}Rb$. Below 130 K, there is a gradual decrease with T, which is expected[6] for a constant mass of N_2 hit by the γ beam. Another feature revealed here is that the intercalation process is reversible in the sense that all the intercalated gas could be extracted from the sample on heating it. In addition, at each T, the intercalated amount of gas reaches equilibrium relatively quickly (within a few hours). This is in marked contrast with the behavior of $C_{24}K$ (based on HOPG),[1] where the intercalation of N_2 started only below 200 K and was very slow, reaching equilibrium only after about two weeks.[1] The reversibility of intercalating nitrogen seems to show that molecular N_2 is the intercalated species.

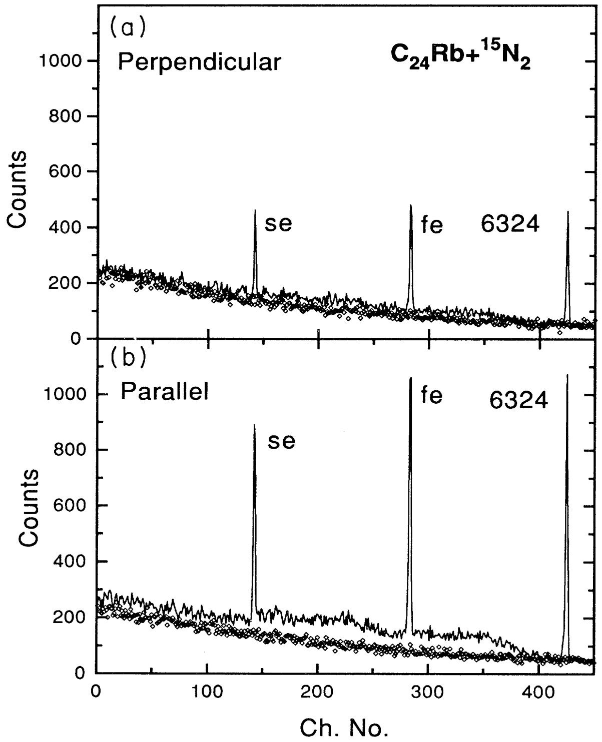

FIG. 3. Sum of scattered radiation spectra obtained at $T=12$–70 K, from $^{15}N_2$ physintercalated in a $C_{24}Rb$ sample and using a 150-cm^3 HPGe detector with the beam parallel and perpendicular to the graphene planes. The "background" scattered spectra were obtained by evacuating the $^{15}N_2$ gas from the container. The three peaks correspond to the photopeak, first escape (fe), and second escape (se) peaks of the resonantly scattered 6324-keV γ line.

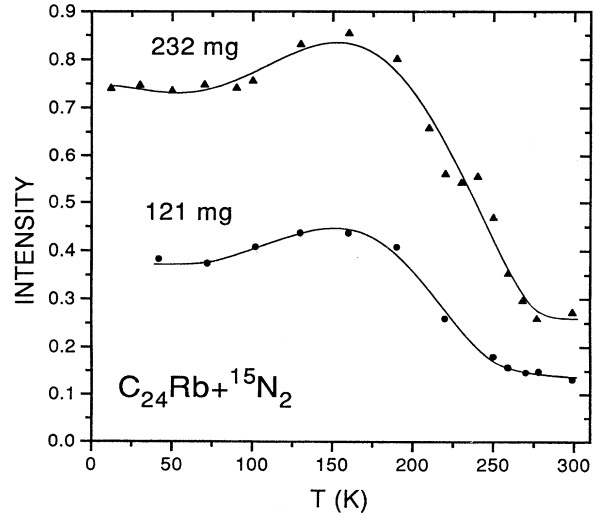

FIG. 4. Scattered intensities vs T for the two separate amounts of $^{15}N_2$ gas (232 and 121 mg) in the $C_{24}Rb$ sample container. The intensities were deduced from the relation $\sigma=(2\sigma_{\parallel}+\sigma_{\perp})/3$, where $\sigma_{\parallel}$ and $\sigma_{\perp}$ are the scattering intensities measured with the photon beam parallel and perpendicular to the graphite planes of the sample. Solid lines are passed through the data points to lead the eye.

This conclusion is also supported by other evidence:

(1) The scattering cross section from the intercalated nitrogen was found to be very close to that of a pure diatomic N_2 gas. Since the scattered intensity is strongly dependent on the effective temperature of the N atom, which in turn is characterized by its chemical nature, we conclude with certainty that the nitrogen residing inside the $C_{24}Rb$ sample is in a molecular N_2 form. Quantitatively, the effective temperature T_e of the ^{15}N atom in a pure, free, gaseous N_2 at $T=120$ K is[1,6] $T_e=374$ K. This is a few percent smaller than $T_e=383$ and 402 K estimated for N_2 residing inside a $C_{24}Rb$ sample and obtained using the two sets of parameters of Ref. 1.

(2) Further strong supporting evidence for the molecular nature of the physintercalated nitrogen is obtained by measuring the asymmetry ratio of the scattered radiation as explained below.

B. Asymmetry ratio and tilt angle of nitrogen

The asymmetry ratio is given by $R=\sigma_{\parallel}/\sigma_{\perp}$, where $\sigma_{\parallel}$ and $\sigma_{\perp}$ were defined above. This measured ratio was found at $T<130$ K to be around $R=2.8$ (Fig. 5), and hence agrees nicely with that calculated for N_2 molecules lying flat on the graphene planes. The two solid lines in Fig. 5 represent two models obtained using two different sets of parameters (see Ref. 1). The predicted R, at $T<130$ K, may be seen to be between 2.5 and 3.2, depending on T and the parameter set. The measured R is between the above two estimates, indicating that the N_2 molecules should be parallel to the graphite planes. Figure 5 shows that R decreases with increasing T above 130 K. This is caused by the contribution of *free* N_2 gas, which has no preferred orientation, and hence its asymmetry ratio $R=1$. Thus any measured value, $R<2.8$, is due either to the contribution of some free N_2 gas in the vicinity of the sample or to the effect of a tilt angle larger than zero. Hence the data of Fig. 5 are easily interpreted: At $T<130$ K, the measured R (around 2.8) means that at this T range all N_2 molecules in the container reside inside the C_{24} Rb sample with their molecular axes parallel to the graphite planes. At $T>130$ K, R gradually decreases with increasing T, implying that the N_2 gas leaves the $C_{24}Rb$ sample and passes to the container. This process continues, reaching $R\sim 1.1$ at 296 K, which may be explained if one assumes that 6% of the total amount of N_2 resides in the sample with the molecular axes lying flat on the graphene planes, while the rest are in a pure gaseous form and hence nonoriented. The measured R for the present case ($R=2.8$ at $T<130$ K) is larger by 7% than that of the $C_{24}K+N_2$ system; it indicates that the tilt angle in the present case is smaller than that of N_2 inside $C_{24}K$. We may estimate the upper limit of the tilt angle for $T<130$ K in a similar manner to that of Ref. 1. The result is $\vartheta=9°$; compared with $\vartheta=15°$, which is the upper limit for the tilt angle at $T<130$ K of the ($C_{24}K+N_2$) system.[1] Finally, one of the most remarkable results of the present work is that about 15 out of 232 mg of N_2 were found to intercalate inside $C_{24}Rb$ at a temperature as high as 296 K with their molecular axes parallel to the G planes.

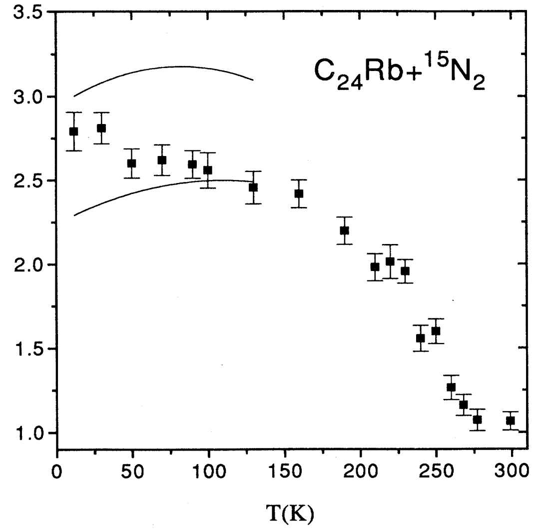

FIG. 5. Measured scattered intensity ratios $R=\sigma_{\parallel}/\sigma_{\perp}$ vs T from the $C_{24}Rb$ + N_2 target for a 232 mg $^{15}N_2$ in the cell. The signal is contributed by both the intercalated N_2 and by the "free" N_2 present in the dead volume of the sample holder. The solid lines, taken from Ref. 1, were calculated for purely intercalated N_2 molecules lying flat on the graphene planes at $T=12-130$ K, where all N_2 is experimentally known to be intercalated in $C_{24}Rb$ with no free gas left.

C. Diameter of the intercalated N_2 molecules

At RT, the identity period of $C_{24}Rb$ is 0.903 nm and is larger by 0.029 nm than that of $C_{24}K$ (see Sec. II B). The difference is due to the larger thickness of the Rb layer. Thus the expected "swelling" of the $C_{24}Rb$ at 120 K caused by inserting the N_2 gas into the Rb layer, being 0.046 nm thick ($=0.947-0.901$) is smaller than the corresponding case of $C_{24}K$, and hence is much "easier" for the gas to intercalate inside the $C_{24}Rb$ sample.[7] This qualitatively explains the much faster intercalation occurring in $C_{24}Rb$ as compared with $C_{24}K$. The fact that the value $d_i=0.901$ nm at 120 K is smaller by 0.002 nm than $d_i=0.903$ nm measured at RT is very probably due to thermal contraction of the $C_{24}Rb$ sample.

It may be noted that the N_2 molecules reside within the vacancies occurring in the Rb layer;[7] those vacancies are large enough to allow N_2 intercalation in second- and higher-stage compounds and not in C_8Rb, which has smaller vacancies; the density of the Rb layer is larger by a factor of 1.5, thus not allowing any N_2 molecules to reside there. Thus is it unlikely that the N_2 molecules could reside within the Daumas-Herold boundaries, which could in principle be present in the sample.

It should be noted that the small van der Waals diameter D of a lying N_2 molecule may be obtained by subtracting the identity period of the ($C_{24}Rb+N_2$) system from that of the pure $C_{24}Rb$ compound; thus $D=0.947-0.667=0.280$ nm at $T=120$ K, where $c_i=0.667$ nm is the lattice parameter of graphite at $T=120$ K and is smaller than that determined at RT ($c_i=0.670$ nm).[11] Here, we refer to a "small" diameter because the N_2 molecule is not spherical; its larger diameter is known to be around 0.4 nm. The above should be compared with $D=0.289$ nm, deduced in a similar manner from the $C_{24}K+N_2$ system.[10] The 3% difference deduced from the two samples is not entirely clear. It may be due to an apparent tilt of $\phi=15°$ of the N_2 molecular axes with respect to the graphene planes in the $C_{24}K+N_2$ system. This explanation is supported by the fact that the asymmetry ratio for the $(C_{24}K+N_2)$ system whose maximum value $R=2.6$ at 12 K is actually smaller than that of the $(C_{24}Rb+N_2)$ system, being $R=2.8$ at 12 K (Fig. 5) where the N_2 molecules are taken to lay flat at the graphene surface, $\phi=0°$. Obviously, any out-of-plane tilt of the N_2 molecular axes tends to decrease the value of R. In fact, the calculated asymmetry ratio corresponding to an effective tilt of $\phi=15°$ is indeed $R=2.6$, which agrees with that measured at 12 K in the $(C_{24}K+N_2)$ system.

In the above estimate we are neglecting possible atomic corrugation effects of the graphite and its atomic surface is assumed to be smooth.

IV. CONCLUSIONS

We have shown that the N_2 molecule physintercalates in $C_{24}Rb$ with its molecular axes parallel to the graphene planes at temperatures as high as 296 K. The amount of physintercalated N_2 at any T is proportional to the external pressure acting on the $C_{24}Rb$ sample; it also increases with decreasing T, reaching saturation at around 130 K. It is of interest to study also the $(C_{24}Cs+N_2)$ system where the diameter of the Cs atom is larger than Rb, and hence the expected swelling caused by N_2 intercalation will be much smaller. One would therefore expect the N_2 gas to intercalate easily at room temperature. Because of the larger "thickness" of the Cs layer, it is speculated that a large fraction of the N_2 molecules may enter the $C_{24}Cs$ compound at RT with the symmetry axes parallel to the graphene planes. It will be interesting to see if the larger spacing can allow some N_2 molecules to stand perpendicular to the graphene planes.

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