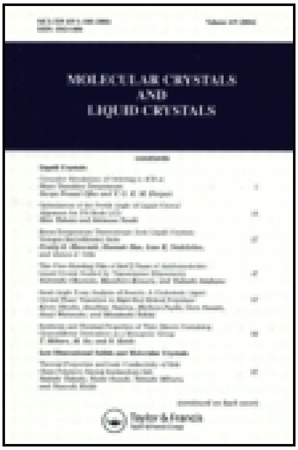

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R. Moreh [a] [b] , H. Pinto [a] , M. Melamud [a] & H. Shared [a] [b]
[a] Nuclear Research Center - Negev, Beer-Sheva, POB 9001, Israel
[b] Ben-Gurion University, Beer-Sheva, 84105, Israel

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NEUTRON DIFFRACTION AND NUCLEAR RESONANCE PHOTON SCATTERING STUDY OF THE $C_{24}K + N_2$ SYSTEM

R. MOREH[#], H. PINTO, M. MELAMUD, H. SHAKED[#]
Nuclear Research Center - Negev, Beer-Sheva,
POB 9001, Israel
[#]Ben-Gurion University, Beer-Sheva 84105, Israel

Abstract N_2 gas was physintercalated into $C_{24}K$ prepared from HOPG and the properties of the system was studied by n-diffraction and nuclear resonance photon scattering. The tilt of the N_2 molecular axis was found to be very nearly parallel to the graphite planes.' The identity period was determined before and after gas intercalation. The mosaicity of the system was destroyed by repeated intercalation and deintercalation of the gas.

INTRODUCTION

Non-polar molecules of small dimensions such as nitrogen are known[1] to physintercalate into binary 2nd-stage GICs such as $C_{24}K$. Such a process involves a "swelling" of the alkali layer to allow for the accomodation of the N_2 molecules in the alkali plane. This system was studied using neutron diffraction (ND) to determine the identity period before and after the "insertion" of N_2. The system was also studied using nuclear resonance photon scattering (NRPS) in order to determine the tilt angle of N_2 molecules with respect to the graphite planes.

The NRPS technique

The basic idea of the NRPS technique rely on monitoring the Doppler broadening of a nuclear level in ^{15}N caused by the internal zero-point vibrational motion of the N_2 molecule. Because of the internal motion of the atoms in the molecule, the Doppler width of the nuclear level is maximum along the molecular axis and minimum in the perpendicular direction. In such a resonance photon scattering process[2] (involving the 6324 keV level of ^{15}N), the scattering cross section was shown to be proportional to the Doppler broadening of the nuclear level and hence was utilized for the determination of the tilt angle of the molecular axis with respect to the graphite planes.

EXPERIMENTAL METHOD

The sample consisted of 380 mg of isotopically enriched nitrogen (99% ^{15}N) and $C_{24}K$ (prepared using 30x15x13 mm^3 HOPG and weighing 4.2 g) both enclosed in an aluminium cylinder of 1 mm wall thickness. The mosaic spread of the initial sample was about 8°. The cylinder was connected to a 48 mm diameter 10 mm high stainless steel cylinder which served as a gas reservoir. The target assembly was positioned in such a way that only the $C_{24}K$ sample was hit by the photon beam and the N_2 reservoir was outside the beam region. At room temperature (RT) the pressure of the N_2 gas was around 320 psi and no intercalation occurred into the sample. The nuclear resonance occurs only in ^{15}N (which has a level at the 6324 keV) thus requiring the use of isotopic N_2. The target was placed inside a cryostat and the temperature was varied between RT and 10 K. The scattered radiation was detected using two hyper-pure Ge detectors of about 150 cc. The photon beam was obtained from the (n,γ) reaction on disks of metallic Cr placed near the core of the IRR-2 reactor. Details of the scattering facility and target are described elsewhere.[3]

The ND was performed at the KANDI-III diffractometer of IRR-2 with $\lambda = 0.24$ nm, after finishing the NRPS measurments, using the same target and cryostat. At RT the (00ℓ) and (hk0) spectra were measured. Rocking curves of the (006) and (009) reflections were taken and the scattering angle was kept fixed at an angle corresponding to the (00ℓ) while the sample was rocked around its axis. For studying gas intercalation, the sample was cooled slowly at a rate of 30 K/min to 170 K and was kept for more than 250 h and then warmed up to RT.

RESULTS AND DISCUSSION

We first discuss the NRPS results. At 297 K no gas was intercalated into the sample and the photon scattering signal was entirely due to the free N_2 gas present in the Al container and hit by the beam. When the temperature of the sample was reduced below 200 K, the scattering signal increased; this can only happen if N_2 "enters" the $C_{24}K$ sample thus indicating the onset of intercalation. This process was monitored as a function of T for 200 K > T > 10 K and was found to have the highest speed at around 170 K while at T < 80 K, the gas intercalation stopped. At 170 K, the amount of gas "entering" the GIC reached saturation after about a week. At T > 200 K, deintercalation occurred taking the gas several hours to leave the $C_{24}K$ sample. The ratio of the scattered intensities with the photon beam parallel and perpendicular to the graphite planes of the sample were also measured. The

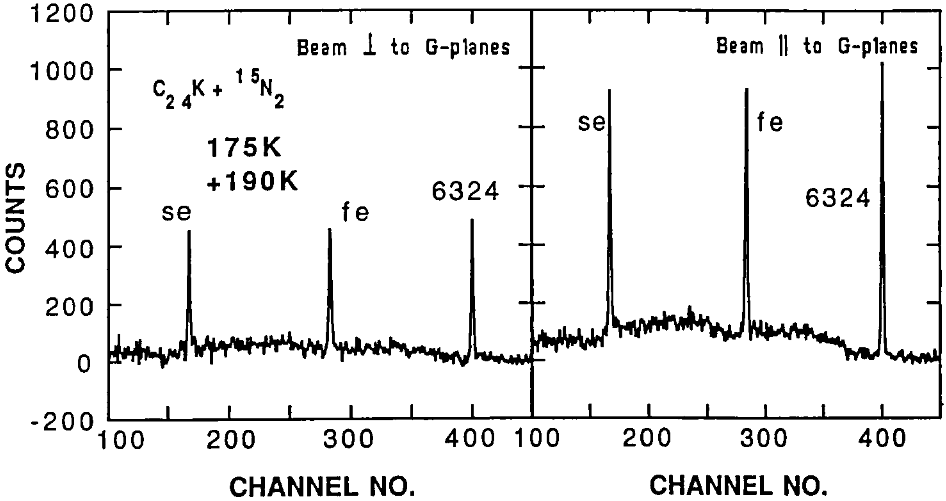

FIGURE 1 Portions of spectra of photons scattered from ${}^{15}N_2$ intercalated in $C_{24}K$ obtained with the photon beam parallel and perpendicular to the graphite planes. Each spectrum was obtained by summing data taken at 190 K and 175 K for a total running time of 35 h. The lines refer to the photo, first (fe) and second escape (se) peaks.

scattered radiation spectra, normalized to the same incident photon flux, are shown in figure 1 for the two geometries and are obtained by summing measurements carried out at 175 K and 190 K for enhancing the statistics. Similar measurements were done as a function of T. From fig. 1, the anisotropy were deduced after accounting for the contribution of the free (non intercalated) gas present in the sample and hit by the beam. A large ratio: $R = 2.5 \pm 0.2$ was found at $10\ K < T < 200\ K$ corresponding to a huge anisotropy which could only be caused by the physintercalated molecular N_2 axes being parallel to the carbon planes. The mathematical relation connecting the tilt angle and the scattering cross section ratio was derived in detail[3] for the case of N_2 physisorbed on Grafoil and was applied to the present case to deduce the tilt angle of the N_2 molecular axes and was found to be: $\vartheta \leq 15°$.

By repeating the intercalation and deintercalation of the gas,

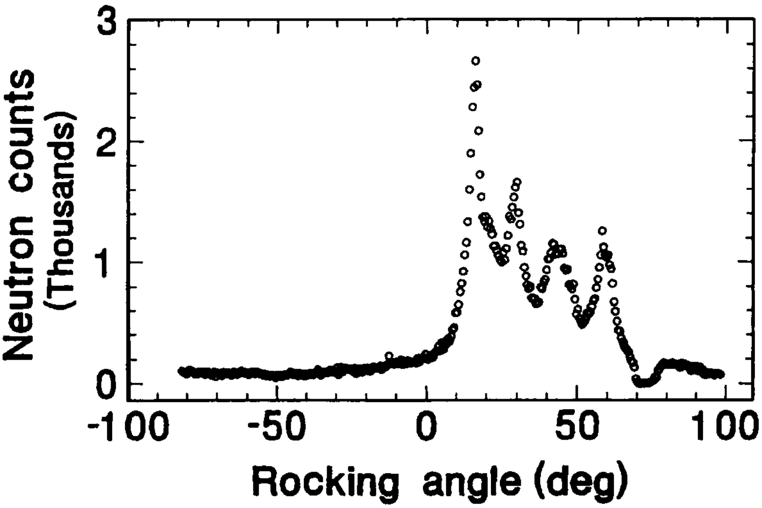

Figure 2 Rocking curve of the (009) reflection of $C_{24}K$ measured by n-diffraction at RT, showing at least four subsamples, being "produced" by intercalation and deintercalation of the N_2 gas. The corresponding c-axes are inclined to each other by about 13 degrees. The mosaic spread of the original $C_{24}K$ sample was about 8°.

we observed a decrease in anisotropy of the system. It was thus suspected that a disruption of the mosaicity of the $C_{24}K$ sample was occuring. We thus decided to study it using ND.

The ND spectrum was measured first at RT and the identity period was d = 0.874 nm which agrees with the literature value for $C_{24}K$. To test the mosaicity of the sample, following the intercalation and deintercalation processes, we carried out a rocking curve measurement. The result (figure 2) imply that the $C_{24}K$ is composed of at least four discrete subsamples inclined to each other by about 13 degrees. All the ND results are given for the largest subsample which revealed the strongest reflections. The (hk0) spectrum was measured with the sample set at 90 degrees relative to the [001] direction. All the (00ℓ) reflections are found in this spectrum, although with low intensity. After cooling to 170 K, the intensities of the (00ℓ) reflections were checked as a function of time,

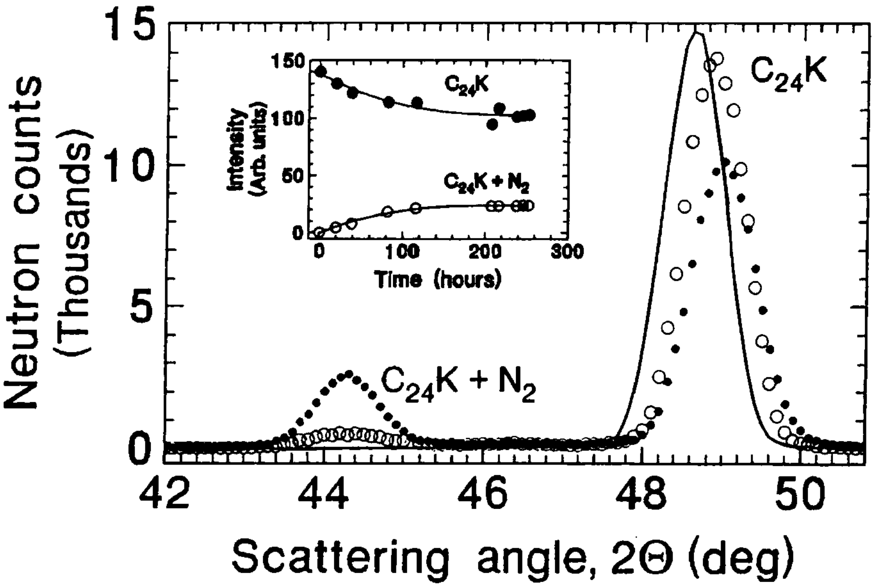

Figure 3 The (009) reflections of $C_{24}K$ and $C_{24}K + N_2$ observed by ND during the physintercalation of N_2 at 170 K. The solid line is the RT result; open circles - 5 h after the start of cooling. Full circles - 250 h after cooling. The insert shows the change of the integrated intensities of the two reflections versus time at 170 K.

representative results are shown in fig. 3 for the (009) reflection. A shift in the position of the reflections occurred during the cool-down period, as expected because of the thermal contraction of the material, saturating in an identity period of 0.868 nm for the $C_{24}K$ layers. At the same time, new superlattice (00ℓ) reflections appeared at lower angles concuring with d = 0.957 nm for the $C_{24}K + N_2$ system, namely a "swelling" of 0.089 nm caused by the N_2 intercalation. This amount of "swelling" corresponds to a Van der Waals diameter of 0.289 nm = (0.200 + 0.089) nm of a "lying" N_2 molecule (where 0.200 nm is the "thickness" of the K-layer). The 0.289 nm may be compared with a diameter of 0.4 nm of a "standing" N_2. The new set of (00ℓ) reflections increased with time saturating after about 170 h whereby 30% of the sample seemed to have been intercalated with molecular N_2 whereas the identity period of the remaining 70% remained unchanged. The rocking curves of the (009) reflection at 170 K did not show any significant change during the 250 h period. But after warming up to RT a different rocking curve was observed, showing a larger dispersion angle of approximately 20 degrees. After the end of the ND runs, the sample container was opened and the sample was found to have expanded considerably pressing itself against the canister wall. This fact could explain the observed changes in the rocking curve.

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