



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

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Version of record first published: 04 Oct 2006

To cite this article: H. Shaked, R. Moreh, H. Pinto, M. Melamud & Y. Finkelstein (1998): Second Stage Physintercalation of N₂ Molecules into C₂₄Rb, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 310:1, 105-110

To link to this article: <http://dx.doi.org/10.1080/10587259808045322>

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Second Stage Physintercalation of N₂ Molecules Into C₂₄Rb

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Using neutron diffraction, a second stage physintercalation of molecular N₂ into C₂₄Rb has been observed in which the N₂ molecules reside inside every *second* Rb layer. The new phase, C₄₈Rb₂(N₂)_x, coexists below 175 K with pure C₂₄Rb and the 1st stage C₂₄Rb(N₂)_x. The tilt of the N₂ molecular axes relative to the graphene planes was determined versus T using the nuclear resonance photon scattering (NRPS) technique and found to be almost parallel to the graphene planes of the C₂₄Rb sample.

Keywords: N₂ adsorption, Graphite intercalation compounds, C₂₄Rb, molecular orientation, n-diffraction, γ -ray resonance scattering.

INTRODUCTION

Second stage binary compounds such as C₂₄Rb are known¹ to physintercalate molecules such as N₂, forming compounds of the form C₂₄Rb(N₂)_x in which the N₂ resides in the Rb planes. The adsorption of N₂ causes a swelling of the Rb layer of the GIC because of the larger "thickness" of N₂. Previously, we studied² this system using both n-diffraction and nuclear resonance photon scattering (NRPS) and the structural properties were obtained³. In the present work, the amount of N₂ was increased and a search for a new phase of N₂ inside C₂₄Rb was conducted using n-diffraction. Also the average tilt angle of N₂ was measured. using the NRPS technique.

EXPERIMENTAL METHOD

The graphite intercalated sample C₂₄Rb (weighing ~ 3.5 g) was prepared using 25x11x4.5 mm³ HOPG plate, 2.7 g (with its c-axis perpendicular to

the 25x11 mm² plane) using the two bulbs method⁴. The HOPG and glass container were heated at ~ 350 C in vacuum for 12 h before intercalation in order to clean all moisture. Pure C₂₄Rb was formed; it was transferred to a sample holder described in ref. 2. A 320 mg of isotopic ¹⁵N₂ (99%) was inserted into the container building a pressure of ~ 5 atm at 300 K.

Neutron Diffraction

Figure 1(a) is a (00 l) spectrum of C₂₄Rb+N₂ at 300 K using a KANDI diffractometer ($\lambda \sim 2.405$ Å), revealing a pure C₂₄Rb phase³. Fig. 1(b) is a 3h scan taken at 120 K obtained by cooling from 300 K at a rate of 1 K/min; it reveals more (00 l) lines corresponding to two more phases. The first, C₂₄Rb(N₂)_x, is known^{2,3} where, the N₂ occupy *each* Rb layer. Here, $I_c = 9.47$ Å, with $I_c = c/3$ and c the lattice parameter where C₂₄Rb have the stacking order AB|BC|CA). The second phase, C₄₈Rb₂(N₂)_x, is *new* and the N₂ molecules occupy every *second* Rb layer. Note that the new lines can not

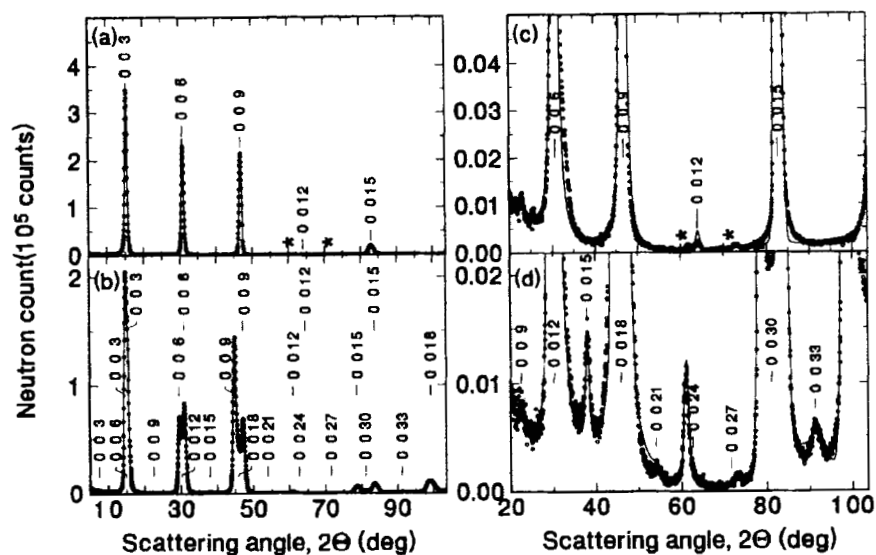


FIGURE 1 N-diffraction from (C₂₄Rb+N₂) corrected by dividing the count at each 2θ by sinθ yielding a powdered sample spectrum. (a) Pure C₂₄Rb phase at 300 K. (b) Three phases: C₂₄Rb, C₂₄Rb(N₂)_x, C₄₈Rb₂(N₂)_x coexist at 120 K. The top, middle and lower (00 l) indices correspond to those phases. (c), (d) Expanded view of (a) and (b) show the (0015), (0021), (0033) lines of the new third phase. In (d), only indices of this phase are given. The solid lines are Rietveld profile fits.

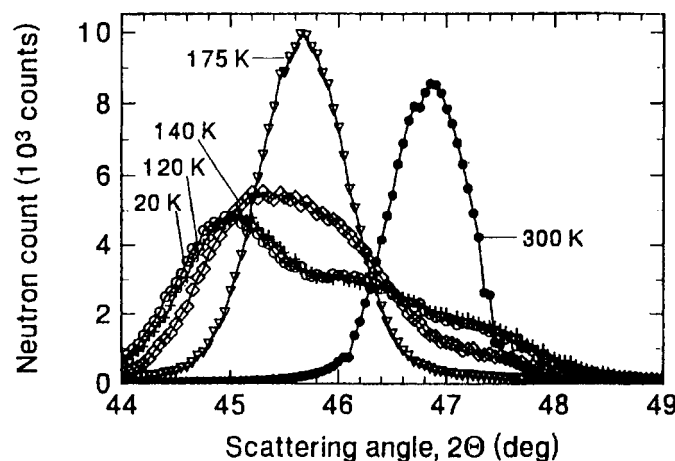


FIGURE 2 Change of the n-diffraction pattern around $2\theta \sim 46^\circ$ as a function of T , marking the evolution of the two phases.

be explained by assuming a random distribution of interstratified layers of $C_{24}Rb$ and $C_{24}Rb(N_2)_x$, since n-diffraction requires ordered regions with dimension of $\sim 500 \text{ \AA}$.

In other measurements the sample was cooled from 300 K by $\sim 25 \text{ K}$ steps to 20 K. Each scan took 3h, and the equilibration time between two runs was 2 h. The evolution of the N_2 -containing phases in the angular range $44^\circ - 49^\circ$ is shown in fig. 2. In the normal phase, $C_{24}Rb(N_2)_x$, the N_2 enters gradually the galleries of every Rb layer causing an increase in the swelling of the identity period l_c with decreasing T , reaching saturation at $\sim 120 \text{ K}$. The data was the same down to 20 K. Fig. 3 shows the swelling, Δl_c versus T .

Resonance Photon Scattering

The photon beam for the NRPS measurements was generated from the $Cr(n,\gamma)$ reaction using Cr disks placed near the core of the IRR-2 reactor. The basic idea of the NRPS technique^{5,6} is a chance overlap between one γ -line of the $Cr(n,\gamma)$ reaction and the 6324 keV level in ^{15}N . It turned out that the scattering cross section in this case depends on the tilt angle of the N_2 molecule relative to the incident photon beam. This dependence is related to the Doppler broadening of the nuclear level in ^{15}N caused by the internal zero-point vibrational motion of N_2 . The Doppler broadening is maximum along the N_2 molecular axis direction and minimum in the direction of the normal. This causes the photon scattered intensity to behave in a similar

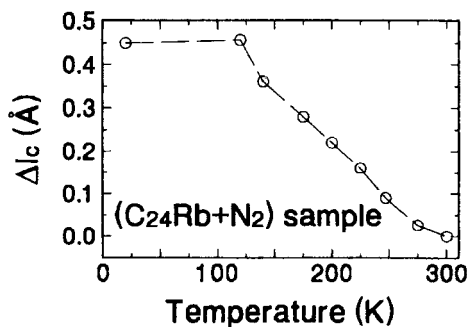


FIGURE 3 Observed expansion (ΔI_c) of the identity period versus temperature. The amount of adsorbed N_2 increases with decreasing T .

manner. Thus, the tilt of N_2 with respect to the graphene planes is obtained from the scattered intensity ratios R with the beam parallel and normal to the graphene planes of the $C_{24}Rb+N_2$ sample. The corresponding scattered radiation spectra from ^{15}N in the sample, at 130 K, are shown in fig. 4. A huge *average* ratio $R = \sigma_{\parallel}/\sigma_{\perp} = 2.72$ was measured in the range 20 K to 130 K showing that the N_2 molecular axes are tilted nearly flat on the graphene planes of the $C_{24}Rb$ sample as discussed below. The total scattering intensity was also used to determine^{2,3} the adsorbed amount of N_2 versus T .

RESULTS and DISCUSSION

Rietveld powder analysis was applied to the data of fig. 1 (obtained from the raw data by dividing by $\sin\theta$ to convert it to that of a cylindrical powder sample). The Rietveld fits yielded the x in the three phases at 120 K: $C_{24}Rb$, $C_{24}Rb(N_2)_x$ and $C_{48}Rb_2(N_2)_x$. The results are: $x = 0$, 1.2(1) and 0.6(2) respectively, where the enclosed values are the errors in the last digit. The deduced weight fractions at 120 K of the 3 phases are: 0.39, 0.51, 0.13 respectively. In addition, the I_c of $C_{24}Rb$ (9.016 Å) was found to expand by 0.456 Å to 9.472 Å after N_2 intercalation, thus the deduced thickness of the N_2 layer is 2.82 Å. This is smaller than 2.89 Å, obtained from the $C_{24}K+N_2$ system⁷; it may be due to the smaller tilt angle of N_2 in the $C_{24}Rb+N_2$ case. This claim is supported by the measured larger ratio of scattered intensities, $R = \sigma_{\parallel}/\sigma_{\perp} = 2.67$, obtained at 130 K, using the NRPS technique, which leads to a tilt, $\phi \leq 9^\circ$, smaller than $\phi \leq 15^\circ$ of the $C_{24}K+N_2$ case⁷. In fig. 5 we show another strong support for the presence of the new phase where the expanded view of (0012) reflection (at $2\theta \sim 31^\circ$) may be seen to be in much

better agreement with a three phase Rietveld analysis (solid line) compared to that of a 2-phase analysis (dashed line). Another result from the Rietveld fits is the occurrence of corrugations in the C-planes of the sample, with amplitudes of ~ 0.43 Å which are larger than the value ~ 0.35 Å reported for some pristine graphites⁸.

The adsorption of N₂ in C₂₄Rb between 300 K and 175 K causes a swelling of the sample and shows up as a “single” peak (fig. 2), being a combination of the pure C₂₄Rb and the C₂₄Rb(N₂)_x phases. At 140 K, a clear phase transition occurs where the single peak splits into 3 peaks, related to the above two phases and the new C₄₈Rb₂(N₂)_x phase. The behavior of the present data is understood by noting that the “entrance” of the N₂ inside the C₂₄Rb crystallites is a continuous process occurring simultaneously over all parts of the entire sample. The identity period expands gradually to a maximum, $\Delta l_c \sim 0.45$ Å to accommodate the N₂ molecule and the expansion process starts at 300 K. The above is in contrast to the C₂₄K case where another peak, appeared below 200 K (corresponding to a *constant* expansion $\Delta l_c \sim 0.89$ Å) when N₂ adsorption starts. The adsorption was extremely slow taking weeks. This different behavior is due to the fact that in C₂₄K, only few selected crystallites allow the entrance of the N₂ molecules. Once the adsorption process starts, it is easier for more molecules to enter the expanded regions formed in the selected crystallites. This explanation is

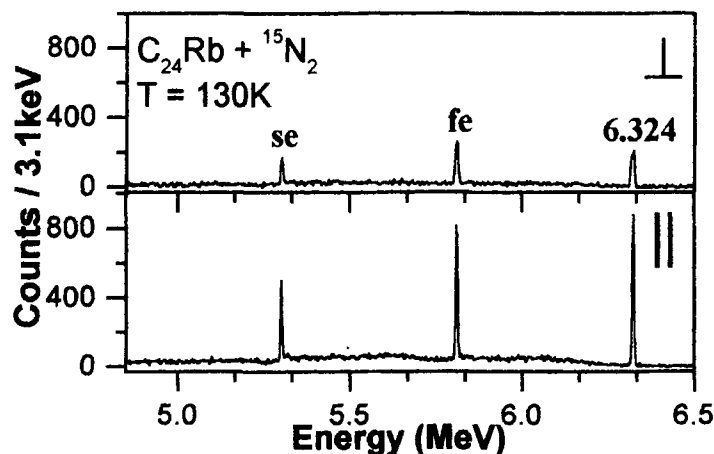


FIGURE 4 Nuclear photon scattering at 130 K from ¹⁵N in C₂₄Rb+N₂. (after background subtraction). A 150 cm³ Ge detector is used. The spectra were measured with the photon beam parallel (||) and perpendicular (⊥) to the graphene planes of the sample. The lines are the photo, first (fe) and second (se) escape peaks of the 6.324-MeV photons.

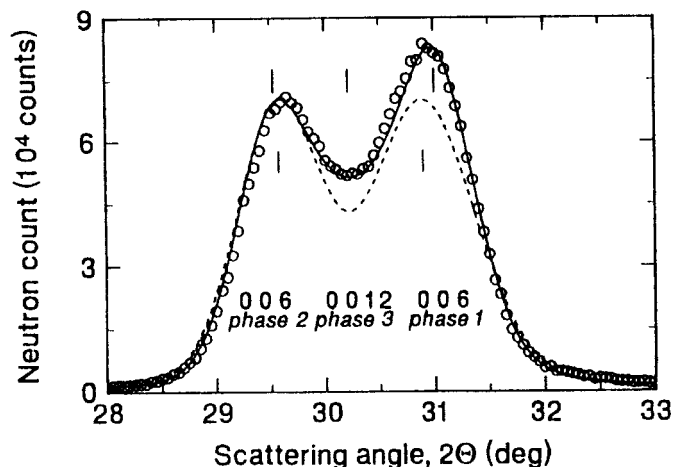


FIGURE 5 Rietveld profiles for 2-phase (dashed line) and 3-phase analysis (solid lines) at 120 K. Open circles are the observed data.

supported by the NRPS findings⁷ where the total amount of adsorbed N_2 in $C_{24}K$ was found to increase with the number of cooling and heating cycles between 300 K and 20 K, reaching saturation after several cycles.

Acknowledgments

This work was supported by the German-Israeli Foundation for Scientific Research and Development (G.I.F.).

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