

X-RAY CRYSTALLOGRAPHIC STUDY OF DISORDERED C₂₄Rb

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ABSTRACT

An X-ray crystallographic analysis was performed on an HOPG sample of stage-2 Rb-intercalated graphite (C₂₄Rb) at room temperature. A q-scan in the circularly averaged (hk.0) reciprocal lattice plane shows the familiar liquid-like pattern with a suggestion of substrate modulation effects. Assuming partial registry of the Rb with its graphite host, an analysis of 85 Bragg peaks, to which a Rb contribution was included, was performed. The registered fraction (x) was thereby estimated to be 0.71±0.02. The in-plane combined thermal and static displacement amplitude of the assumed registered Rb atoms was $\langle u^2 \rangle^{1/2} \approx 0.32$ Å. This large amplitude suggests that the standard Debye-Waller treatment is inappropriate here and that substrate modulation effects on the 2-D liquid, as they appear at the graphite peaks, may be more important.

INTRODUCTION

Parry *et al.* [1,2,3] have performed pioneering studies on stage-2 HOPG intercalated with K, Rb and Cs in which they demonstrated several important aspects of the structure at room temperature using an X-ray photographic method. The first is that the average stacking sequence along the hexagonal c axis is A/A B/B C/C, i.e., every second hexagonal graphite plane is followed by an alkali layer, regularly stacked together along the c axis, where Roman letters A, B and C refer to graphite layers and the lines refer to the disordered alkali intercalant layers. The second result is that the scattering from the intercalated alkali atoms is streaked along the c* axis (c* is the reciprocal lattice parallel to the c axis), which confirms the essential 2-D (two-dimensional) character of the disordered intercalant layers. Nixon and Parry [2] and Parry *et al.* [3] also deduced, from a qualitative structure analysis, that within each intercalated layer the alkali atoms are distributed irregularly with a fractional occupation of the hexagon centers in the adjacent graphite layers.

In a more recent study, Parry [4] presented a room temperature single crystal X-ray photograph of stage-2 disordered $C_{24}Cs$ in which an anisotropic liquid-like diffuse scattering is observed in the $(hk.0)$ reciprocal lattice plane with distinct lobes in $[11.0]$. This result supports the idea that the intercalated alkali atoms demonstrate some type of registry or interaction with the graphite because the alkali pattern appears, as well, to be repeated about the $\{10.0\}$ graphite reciprocal lattice points. In a single crystal study of $C_{24}Rb$, Naiki and Yamada [5] find the disordered state to be similar to that of $C_{24}Cs$ [4].

In this paper we report the result of an X-ray room temperature crystal structure analysis of stage-2 HOPG intercalated with Rb to determine the intercalated gallery spacing, the registered fraction of alkali, as above, and the thermal parameters of graphite and Rb atoms. We also estimate the probability of graphite stacking faults along the c axis using a simple model given by Wilson [6] to analyse the streaking parallel to c^* associated with Bragg reflections of the $\{10.l\}$ class which, along with twin patterns, can be seen in Fig. 4(c) of Nixon and Parry [2].

EXPERIMENTAL

An HOPG sample with a c axis mosaic spread of ~ 0.6 degrees, provided by A.W. Moore, was used. Sample preparation is described in detail elsewhere [7]. Our $C_{24}Rb$ sample was mounted in an evacuated thin glass bulb whose scattering could be eliminated with appropriate slits.

The X-ray measurements were performed on a two-circle HUBER goniometer using CuK_{α} ($\lambda=1.54178$ Å) and MoK_{α} ($\lambda=0.7107$ Å) radiation generated by a 12 KW RIGAKU Rotaflex (RU-200). Both flat and vertically bent graphite monochromators were used. Diffracted $hk.0$ and $hk.l$ diffuse and $HK.L$ Bragg intensities were measured in a normal scan using a scintillation detector. The a and c unit cell parameters of our sample were 2.472 ± 0.001 Å and $27.09 \text{ Å} \pm 0.01$ Å, respectively, at room temperature.

RESULTS AND INTERPRETATION

To confirm the two-dimensionality of the disordered state, a series of diffracted diffuse scattering profiles were measured using the flat graphite monochromator and CuK_{α} radiation. In Fig. 1, the experimental result of a q -scan in the circularly averaged $(hk.0)$ reciprocal lattice plane is shown, where q is defined as $4\pi \sin\theta/\lambda$. The main diffuse peak is centered at $q=1.175 \text{ Å}^{-1}$, designated as 1, along with the second maximum at $\sim 2.25 \text{ Å}^{-1}$, designated as 3. Bragg reflections come at 2.94 and 5.08 Å^{-1} . The subsidiary diffuse peak labelled 2, is also observed at $\sim 1.80 \text{ Å}^{-1}$. The interpretation follows the (schematic)

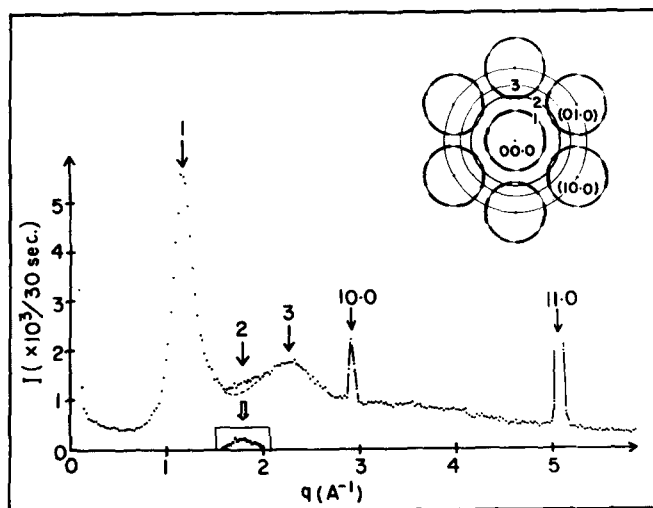


Fig. 1. The experimental result for a circularly averaged q -scan in the $(hk.0)$ plane of HOPG $C_{24}Rb$. q is defined as $4\pi\sin\theta/\lambda$. A schematic single crystal $hk.0$ diffuse scattering pattern, based on the photographic result of Parry [4] on $C_{24}Cs$, is inserted for interpretation.

single crystal $hk.0$ diffuse scattering pattern from the photographic result on $C_{24}Cs$ of Parry [4] which is inserted in Fig. 1. We may identify the three diffuse maxima, within the (10.0) Debye circle, as shown by the circles 1, 2 and 3 in Fig. 1. The first (1) is the principal maximum of the anisotropic liquid-like scattering of Rb. The third (3) is as noted above, while the weak shoulder at $q=1.80 \text{ \AA}^{-1}$ (2) arises, as indicated, from the intersection of the Debye circle about (00.0) with liquid-like modulation pattern repeated about every graphite (10.0) . It should peak approximately midway between the point of tangency and the center of the anisotropic maximum about (10.0) , as observed.

The results of a q -scan along the c^* axis, i.e. an l -scan, are shown in Fig. 2 at $q=0.50$ and 1.175 \AA^{-1} . This l -dependent feature of the Rb diffuse scattering reflects the angular-dependent X-ray form factor including thermal effects, Lorentz-polarization factor and background. The fall-off, of course, is much too gradual to be due to interplanar correlations.

To determine the structural parameters in the intercalated Rb plane, we assume a fraction, x , of Rb atoms registered with graphite. A series of integrated intensities were then measured at the Bragg reflections : $10.L$, $20.L$, $11.L$, $21.L$, $30.L$, $22.L$ and $41.L$ where L =integer. In this experiment we used a vertically bent graphite monochromator and MoK_{α} radiation. The probability, x , of finding an intercalated Rb atom at a hexagon center in adjacent graphite layers, assumes an in-plane concentration of $C_{12}Rb$, so that the unit cell structure factor is given as :

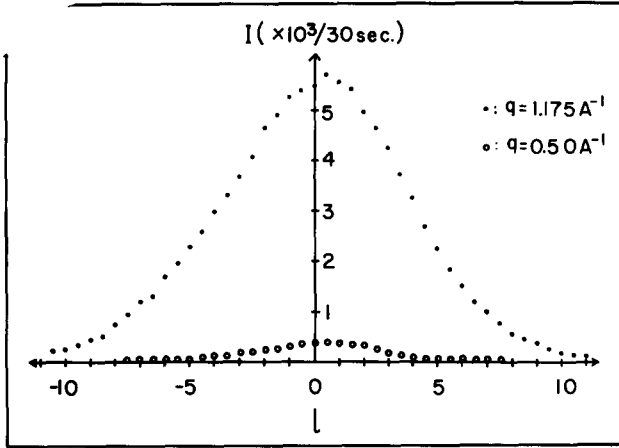


Fig. 2. The result of a q -scan along the c^* axis ; i.e., l -scans at $q(hk.0)=0.50$ and 1.175 \AA^{-1} , where l is a continuous variable along c^* .

$$F_{HK.L} = \left\{ 4f_c \cos^2 \frac{2\pi}{3} (H+2K) \cos 2\pi L \frac{C_1}{2} + \frac{x}{6} f_{Rb} \right\} \left\{ 1 + 2 \cos \frac{2\pi}{3} (H+2K \pm L) \right\} \quad (1)$$

f_i is the scattering factor of the i^{th} atom, including thermal effects, C_1 is the ratio of the separation of one graphite-Rb-graphite sandwich to the total c axis, and H and K are integers (for $00.L$, $x \neq 1.0$). In eq. (1), we consider two types of stacking sequences along the c axis; A/A B/B C/C... or A/A C/C B/B... Using a non-linear least squares fitting procedure, four temperature factors (B_c^{\parallel} , B_c^{\perp} , B_{Rb}^{\parallel} and B_{Rb}^{\perp} where \parallel and \perp refer to the hexagonal ab and the c axis resp.), C_1 and x were determined and are given in Table I. The distance for the graphite-Rb-

Table I. Structural Parameters and Reliability Factor, R.

$B_c^{\parallel} (\text{\AA}^2)$	$B_c^{\perp} (\text{\AA}^2)$	$B_{Rb}^{\parallel} (\text{\AA}^2)$	$B_{Rb}^{\perp} (\text{\AA}^2)$	C_1	x	R
0.67(2)	0.54(4)	8.32(9)	0.98(2)	0.2103(2)	0.71(2)	0.086

graphite spacing, calculated from the C_1 value, is $5.70 \pm 0.01 \text{ \AA}$. The spacing for an unintercalated graphite-graphite layer is $3.33 \pm 0.01 \text{ \AA}$. These spacings are quite close to the previous data of Leung *et al.* [8]. An important result is that the probability, x , of finding the intercalated Rb atoms at hexagon centers of the adjacent graphite layers is 0.71 ± 0.02 in which estimate is also included the deviation of the in-plane concentration from $C_{12}Rb$. Parry *et al.* [3] deduced that x lies between $1/2$ and $3/4$ for $C_{24}Rb$ depending on the temperature parameters. Finally, a very large temperature parameter for B_{Rb}^{\parallel} was obtained. It may be said that, if 71% of the Rb atoms are registered at the hexagon centers of adjacent graphite planes, each registered Rb atom must undergo a very large mean square displacement whose RMS value is about 0.32 \AA or 13% of a hexagon "diameter"!

The diffraction profiles along the c^* axis for $H+2K\#3n$ (n : integer) were considerably broader than for $H+2K=3n$. Using the simple analysis of Wilson [6], we concluded that conventional stacking faults existed with a fault probability, α , of 0.16 ± 0.02 determined after performing a Gaussian instrumental resolution correction using the FWHM of 11.L reflections. This value of α means that there is one stacking mistake in every seven units of stacking which is a rather low probability for intercalated graphite when compared, say, with $C_{24}K$ [9] for which $\alpha \sim 1/3$ and where appreciable peak shifts were also seen. This low value of α enabled us to make reasonable estimates of the integrated intensities of these broadened peaks.

DISCUSSION

Two familiar features of the intercalation process have been confirmed here in a more quantitative fashion. The first is the 2-D character of the alkali diffuse scattering in the disordered state as shown in Fig. 2. The second is that the value of x , the fraction of Rb atoms centered in hexagons, is 0.71 ± 0.02 , as suggested by Parry *et al.* [3].

The large value of B_{Rb}'' , which is extremely insensitive to variations in the other fitting parameters requires interpretation, however, especially as $2B(\sin\theta/\lambda)^2 = \langle u^2 \rangle q^2 > 1$ for most of our reflections! By way of comparison, the in-plane motion of Ag atoms in stage-2 $Ag_{0.18}TiS_2$ [10] is $B_{Ag}'' = 3.0 \text{ \AA}^2$. Because the masses of Rb and Ag are not so disparate ($M_{Rb}/M_{Ag} \approx 0.8$), the large difference in in-plane B parameters reflects a fundamental difference between the commensurate registered (2-D) Ag lattice gas in TiS_2 and the incommensurate (modulated) liquid in these alkali-graphite compounds. If we treat B_{Rb}'' , for the moment, as a proper Debye-Waller factor, we may then compare it to the thermal Debye-Waller factor extracted by Kamitakahara and Zabel from their neutron study of the in-plane Rb phonon density of states in $C_{24}Rb$ [11]. They obtained $B_{Rb}'' = 3.94 \text{ \AA}^2$ compared to our 8.32 \AA^2 . This leaves a large mean-square static displacement of the "registered" Rb atoms off their hexagon centers and renders the distinction between registered and unregistered more tenuous. A further interpretation of the present results has been made in a preliminary fashion by Moss *et al.* [12] in which the alkali layer is discussed as a true 2-D liquid perturbed by its periodic substrate. In this interpretation, the effects induced in the liquid are restricted to 2-D density modulation waves within the confined alkali layer and give rise principally to Rb contributions at the graphite reciprocal lattice points along with the modulation effects described in Fig. 1. This alternate interpretation of the present results is very encouraging and is developed further in these proceedings [13].

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