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Orientation of nitrate molecules in graphite-HNO_3 residue compounds

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With the use of nuclear resonance fluorescence of 6.324-MeV photons from ^{15}N, it is shown that in third-stage graphite-HNO_3 residue compounds (characterized by a distance $I_3 = 13.25$ Å), the intercalant molecules are in the form of nitrates and are oriented at $\theta_0 = 13° \pm 5°$ to the graphite planes. The procedure for preparing and characterizing thick residue samples using highly oriented pyrolytic graphite is discussed.

I. INTRODUCTION

Pure fuming HMO_3 is known to react with graphite and form intercalated compounds of the form C_{5n} (HNO_3), where the particular stage depends on the preparation as described in detail elsewhere.[1,2]. It was reported that such compounds are unstable upon exposure to air turning gradually to residue compounds of the form C_{8n} (HNO_3).

The present work is unique in two respects. First, a relatively new technique which involves nuclear resonance photon scattering from the 6.324-MeV level in ^{15}N was employed. This method was applied in a previous work[3] for the study of the orientation of the nitrate molecule with respect to the graphite planes using a *normal* second-stage intercalated compound C_{10} (HNO_3). Second, the sample required by the present technique is large, with dimensions of ≈ 1 cm and weighing about 2 g. It turns out that the preparation of such samples is markedly different from that of the thin samples (≈ 0.2 mm thick) employed in previous investigations.[2,4]

Using the usual notation, a sample of stage n in which n graphite layers are sandwiched between two intercalant layers has an identity period I_n given by

$$I_n = d_i + 3.35(n-1)\ ,$$

where d_i is the identity period for the first-stage compound and 3.35 Å is the thickness of one layer of pure graphite. For the normal intercalated compounds of the form C_{5n} (HNO_3), the literature value[2] is $d_i = 7.80$ Å, while for the residue compounds the value is $d_i = 6.55$ Å. Apart from the determination of the orientation of the intercalant molecules, the aim of the present work was also to characterize their chemical form.

II. EXPERIMENTAL METHOD

As mentioned above, we deal here with a nuclear resonance photon scattering process in which the 6.324-MeV level in ^{15}N is photoexcited by a chance overlap to within ≈ 30 eV with one of the γ lines of the $Cr(n,\gamma)$ reaction. The incident photon beam was generated from the (n,γ) reaction on three separated chromium discs, 7.5 cm in diameter and 1.5 cm thick, placed along a tangential beam tube and near the core of the IRR-2 nuclear reactor.[5] The intensity of the γ line photoexciting the 6.324-MeV nuclear level in ^{15}N is 10^4 photons/cm^2 s at the target position. The intercalated sample was placed in the beam path with its c axis in the scattering plane and could be rotated from one geometry where the beam direction and the c axis are parallel, to a perpendicular geometry. For low-temperature measurements (20 K), the sample was placed inside a Displex cryostat which could be rotated so that the angle between the photon beam and the sample c axis can be varied back and forth by 90°. The scattered radiation was detected using a 100-cm^3 GeLi detector (having a full width at half maximum resolution of 10 keV at 6.3 MeV) placed at a distance of 20 cm from the sample.

The sample consisted of a third-stage *residue* compound having $d_i = 6.55$ Å and $I_3 = 13.25$ Å. It was prepared from a *normal graphite nitrate sample of the form C_{5n} (HNO_3)* and containing a mixture of second- and third-stage compounds (characterized by $d_i = 7.80$ Å with $I_2 = 11.15$ Å and $I_3 = 14.45$ Å, respectively). This mixture sample was exposed to air and was transformed after two years to a third-stage residue compound. The *normal* graphite nitrate sample was prepared using a 5 mm thick rectangular 1.5×0.9-cm^2 highly oriented pyrolitic graphite (HOPG) plate (weighing 1.49 g) and pure isotopic $H^{15}NO_3$ (99% ^{15}N) using the two-zone vapor-transport method.[2] In this method, the $H^{15}NO_3$ was placed in one zone and the HOPG in the second zone, both kept at room temperature. After seven days, the amount of the $H^{15}NO_3$ intake was 46% corresponding to the formation of a mixture of second- and third-stage *normal* compounds of the form $C_{5n}(HNO_3)$, where the weight intake is expected to be 53% and 35%, respectively. The analysis of this sample by neutron diffraction[6] confirmed the presence of this mixture. Initially, an attempt was made to convert this normal graphite nitrate sample to the residue compound by following the procedure given in the literature and passing N_2 over the sample for a few weeks or exposing it to air for about the same period. However, the loss in weight of the sample under this procedure was small and did not correspond to the formation of the residue compound. In addition, the study of the nuclear scattering intensities of the photons from the two perpendicular geometries of the sample (as described in a previous publication[3]) indicated that the nitrate molecular planes lay almost perpendicular to the graphite planes and, hence, *most* of the compound was still a normal form having the formula $C_{5n}(HNO_3)$. Thus, it appears that the preparation of the residue compounds depends strongly on the size and thickness of the sample, which seems to change the kinetics of the intercalation process. After the initial "unsuccessful" treatment, the sample was left exposed to air and tested every few months. A gradual change was found to take place in which the weight of the sample was decreasing and the scattering cross-section ratio was increasing little by little. The x-ray analysis of the sample have indicated that the amount of the third-stage residue compound was increasing with time. Thus after about two years, the sample seems to have transformed to a stable residue as evidenced by the fact that its weight remained constant for at least a year. This is a third-stage residue compound characterized by the distances $d_i = 6.55$ Å and $I_3 = 13.25$ Å as shown in Fig. 1 which displays the x-ray diffraction pattern obtained using the K_α line of Cu. It can be seen that all strong lines are related to third-stage residue. However, on the basis of Fig. 1 and by considering the calculated intensities and positions of the $(0,0,l)$ x-ray lines, it is possible that a $\simeq 5\%$ impurity of $C_{15}(HNO_3)$ could be present in our sample. It is very important to note that the total weight of the intercalated residue sample was 1.90 g (consisting of 1.49 g HOPG and 0.41 g $H^{15}NO_3$), which corresponds to the formula $C_{19}(H^{15}NO_3)$. Thus the third-stage compound obtained here does not conform to the formula $C_{8n}(HNO_3)$ reported in Ref. 2. This means that the $H^{15}NO_3$ weight intake for a particular stage of a residue compound can vary within a wide range. The possible presence of a $\simeq 5\%$ impurity of $C_{15}(HNO_3)$ does not change the last conclusion substantially.

From the known distance, $d_i = 6.55$ Å, one may note that the thickness of the intercalant layer is $6.55 - 3.55 = 3.20$ Å implying that the nitrate group can either be inclined at an angle $\theta_0 < 20°$ or lay flat on graphite planes depending on the van der Waals radius of the O atoms for this intercalated compound. In order to determine the angle θ_0 we used the nuclear technique[3] described below. It should be remarked that an electron diffraction study[7] of a second-stage residue compound has indicated that the nitrate planes are inclined at about 8° with respect to the graphite planes. In addition, a very recent infrared transmission study[8] has concluded that the nitrate planes are approximately parallel to the graphite plane in the residue compound.

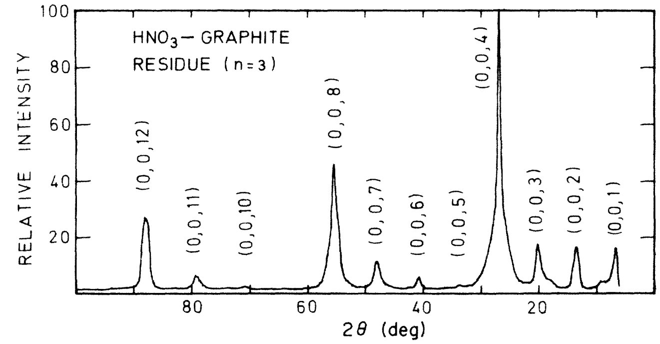

FIG. 1. X-ray diffraction pattern obtained using the $K\alpha$ line of Cu. The indexing of the $(0,0,l)$ lines corresponds to $I_3 = 13.25$ Å (stage three) of the residue compound $C_{19}(HNO_3)$. The small shifts and broadening of the lines are due to transparency aberration caused by the thick target used.

III. THE NUCLEAR TECHNIQUE

In the present technique which employs nuclear resonance photon scattering from the 6.324-MeV level in ^{15}N, one monitors the Doppler broadening of the ^{15}N nuclear level arising from the *zero-point* vibrational energy of the molecule. The nitrate NO_3 molecule is a planar molecule and highly anisotropic in the sense that the average kinetic energy of the N atom, due to the normal modes of molecular vibrations,[9] is maximum along the plane and minimum in the perpendicular direction. Thus the Doppler broadening, being dependent on the ^{15}N kinetic energy, will also be directional and changes from maximum to minimum in the same manner as the ^{15}N kinetic energy. The resonance scattering cross section σ_s, which monitors the Doppler broadening, is expected also to be highly anisotropic. Thus, σ_s increases with the Doppler broadening and is almost linearly proportional to the effective temperature T_e of the scattering nucleus. In fact, it was shown by Shahal and Moreh[9] that the resonance scattering cross section σ_s of the 6.324-MeV photons from ^{15}N in the form of $Na^{15}NO_3$ single crystal increases by 43% when the orientation of the NO_3 planes is changed from a perpendicular geometry (relative to the photon beam) to a parallel geometry. One therefore expects a similar dependence on σ_s when a residue compound is used, provided that the NO_3 molecular planes are parallel to the graphite planes. This should be true because the van der Waals forces binding the nitrate molecules to the graphite planes are much weaker than the covalent forces binding the N atom in the NO_3 molecule. For NO_3 molecules inclined at angle θ_0 with respect to the graphite planes, the effect on σ_s of a vibrating atom varies as $\cos^2\theta_0$, where θ_0 is the angle between the direction of vibration and that of the incident photon. Thus, we may write[3,9]

$$\sigma_\perp = \sigma_a \sin^2\theta_0 + \sigma_c \cos^2\theta_0 , \tag{1}$$

$$\sigma_\parallel = 0.5\sigma_a(1+\cos^2\theta_0) + 0.5\sigma_c \sin^2\theta_0 , \tag{2}$$

where the cross sections $\sigma_\parallel$ and $\sigma_\perp$ are the scattering cross sections of ^{15}N obtained when the photon beam is parallel and perpendicular to the *graphite* planes, respectively, while σ_a and σ_c are the cross sections obtained when the photon beam is parallel and perpendicular to the *nitrate* planes, respectively. Obviously, one obtains $\sigma_\parallel = \sigma_a$ and $\sigma_\perp = \sigma_c$ when the nitrate planes are exactly parallel to the graphite planes in the intercalated sample namely when $\theta_0 = 0°$ as can be seen from Eqs. (1) and (2). A plot of the calculated ratio $R = \sigma_\parallel / \sigma_\perp$ versus θ_0 is given in Fig. 2.

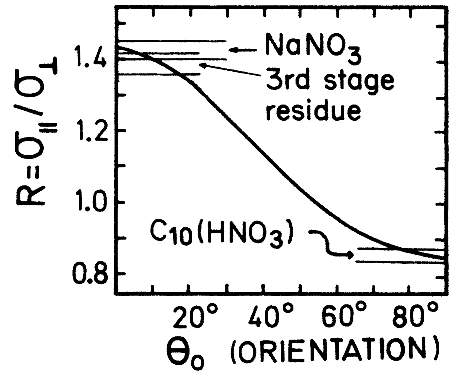

FIG. 2. Calculated and measured ratios of $R=\sigma_{\parallel}/\sigma_{\perp}$ vs θ_0 (the angle of orientation of the NO_3 planes with respect to the graphite planes). The horizontal parallel lines indicate the measured ratio including the error bar for the residue compound, for $NaNO_3$ and for the normal second-stage compound $C_{10}(HNO_3)$.

IV. RESULTS

A. Scattered intensities

The scattered radiation spectrum for the two geometries of the sample is shown in Fig. 3 which shows that the scattering cross section $\sigma_{\parallel}$, for the case where the photon beam is parallel to the graphite planes, is much larger than that for the perpendicular geometry. The two spectra were accumulated during a total running time of four days using alternate 30 min runs for averaging out effects of electronic drifts and intensity variations of the photon beam. The background was measured using a graphite sample having the same weight as the residue sample.

Experimentally, we found $R=\sigma_{\parallel}/\sigma_{\perp}=1.36\pm0.03$ for the third-stage residue intercalated sample. This is to be compared with a ratio $R=0.86\mp0.02$ obtained for the second-stage normal compound $C_{10}(HNO_3)$, where the NO_3^- planes were found to be nearly perpendicular[3] to the graphite planes (Fig. 2). This should also be compared to $R=1.43\mp0.03$, which would be obtained for a parallel orientation of NO_3 relative to the graphite planes; this value was measured experimentally using a $NaNO_3$ single crystal, where the NO_3 planes were positioned parallel and perpendicular to the photon beam.[9] The present value of R should be corrected for possible disorientation effects caused by the intercalation process and for the possible presence of $\simeq$5% impurity of $C_{15}(HNO_3)$. The influence of disorientation was deduced from a measurement of the mosaic spread of the intercalated sample using x-ray diffraction and was found to have a full width at half maximum of $\Delta\phi=2.5°$, and, hence, has a negligible effect on the value of R. Furthermore, the possible presence of $\simeq$5% impurity of $C_{15}(HNO_3)$ would tend to decrease R by about 2% and, hence, the corrected value would be $R=1.39\mp0.03$, which implies that the nitrate planes make an angle $\theta_0=13\mp5°$ with the graphite planes. This is to be compared with $\theta_0=8\mp2°$ reported in Ref. 7 using the low-energy electron diffraction technique and employing a very thin target.

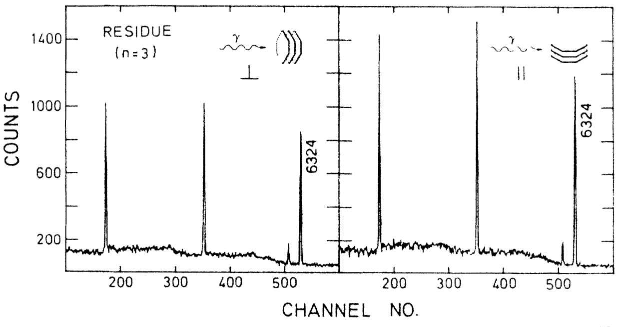

FIG. 3. Portions of the scattered photon spectra from ^{15}N appearing in the residue sample $C_{19}(HNO_3)$ obtained using 100-cm^3 GeLi detector with the photon beam parallel (||) and perpendicular (⊥) to the graphite planes. The three strong peaks correspond to the photo, first, and second escape peaks of the scattered 6324-keV γ line.

TABLE I. Scattering cross-section ratios R_T at $T=20$ K relative to $T=296$ K for parallel and perpendicular geometries of the photon beam with respect to the graphite planes.

	$R_T=\sigma_s(20\ K)/\sigma_s(296\ K)$	
	Experiment	Calculated
Parallel	0.92 ± 0.02	0.93
Perpendicular	0.83 ± 0.03	0.88

B. Variation of σ_s with T

One interesting feature of the present technique is that it enables us to characterize the particular chemical species of the intercalant residing between the graphite planes. This may be done by measuring the ratio R_T of the scattering cross section σ_s at $T=20$ K relative to $T=296$ K. This ratio was measured for two geometries where the incident photon beam was perpendicular and parallel to the graphite planes of the residue sample. The results of such measurement characterize the chemical form of the intercalant because different molecules have different ratios. The results for the residue sample are compared in Table I with that calculated for a nitrate single crystal (such as $NaNO_3$). Table I reveals a remarkable agreement especially for the parallel case with calculated cross sections. For the perpendicular case, a small deviation occurs which can be attributed to the anisotropic binding of the entire NO_3 molecule to the graphite plane. This is because in the calculated values of Table I, it is tacitly assumed that the forces holding the entire nitrate molecule in $NaNO_3$ are isotropic. Thus, the lower measured value (Table I) for the perpendicular case would indicate a weaker binding of the nitrate molecules perpendicular to the graphite planes as compared to the parallel binding.

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