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Resonance Photon Scattering from $^{15}N_2$ Monolayers Adsorbed on Grafoil

R. Moreh[a] and O. Shahal
Nuclear Research Center, Negev, Beer Sheva, Israel, and Ben-Gurion, University of the Negev, Beer Sheva, Israel

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Nuclear resonance scattering of photons from ^{15}N has been used to study the orientation of the N_2 molecular axis with respect to the adsorbing Grafoil plane. At 78 °K, and around 1 monolayer coverage, the N_2 molecules were found to be aligned preferentially parallel to the plane of graphite. At lower coverage, of ~0.8 monolayer, some parallel orientation is retained while at a coverage of 1.5 monolayers no preferred orientation was obtained.

The nuclear-resonance-scattering cross section of 6.324-MeV photons from $^{15}N_2$ molecules adsorbed on Grafoil has been measured as a function of the coverage. Film thicknesses of N_2 ranging from ~0.8 to ~1.5 monolayers have been used. A strong dependence of the photon scattering intensity on the angle between the *c* axis of the Grafoil and the direction of the photon beam was observed. This is interpreted as due to the particular orientation of the adsorbed N_2 molecule with respect to the *c* axis of graphite.

The present technique is entirely new and can be applied to the adsorption of $^{15}N_2$ gas only as it depends on the fact that the 6.324-MeV level in ^{15}N is photoexcited[1,2] by a chance overlap (to within ~30 eV) with one of the γ lines of the reaction Cr(n, γ). The nuclear-scattering cross section σ_s is so high (~1.4 b) and the background is so low that detectable scattered signals are obtained even from targets containing ~10 mg of ^{15}N. In addition, since a resonance-scattering process is involved the graphite substrate is essentially transparent to the incident photon beam.

In a recent publication,[3] it was noted that σ_s is strongly dependent on the kinetic-energy component of the N atom (including that of its *zero-point* motion) along the photon-beam direction. This is because σ_s is determined by the overlap between the two Doppler-broadened shapes of the incident γ line and the resonance level. In fact, a one-to-one correspondence was established[3] between σ_s and the effective[4] temperature T_e of the N atom, where T_e gives a measure of the total kinetic energy of the N atom including that of its zero-point motion.

From the above it may be seen that σ_s would be highest when the axis of the linear $^{15}N_2$ molecule coincides with the γ-beam direction because of the increased kinetic energy of the N atom contributed by the *zero-point* vibrational energy of the N_2 molecule. Hence σ_s can be used as a very sensitive monitor of the angle between the line joining the diatomic N_2 molecule and the photon direction. In the present work we used this fact for studying the orientation of adsorbed $^{15}N_2$ molecules on partially oriented graphite foil known commercially as "Grafoil."

Experimentally, the photon beam is obtained from the (n, γ) reaction on some chromium disks placed along a tangential beam tube and near the core of the IRR-2 reactor.[1] The intensity of the 6.324-MeV γ line emitted by the reaction ^{53}Cr(n, γ) is relatively weak amounting to ~10^4 photons/cm^2 sec at the target position. The target consisted of variable amounts of enriched $^{15}N_2$ gas (99.3%) adsorbed on Grafoil. A total of 84 rec-

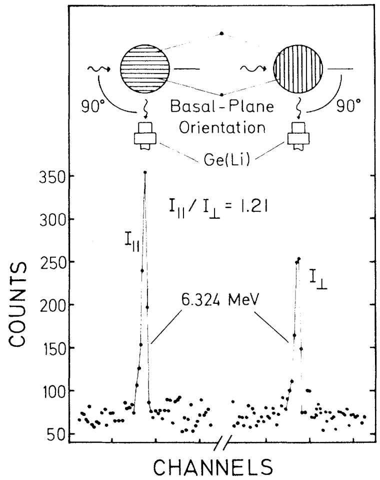

FIG. 1. Small portions of the scattered photon spectra from $^{15}N_2$ adsorbed on Grafoil showing the double escape peaks of the 6.324-MeV γ line, obtained with use of a 50-cm^3 Ge(Li) detector. The scattered intensity $\sigma_{\parallel}$ from the parallel geometry (i.e., with the photon beam parallel to the plane of the Grafoil) is higher than $\sigma_{\perp}$ which is the scattered intensity from the perpendicular geometry. The γ source is obtained from the reaction Cr(n,γ).

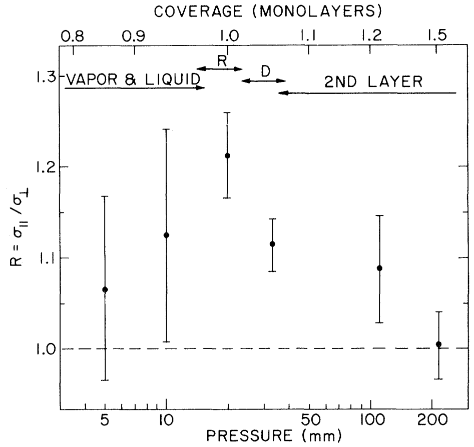

FIG. 2. Measured-scattering cross-section ratios $\sigma_{\parallel}/\sigma_{\perp}$ from $^{15}N_2$ adsorbed on Grafoil as a function of the vapor pressure ($T = 78$ °K). The extreme points at $P = 5$ mm and $P = 216$ mm correspond to a coverage of ~ 0.8 and ~ 1.5 monolayers, respectively. The upper scale, showing the coverage in units of registered monolayers, was deduced from the data of Kjem *et al.* (Ref. 5). The top part of the figure, taken from Refs. 5–7, shows roughly the vapor-pressure boundaries of the different phases of adsorbed N_2, where R denotes a $\sqrt{3}\times\sqrt{3}$ registered phase and D denotes a dense solid phase.

tangular Grafoil sheets of variable width were packed inside a cylindrical quartz container (of inner dimensions 2.7 cm diam × 2.8 cm high) so that the foil planes were parallel to the axis of the quartz cylinder. The sample was heated to 750 °C under vacuum for 7 h to remove the impurities before gas adsorption. The weight of adsorbed $^{15}N_2$ at 78 °K and 20 mm pressure was 64 mg. The pressure of the gas was measured with an electronic transducer. The sample was placed in a nitrogen Dewar in such a way that the region traversed by the photon beam was free from liquid nitrogen. The design of the system permitted the rotation of the sample from a position where the photon beam and the Grafoil c axis are parallel, to a perpendicular position, without breaking the vacuum. The scattered radiation was detected with two 50-cm^3 Ge(Li) detectors, at 90° to the photon beam, placed symmetrically at a distance of 18 cm from the target. Because of the smallness of the target material and the weakness of the incident γ line, such measurements are time consuming, requiring running times of the order of days per spectrum.

Figure 1 shows the scattered spectra for the parallel and perpendicular positions at 78 °K and a pressure of 20 mm. The ratio of the scattered intensities as a function of $^{15}N_2$ pressure is given in Fig. 2 which shows a sharp rise of the ratio reaching a maximum, $R = \sigma_{\parallel}/\sigma_{\perp} = 1.21$, at $P = 20$ mm. The ratio then drops gradually reaching $R \sim 1$ at $P \sim 220$ mm. Figure 2 also shows the different phases of adsorbed N_2 on grafoil at ($T = 78$ °K) taken from Kjems *et al.*,[5] Chung and Dash,[8] and Ostlund and Berker.[7] The region in Fig. 2 around $P \sim 20$ mm corresponds to a completion of 1 monolayer of N_2 molecules on Grafoil. At this coverage, the N_2 molecules were found to form a $\sqrt{3}\times\sqrt{3}$ registered structure.[6,8]

As mentioned earlier, the ratio R (Fig. 2) is expected to be a sensitive monitor of the angle of the N_2 symmetry axis with respect to the Grafoil plane. A value $R > 1$ indicates a preferred orientation parallel to the graphite planes. We interpret the behavior of the values of R versus P as follows: At $T = 78$ °K and coverages around 0.9 monolayer ($P = 5$ and 10 mm) there is a preference for a parallel orientation because $R = 1.07 \pm 0.10$ and 1.13 ± 0.12 (Fig. 2). This is a very remarkable result because it means that when N_2 on Grafoil is in a liquid and possibly partly vapor form, some molecular orientation still persists. When the coverage is increased to around 1 monolayer (at $P = 20$ mm) the extent of parallel orientation increases to a maximum value $R = 1.21 \pm 0.06$. At this coverage the N_2 monolayer film forms a

$\sqrt{3}\times\sqrt{3}$ structure in registry with the Grafoil plane. It should be noted, however, that this value of R corresponds to partial parallel orientation only and the molecules must tilt slightly from the surface plane (see below). With increasing coverage, R decreases gradually and also the extent of parallel molecular orientation; this is probably expected because with higher coverage, the N_2 film is first forced out of registry and the N_2 molecular axes could be tilted more out of the film plane by a formation of an incommensurable dense solid phase in which the nearest-neighbor distance decreases from 4.26 to 4.04 Å. With further increase in coverage, the decreasing trend of R continues because a second layer starts to form which forces out the N_2 molecules of their partial parallel orientation, until at a coverage of 1.5 monolayers ($P \sim 220$ mm), the molecular orientation gradually disappears and $\sigma_{\parallel}$ approaches $\sigma_{\perp}$. Qualitatively, this behavior is in line with the theoretical results of Steele,[6] and of Berlinsky and Harris,[9] and also with speculations made by Chung and Dash[8] based on heat capacity data.

As noted earlier, our data imply only a partial alignment of the $^{15}N_2$ molecules parallel to the Grafoil surface because the calculated ratio for complete alignment with the basal plane of graphite is $R = \sigma_{\parallel}/\sigma_{\perp} = 1.9$, compared with a measured value of 1.21 ± 0.06.

The ratio of the cross sections may be calculated by first noting that the effective temperature T_e of an N atom in $^{15}N_2$ gas at $T = 78\,^{\circ}\mathrm{K}$ is given by[2]

$$T_e \approx \tfrac{5}{6}T + \tfrac{1}{12}h\nu_0 = \tfrac{5}{6}T + 274, \qquad (1)$$

where $h\nu_0/12 = 274\,^{\circ}\mathrm{K}$ is contributed by the zero-point vibration of the N_2 molecule to the kinetic energy of the atom at $T = 78\,^{\circ}\mathrm{K}$. Second, we consider an N_2 molecule lying flat on the graphite substrate and define two effective temperatures T_c and T_a characterizing the motion of the N atom along the c axis and perpendicular to it (i.e., within the plane of the graphite substrate). The motion along the c axis consists of two degrees of freedom: One is vibrational, $h\nu_1$, of the whole N_2 molecule with respect to the graphite surface and characterizes the binding energy of physisorption of N_2 on graphite. The second, $h\nu_2$, is a librational motion of N_2 around an axis lying in the graphite plane. The motion of N_2 within the plane has four degrees of freedom, two of which are translational of the whole N_2 molecule, one for internal vibration, $h\nu_0$, and one for free rotation around the c axis; thus,

$$T_c = \sum_{I}^{2} \frac{h\nu_i}{2}\left(\frac{1}{\exp(h\nu_i/kT) - 1} + \frac{1}{2}\right), \qquad (2)$$

$$T_a = \tfrac{3}{4}kT + \tfrac{1}{8}h\nu_0. \qquad (3)$$

Adopting the values of Steele,[6] namely, $h\nu_2 = 47\,^{\circ}\mathrm{K}$ and $h\nu_1 = 58\,^{\circ}\mathrm{K}$, we obtain $T_c = 81\,^{\circ}\mathrm{K}$, $T_a = 470\,^{\circ}\mathrm{K}$, and hence $T_g = \frac{1}{3}(2T_a + T_a)$ for the effective temperature of N_2 on nonoriented graphite. The corresponding scattering cross sections may then be determined by use of the calculated curve of σ_s vs T_e given in Ref. 3, yielding $\sigma_c = 0.43$ b, $\sigma_a = 1.55$ b, and hence $R = \sigma_a/\sigma_c = 3.6$ for the ideal case of flat N_2 molecules adsorbed on absolutely parallell graphite surfaces. In practice, however, one should account for the randomly oriented fraction f of graphite *surfaces* in Grafoil and for the angular spread $\Delta\theta$ of the orientations of the graphite *surfaces* in Grafoil. Further, it may be noted that the contribution to the effective temperature of a vibrating atom varies as $\cos^2\gamma$, where γ is the angle between the axis of vibration and the direction of the incident photon.[3] Assuming reasonable values, $\Delta\theta = 30°$ and $f = 50\%$, for the full width at half maximum angular spread of the crystallite surfaces and for the random fraction,[5,10] we obtain $T_c = 215\,^{\circ}\mathrm{K}$, $T_a = 401\,^{\circ}\mathrm{K}$ yielding $R = \sigma_a/\sigma_c = 1.9$. If instead of $T_c = 81\,^{\circ}\mathrm{K}$ based on Steele's values[6] of $h\nu_i$, we use $T_c \sim 101\,^{\circ}\mathrm{K}$ deduced from our measurement of the *absolute* scattering cross section of the 6.324-MeV γ line from ^{15}N adsorbed on graphite, we find $R = 1.75$ which is still much higher than the measured value. Thus in order to account for the measured low value of R in the registered phase (at $T = 78\,^{\circ}\mathrm{K}$) it is necessary to assume a constant tilt angle, $\beta \sim 70°$, of the N_2 axis with respect to the Grafoil c axis, and a value $\alpha \sim 20°$ for the angular amplitude of the librational motion, to achieve agreement with the measured value of R.

Finally, better quantitative measure of β and α can be obtained by measuring σ_s as a function of T for $T < 78\,^{\circ}\mathrm{K}$. This will require a more refined knowledge of the structure of the Grafoil.

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[a] Present address: Physics Department, University of Illinois at Urbana-Champaign, Urbana, Ill. 61801.

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Electronic Raman Scattering and Antiresonance Behavior in Highly Stressed Photoexcited Silicon

D. Guidotti, Shui Lai, M. V. Klein, and J. P. Wolfe
Physics Department and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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Inelastic light scattering from photoproduced carriers is observed in stressed high-purity silicon at low temperatures. The two electronic Raman structures observed correspond to transitions between stress-split valence bands at the zone center. These transitions can be stress-tuned to the Γ-point phonon energy, thereby exhibiting Fano-type interference between competing scattering amplitudes.

When intrinsic silicon is illuminated with light above the band gap, electron-hole (e-h) pairs are produced which, at low temperatures, bind into excitons near the surface of excitation. Application of uniform compressive stress parallel to the [001] crystallographic direction causes narrowing of the indirect gap and lowers the band energy of indirect excitons. If stress is applied through a spherical contact surface, the resulting nonuniform stress exhibits a relative maximum and, therefore, a potential-energy minimum for excitons inside the bulk. With use of this method of strain confinement, excitons are drawn from the surface, where they are produced by a pump laser, and collect in the strain well where condensation into an electron-hole liquid (EHL) occurs at low temperatures ($T \lesssim 15$ K).[1,2] A feature of strain confinement is that a high concentration of e-h pairs may be created, with moderate excitation levels, in a nearly spherical volume approximately 100 μm in diameter and totally within the bulk of the sample. We probe the strain-confined exciton gas or EHL by inelastic light scattering using Nd-doped $YAlO_3$ (10 796 Å) or yttrium aluminum garnet (10 644 Å) lasers which have photon energies just below the silicon indirect band edge.

We observe, for the first time in elemental semiconductors, two Raman-active inter-valence-band transitions at the Γ point over a wide range of temperatures (1.8–68 K) and applied stress (40–170 kg/mm^2). These transitions, labeled *A* and *B* in Fig. 1, shift with applied stress and thus provide a unique opportunity to tune each one to the $\Gamma_{25'}$ phonon energy. The antiresonance line shapes observed under these conditions are in good agreement with a modified Fano theory[3,4] in which a transition to the discrete phonon state mixes with the finite continuum of inter-valence-band Raman transitions (*A* and *B*) through electron-phonon interaction. This coupling is simi-

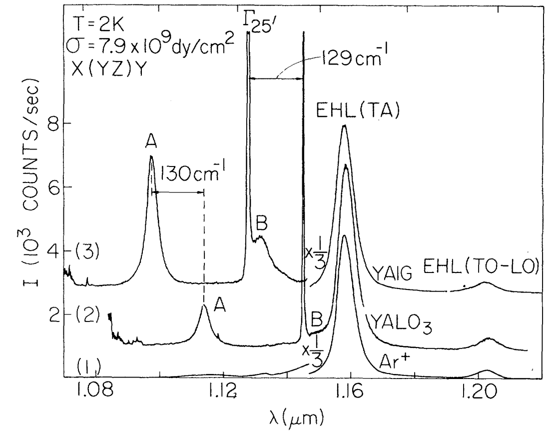

FIG. 1. Overall spectrum from strain well. (1) With argon-ion pump laser only, (2) with $YAlO_3$ probe laser plus the Ar^+ laser, and (3) with yttrium aluminum garnet probe laser plus the Ar^+ laser. The energy difference between the two probe lasers is 132 cm^{-1}.