

Neutron-Scattering Studies of the Structure and Dynamics of ^{36}Ar Monolayer Films Adsorbed on Basal-Plane-Oriented Graphite

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Elastic- and inelastic-neutron-scattering methods have been used to study the low-temperature properties of argon films adsorbed on graphite. At $T=5$ K the film forms a two-dimensional triangular lattice incommensurate with the substrate. The spectrum of neutrons inelastically scattered in the plane of the film is found to be consistent with calculations based on a simple two-dimensional phonon model in which interactions with the substrate are neglected.

We have recently found that elastic neutron diffraction can be used to study adsorbed nitrogen films.¹ To realize the full capability of the neutron-scattering method, however, it is necessary to make inelastic as well as elastic studies so that both the dynamic and static properties of the films can be investigated. While the N_2 films were satisfactory for elastic diffraction, the intensities proved to be marginal for inelastic measurements. Therefore, to explore the potential of neutrons for dynamic studies we turned to a more intense scatterer, ^{36}Ar , adsorbed on Grafoil.² We describe here some of the results of our investigations of the coherent elastic and inelastic scattering from this system at low temperatures.³ These relate to both the structure of the films and their collective excitations.

There are two main reasons for choosing ^{36}Ar as an adsorbed film for neutron scattering. First, it is the most intense coherent neutron scatterer known. Second, since it is monatomic, intramolecular degrees of freedom do not complicate interpretation of the data. As a substrate, Grafoil offers the advantages of large specific areas and surfaces of exceptional uniformity and homogeneity.⁴ It is also attractive from the neutron-scattering point of view because it has a considerable degree of basal-plane order.¹ This not only improves background discrimination but also permits selective study of excitations involving atomic motions parallel and perpendicular to the substrate surface.

Our measurements were made on a triple-axis spectrometer operated with a fixed incident neutron energy of 14.8 meV. A pyrolytic graphite filter was mounted in the beam to reduce higher-order contamination. The Grafoil substrate consisted of 110 disks 4.4 cm in diameter loaded into a close-fitting cylindrical aluminum cell. It formed a stack 5 cm high and weighed 60.5 g. The crystallite c -axis distribution in the foil was found to have a most probable orientation normal to the plane of the foil with a full width at half-maximum of 30° . All scans were made with the sample mounted so that the neutron wave-vector transfer \vec{Q} was *parallel* to the plane of the foils.

Figure 1 shows the diffraction pattern observed

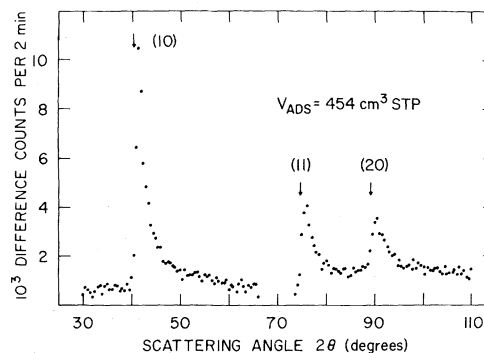


FIG. 1. Neutron diffraction from monolayer films of ^{36}Ar adsorbed on graphite at $T=5$ K. Background scattering from the substrate has been subtracted. The apparent negative swing between 66° and 73° is due to screening of the substrate scattering by ^{36}Ar .

at $T=5$ K with 454 cm^3 STP of ^{36}Ar in the cell. Three peaks are evident, all with the characteristic "sawtooth profile" of diffraction from an ordered two-dimensional array.⁵ These peaks can be indexed as the (10), (11), and (20) Bragg reflections from a two-dimensional triangular lattice with a nearest-neighbor (nn) spacing of 3.88 \AA . The structure is incommensurate with the substrate, the nn distance being about 9% smaller than that of a $\sqrt{3} \times \sqrt{3}$ triangular lattice in registry¹ on the graphite basal-plane surfaces. From the lattice constant of the argon film and a calibration of the substrate surface area made with nitrogen (which forms an easily recognized registered phase), we estimate that 454 cm^3 STP of ^{36}Ar is 10% below the full monolayer capacity of the Grafoil.

It is interesting to note that the nn distance in the adsorbed film is less than 2% larger than the nn distance in three-dimensional solid argon at 20 K. Evidently, the structure of the film is primarily determined by interactions between argon atoms. This conclusion is not unexpected since the attraction between argon atoms is known to be considerably stronger than the variation of the argon-carbon potential from point to point on the substrate surface.⁶

Figure 2 shows some of the inelastic-scattering spectra obtained from the adsorbed argon monolayer. As noted above, the wave-vector transfers \vec{Q} were nominally in the plane of the monolayer films. The spectra represent neutrons which have lost energy by inelastic interactions with the argon film. Note that broad peaks appear at $\sim 3.2 \text{ meV}$ and, for $Q = 2.6 \text{ \AA}^{-1}$, at 5.8 meV as well.

To relate these spectra to collective excitations of the film it is necessary to take account of the fact that the film consists of two-dimensional, planar polycrystals with only partial orientation

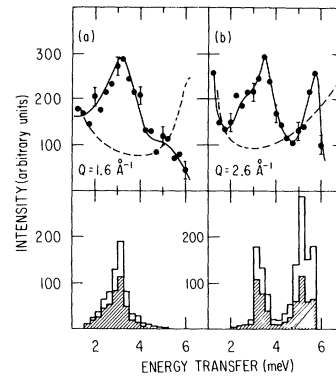


FIG. 2. Inelastic neutron scattering from ^{36}Ar monolayers adsorbed on graphite at $T=5$ K. Background from the substrate has been subtracted. The solid circles are the experimentally observed spectra from in-plane motions of atoms in the film. The abrupt cutoff at about 6 meV in scan (b) is caused by imperfect subtraction of a background peak at 6.5 meV . The solid lines serve as a guide to the eye; the dashed lines indicate the background scattering observed with no argon in the cell. Plotted in the lower part are computer simulations of the scattering based on a simple two-dimensional model of the film. The difference between the shaded and unshaded histograms reflects the effects of including instrumental efficiency in the computations.

of the planes. Hence the spectra cannot be directly identified with discrete phonons propagating in particular directions in the film. To determine the character of the collective modes we have therefore compared the spectra to two-dimensional model calculations analogous to those made by de Wette and Rahman⁷ for three-dimensional fcc polycrystals. As these authors explain, the basic element to be computed is the coherent part of the one-phonon, dynamic structure factor $S_{\text{coh}}(\vec{Q}, \omega)$. For the energy-loss scattering which we have observed, $S_{\text{coh}}(\vec{Q}, \omega)$ for a polycrystal is expressed in the form

$$\{S_{\text{coh}}(\vec{Q}, \omega)\}_{\text{poly}} = \exp(-2W)[n(\omega) + 1](\hbar Q^2/2M\omega) \left\langle \sum_{j=1}^2 [\hat{Q} \cdot \vec{c}_j(\vec{Q})]^2 \delta[\omega - \omega_j(\vec{Q})] \right\rangle, \quad (1)$$

where $\exp(-2W)$ represents the Debye-Waller factor, $n(\omega)$ is the phonon occupation number $[\exp(\hbar\omega/k_B T) - 1]^{-1}$, M is the ^{36}Ar mass, \hat{Q} is a unit vector along \vec{Q} , and the quantities $\vec{c}_j(\vec{Q})$ are the orthonormal phonon eigenvectors corresponding to the eigenfrequencies $\omega_j(\vec{Q})$. The subscript j denotes the mode polarization; the angular brackets indicate the averaging of \vec{Q} over all appropriate orientations.

The phonon eigenvectors $\vec{c}_j(\vec{Q})$ and eigenfrequencies $\omega_j(\vec{Q})$ were calculated in a nearest-neighbor Born-von Karman analysis for a two-dimensional triangular lattice with use of the Lennard-Jones (6-12) potential for argon.⁸ Interaction of the argon film with the graphite substrate was neglected. Except for this, the calculation of $\omega_j(\vec{Q})$ is similar to that of Novaco.⁹ Fig-

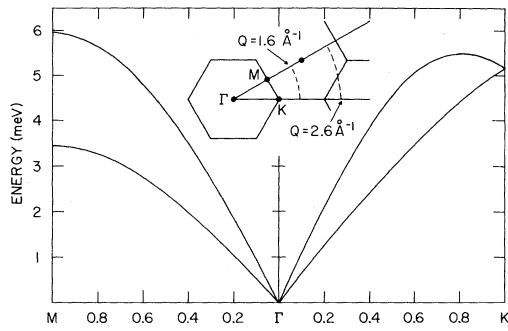


FIG. 3. Dispersion curves along principal symmetry directions of a triangular two-dimensional argon lattice, calculated by assuming the standard Lennard-Jones potential for argon (Ref. 8). The inset shows the region of reciprocal space covered by the scans of Fig. 2.

Figure 3 shows the dispersion curves calculated for phonons propagating along the principal symmetry directions of the Brillouin zone.

The angular average in Eq. (1) involves taking account of both the random x - y orientation and the tilting of the planes of the adsorbed film elements. The former was introduced by calculating the quantity

$$\sum_{j=1}^2 [\hat{Q} \cdot \vec{c}_j(\vec{Q})]^2 \delta(\omega - \omega_j)$$

at randomly selected points along a 30° arc in reciprocal space representing the locus of points of radius Q . Such arcs, shown schematically in the inset to Fig. 3, span the irreducible part of the Brillouin zone. Tilting of the film planes was modeled by adding a finite radial width to Q in the calculation of $\{S_{\text{coh}}(Q, \omega)\}_{\text{poly}}$.

At the bottom of Fig. 2 are histograms representing inelastic spectra computed from Eq. (1) with the Debye-Waller factor set equal to unity. The unshaded histograms indicate the results obtained when instrumental effects are neglected, while the shaded histograms show how the spectra are altered when the variation of the spectrometer efficiency with neutron energy transfer is included in the computations. It is evident that the shaded histograms correspond closely to the experimentally observed spectra not only with regard to the positions of the maxima but also with respect to their shape. The calculations predicted similarly well-defined structure at $Q = 3.5$ and 4.3 \AA^{-1} as was verified experimentally. Spectra at other values of $Q \geq 1 \text{ \AA}^{-1}$ were predicted to have less structure, and this was also observed.

It is possible to see from simple geometrical considerations that the peaks in the inelastic spectra of Fig. 2 are related to the zone-boundary phonon frequencies of the film. The largest contribution to $\{S_{\text{coh}}(Q, \omega)\}_{\text{poly}}$ occurs in regions of reciprocal space near the zone boundaries where the density of phonon states is highest, while the relative weight of the longitudinal and transverse modes is governed by the term $[\hat{Q} \cdot \vec{c}_j(\vec{Q})]^2$ in Eq. (1). For $Q = 1.6 \text{ \AA}^{-1}$ the phonon propagation vector $\vec{q} = \vec{Q} - \vec{\tau}$ is nearly perpendicular to \vec{Q} at the zone boundary ($\vec{\tau}$ is the reciprocal-lattice vector at the zone center). Therefore most of the response comes from the transverse branch at 3.5 meV. On the other hand, for $Q = 2.6 \text{ \AA}^{-1}$, the phonon wave vector at the zone boundary forms an intermediate angle with \vec{Q} ; hence both transverse and longitudinal modes contribute to the scattering.

We can summarize the results of both elastic and inelastic measurements of scattering in the monolayer plane by stating that they are consistent with a model of the adsorbed argon film as a two-dimensional solid whose structure is primarily determined by argon-argon interactions. This lends support to the view that nonregistered monolayer films adsorbed on graphite are good representations of idealized two-dimensional phases, a concept which is also inferred from macroscopic measurements made with other gases.⁴ We emphasize, however, that the model of an isolated two-dimensional system presented here is only applicable to the in-plane modes at low temperatures. Preliminary studies of the out-of-plane modes and of the in-plane and out-of-plane modes at higher temperatures show evidence of the influence of the substrate. More detailed experiments over a wider range in temperature and coverage are now in progress.

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²Grafoil is the trademark of an expanded graphite product marketed by Union Carbide Corp., Carbon Products Division, 270 Park Avenue, New York, N. Y. 10017.

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Nuclear Spin-Lattice Relaxation Associated with Low-Energy Excitations in Glasses

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The nuclear T_1 has been measured between 1.2 and 300 K on ^{11}B , ^{23}Na , ^{29}Si , and ^{77}Se in amorphous B_2O_3 , $(\text{Na}_2\text{O})_{0.3}(\text{SiO}_2)_{0.7}$, $\text{Na}_2\text{B}_4\text{O}_7$, and Se. The measured rates, which for spins $I > \frac{1}{2}$ are much greater than those observed in corresponding crystalline materials, are nearly field independent and vary as T^α with $\alpha \sim 1.3$. Such a quadrupolar relaxation might be explained by a model involving the distribution of two-level systems, as describes the anomalous thermal and ultrasonic-wave properties of similar materials.

Recent measurements of specific heat and thermal conductivity¹ have revealed the existence of low-energy excitations in all insulating glasses so far investigated. One of the models proposed^{2,3} to explain this effect assumes the existence of two-level excitations, whose energy splittings are widely distributed.³ Later experimental results, namely a nonlinear ultrasonic attenuation⁴ and an increase in the sound velocity⁵ at temperatures below 10 K, can also be understood in this model. Such low-energy excitations might induce relaxation of the nuclear magnetization. The nuclear-quadrupole relaxation was indeed found to be faster in amorphous As_2S_3 than in the corresponding crystalline phase between 1.2 and 300 K.⁶

This Letter deals with measurements of the nuclear spin-lattice relaxation time T_1 performed on glasses in which the specific-heat anomaly has already been observed.¹ The results confirm that $(T_1)^{-1}$ is always much higher in the glassy state than in the crystalline. The data further enable us to conclude that the relaxation mechanism involves low-temperature motional excitations rather than paramagnetic centers. The observed frequency dependence of T_1^{-1} will be shown to dis-

agree with the models usually proposed to explain the relaxation through motions in solids. A model for the relaxation process which involves the distribution of two-level systems and might explain the data will be suggested.

Pulsed NMR measurements have been carried out on amorphous samples of B_2O_3 , $(\text{Na}_2\text{O})_{0.3}(\text{SiO}_2)_{0.7}$, $\text{Na}_2\text{B}_4\text{O}_7$, and pure Se. The experimental data obtained at $T = 4.2$ K and in an external field $H_0 \sim 20$ kG will be given first as they enable us to draw straightforward conclusions. The measured T_1 for ^{11}B and ^{23}Na nuclei ($I = \frac{3}{2}$) were always found to be extremely short (~ 2 min) when compared with values of several hours generally found for the same nuclei in crystalline insulating materials.⁷ A direct comparison is possible with crystalline samples for boron oxide and for soda silica. In B_2O_3 T_1 was found to be 20 times longer in crystalline samples (the measured T_1 values were not critically dependent on the preparation procedure for either phase, and this ratio of T_1 's was obtained for a sample on which data were first taken in the crystalline state and then after vitrifying). The difference is even larger in soda silica, with T_1 at least 2 orders of magnitude