

the excitation spectrum in liquid ^3He . Only a microscopic calculation of the particle-hole interaction at finite temperature can lead to a proper description of the dynamical structure factor at finite values of Q and ω over a wide temperature range.

The authors acknowledge valuable discussions with R. Scherm, R. A. Cowley, and G. E. Brown. One of us (H.R.G.) thanks the National Research Council-Center National de la Recherche Scientifique exchange program for support of a visit to the Institut Laue-Langevin.

¹R. Scherm, W. G. Stirling, A. D. B. Woods, R. A. Cowley, and G. J. Coombs, *J. Phys. C* **1**, L341, (1974).

²W. G. Stirling, R. Scherm, V. Volino, and R. A. Cowley, in *Proceedings of the Fourteenth International Conference on Low Temperature Physics, Otaniemi, Finland, 1975*, edited by M. Krusius, and M. Vuorio (North-Holland, Amsterdam, 1975); W. G. Stirling, R. Scherm, P. A. Hilton, and R. A. Cowley, *J. Phys. C* **9**, 1643 (1976).

³K. Sköld, C. A. Pelizzari, R. Kleb, and G. E. Ostrowski, *Phys. Rev. Lett.* **37**, 842 (1976).

⁴V. F. Turchin, *Slow Neutrons* (Israel Program for Scientific Translation, Jerusalem, 1965), p. 108; V. F. Sears, *J. Phys. C* **9**, 409 (1976).

⁵B. E. Keen, P. W. Mathews, and J. Wilkes, *Phys. Lett.* **5**, 5 (1963); W. R. Abel, A. C. Anderson, and J. C. Wheatley, *Phys. Rev. Lett.* **17**, 74 (1966).

⁶D. Pines, in *Quantum Fluids*, edited by D. F. Brewer (North-Holland, Amsterdam, 1965).

⁷D. Pines and P. Nozières, *Theory of Quantum Liquids* (Benjamin, New York, 1966).

⁸C. H. Aldrich, C. J. Pethick, and D. Pines, *Phys. Rev. Lett.* **37**, 845 (1976).

⁹S. W. Lovesey, *J. Phys. C* **8**, 1649 (1975).

¹⁰J. C. Wheatley, in *Quantum Fields*, edited by D. F. Brewer (North-Holland, Amsterdam, 1965).

¹¹S. Babu and G. E. Brown, *Ann. Phys. (N.Y.)* **78**, 1 (1973).

¹²H. R. Glyde and F. C. Khanna, in *Proceedings of Gatlinburg the Conference on Neutron Scattering, Gatlinburg, Tennessee, 1976*, edited by R. Moon, CONF-760601 (National Technical Information Service, Springfield, Va., 1976).

¹³F. C. Khanna and H. R. Glyde, *Can. J. Phys.* **54**, 648 (1976).

¹⁴V. F. Sears and F. C. Khanna, *Phys. Lett.* **56B**, 1 (1975).

¹⁵V. J. Emery, *Ann. Phys. (N.Y.)* **28**, 1 (1964).

Neutron-Scattering Study of the Structure of Adsorbed Helium Monolayers and of the Excitation Spectrum of Few-Atomic-Layer Superfluid Films

K. Carneiro,* W. D. Ellenson, L. Passell, J. P. McTague,† and H. Taub‡
Brookhaven National Laboratory,§ Upton, New York 11973

(Received 13 October 1976)

Elastic diffraction of neutrons from helium adsorbed on Grafoil shows that the surface monolayer forms as a highly compressed, ordered triangular lattice incommensurate with the structure of the underlying graphite basal planes. Inelastic scattering from thin superfluid films on top of the surface monolayers reveals the existence of bulklike rotons in films containing on average as few as three layers of atoms.

We have recently completed a neutron-scattering study of adsorbed helium and would like to report here some of the results relating to both the excitation spectrum of few-atomic-layer superfluid films and the structure of the surface monolayer. Our measurements were made with helium adsorbed on Grafoil,¹ an exfoliated graphite foil widely used for thermodynamic investigations. As has been noted,² Grafoil is an excellent substrate for neutron studies because it is relatively transparent to neutrons and at the same time offers large specific areas and surfaces which are remarkably uniform and free from impurities. In addition, these surfaces (primarily basal planes) exhibit a considerable degree of preferred orientation—a useful property for inelastic investiga-

tions because the adsorbed film planes can be partially oriented either parallel or perpendicular to the direction of momentum transfer, thereby giving different weightings to the in-plane and out-of-plane components of the scattering.

Studies of the heat capacity of the helium-Grafoil system^{3,4} show that at monolayer completion the atoms form a solid with a density of 0.115 atoms/Å². The completed second layer is found to have a much lower density (0.081 atoms/Å²) and does not solidify unless compressed by a third layer.⁵ Superflow begins at about 2½ layers,⁶ suggesting that layers subsequent to the second are liquid.

All of our measurements were made with a triple-axis neutron spectrometer. For elastic scans

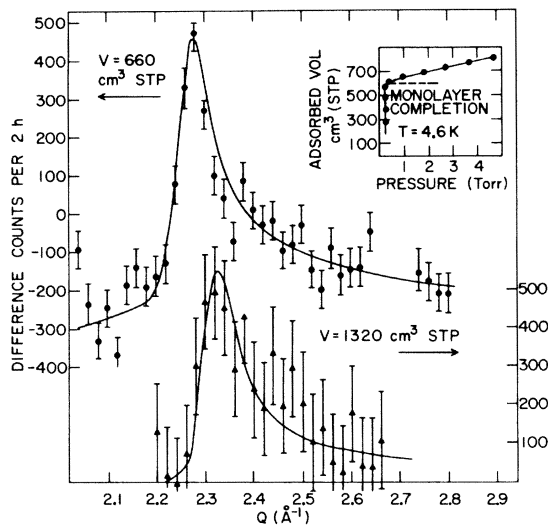


FIG. 1. Diffraction peaks from helium adsorbed on Grafoil; the upper peak was observed with 1.14 monolayers on the surface, the lower with 2.75, both at $T = 1.75$ K. The adsorption isotherm for our sample cell is shown in the inset.

we used neutrons of 2.43-Å wavelength and set the analyzing spectrometer to accept only those scattered without change of energy. Our inelastic scans were made in the constant- Q mode with a fixed incident wavelength of 4.05 Å. Throughout the measurements sample temperatures were maintained between 1.6 and 1.8 K.

The elastic diffraction scans were undertaken to search for evidence of structural ordering in the surface monolayer. Two were made: the first with 0.66 l of helium (STP) in the sample cell and the second with twice that amount. From the adsorption isotherm in the inset to Fig. 1 it can be seen that monolayer completion occurs in our cell at 0.60 l. Under the assumption that the first three layer densities are in the ratio 0.115:0.081:0.077,⁷ we infer that the first scan was made with 1.14 monolayers on the surface and the second with 2.75. Also plotted in the figure are the difference counts representing diffracted intensities with and without helium in the cell. Although there is scatter in the data (reflecting the very small scattering cross section of the helium nucleus), peaks with the "sawtooth" profile characteristic of Bragg reflection from an ordered two-dimensional (2D) array can still be easily recognized. Indexing them as $\{10\}$ reflections from a triangular lattice (the closest packing in 2D), we find from the position of the upper peak a nearest-neighbor distance $a_{nn} = 3.19$ Å.⁸ This corresponds to a surface density of 0.113

atoms/Å², almost identical to the value obtained from the heat capacity measurements of Ref. 2. Together the two experiments establish that the first layer forms an ordered triangular array with a lattice constant some 25% smaller than an epitaxial $\sqrt{3} \times \sqrt{3}$ structure in which every third basal plane hexagon is occupied. The lower peak is outwardly displaced indicating that the additional layers of helium compress the first layer, in this case reducing a_{nn} to 3.13 Å. From the widths of the leading edges of the diffraction peaks the sizes of the diffracting arrays can be estimated to be about 100 Å, i.e., about the size of a typical graphite crystallite.² As far as peaks from the second layer are concerned, we made no attempt to search for these because the $\{10\}$ reflection—the only one likely to be observable—is expected to fall in a region where it would be obscured by the intense background of scattering from the $\{002\}$ reflection of the graphite substrate.

Turning now to our inelastic measurements, these were made with varying amounts of helium in the cell ranging from 2.2 to 7.4 l (STP), the latter being the coverage at which the vapor pressure in the cell coincided with that of bulk liquid helium. For some of the scans the scattering vector \vec{Q} was oriented both parallel and perpendicular to the foil planes to look for evidence of anisotropy in the scattering. All of the low-coverage measurements were made at $Q = 2.0$ Å⁻¹, i.e., as near the roton minimum (the position of maximum inelastic scattered intensity) as background from the substrate would permit. At higher coverages the intensities were sufficient to extend the Q range slightly to cover the region from roughly 1.6 to 2.2 Å⁻¹.

A selection of spectra obtained from films of various thicknesses at $Q = 2.0$ Å⁻¹ is shown in Fig. 2. Also plotted at the top of the figure is the roton line shape observed in bulk superfluid helium under similar but not exactly identical experimental conditions. Attention should be drawn to several features of the spectra. First, there is the simple but surprising fact that well-defined excitations exist in such thin superfluid films. Second, the excitation energies are identical to those found in the bulk liquid. Third, the observed linewidths never exceed the instrumental width; even in the thinnest films there is no indication of intrinsic broadening due to lifetime effects. In fact the only difference between the thin film and bulk liquid spectra is that in the former the lines are less symmetrical—there is relatively more scattering on the high-energy side of the peak. To ex-

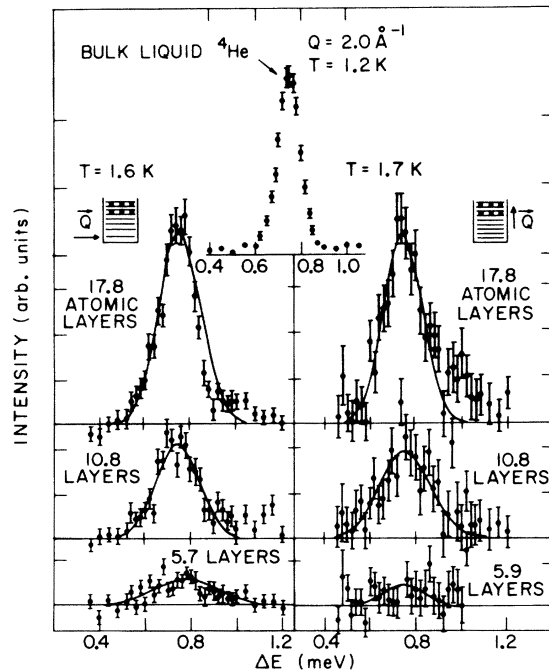


FIG. 2. Representative inelastic spectra from superfluid helium films on Grafoil at $Q = 2.0 \text{ \AA}^{-1}$. The scans on the left- and the right-hand sides were taken with \vec{Q} respectively parallel and perpendicular to the foil planes. At the top is a typical roton peak observed in bulk superfluid helium under nearly identical experiment conditions. The solid lines are Gaussians fitted using only the data between 0.50 and 0.85 meV. The total number of atomic layers on the surface is indicated for each scan; the first two layers are solid, the remainder liquid.

amine this in a more quantitative way we fitted Gaussians to the observed peaks using only the data from 0.50 to 0.85 meV, and divided the spectra into a Gaussian part identified with excitations of 0.74-meV energy (the roton energy in the bulk liquid at 2.0 \AA^{-1}) and an excess part associated with larger energy transfers. The solid circles and triangles plotted in Fig. 3 represent, respectively, the integrated intensity of the Gaussian part and of the excess scattering at larger energies for \vec{Q} parallel and perpendicular to the foil planes. We note that the spectral intensity is proportional to the film thickness; it is also apparent that the excess scattering at higher energies is primarily associated with the out-of-plane component. Multiphonon processes might account for some of the excess scattering but we suggest that the greater part arises from the geometry of the films. Two possible mechanisms come to mind: First, because the films are thin a breakdown of the momentum selection rule can be expected for

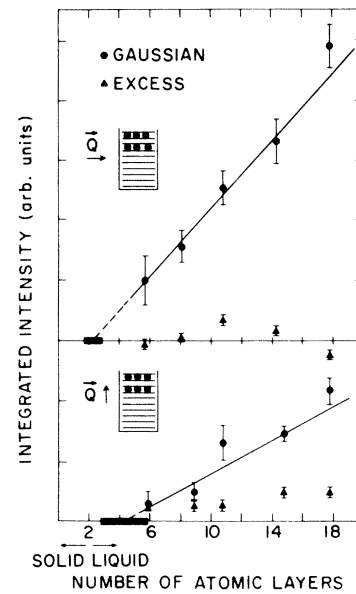


FIG. 3. Variation with film thickness of the intensity of the 0.74-meV roton peak (solid circles) and of the higher energy part of the spectrum (solid triangles) at $Q = 2.0 \text{ \AA}^{-1}$. The upper and lower plots represent scans with \vec{Q} respectively parallel and perpendicular to the foil planes. The first two surface layers are solid, the remainder liquid.

the momentum component perpendicular to the film planes. This will shift part of the spectral response away from the energy at the roton minimum to higher energies. Second, out-of-plane, single-particle motions could also be involved since these are thought to have energies within roughly the same range.⁹ Both contributions will clearly be more pronounced when \vec{Q} is oriented perpendicular to the foil planes.

In fact it is not at all obvious that there ought to be a significant contribution to the scattering from excitations propagating in directions nearly normal to the film planes because of the stringent boundary conditions required for their stability. If, as might be expected, the population of these modes is depressed in the thinnest films, then it may well be that in what we call the out-of-plane orientation we are only detecting excitations propagating along in-plane directions in misaligned films. Some suggestion of this can be seen in the fact that the extrapolated end point of the predominantly in-plane scattering (plotted in the upper part of Fig. 3) falls at $2\frac{1}{2}$ layers (total), which is exactly the thickness at which superflow begins, while for the predominantly out-of-plane scattering (plotted in the lower part of the figure) the end point is shifted to about $4\frac{1}{2}$ layers (total). Un-

fortunately there is too much scatter in the out-of-plane data to be confident that the difference in extrapolated end points is significant.

In conclusion we would like to comment briefly on the interpretation of our data in terms of current thinking regarding thin superfluid films and the properties of their collective excitations. If neutrons couple to surface modes (which is far from certain) the fact that we see only bulklike spectra probably favors the prediction¹⁰ that these modes have the same energies as rotons in the Q range near 2.0 \AA^{-1} . As far as roton energy renormalization is concerned, nothing in our data gives any indication of changes in the roton gap with film thickness. Furthermore, in the thicker films we looked for evidence of changes in the roton effective mass as indicated by changes in the shape of the roton region of the dispersion curve and could find none. To our view this implies that the atomic density of the liquid component of the surface film is the same as that of bulk superfluid, at least within the range (≥ 3 layers) accessible to our investigation. It also suggests that roton renormalization^{11,12} is unlikely to account for the decrease in superfluid fraction observed in films on many surfaces.^{13,14}

We would like to express our appreciation to J. G. Dash and A. D. Novaco for their many helpful comments and suggestions.

*Present address: Physics Laboratory I, University

of Copenhagen, Copenhagen, Denmark.

†Guest Scientist. Permanent address: Department of Chemistry, University of California, Los Angeles, Calif. 90024.

‡Present address: Physics Department, University of Missouri, Columbia, Mo. 65201.

§Work supported by the U. S. Energy Research and Development Agency.

¹Grafoil is the trademark of an expanded graphite product marketed by the Union Carbide Corp., Carbon Products Division, 270 Park Avenue, New York, N. Y. 10017.

²J. K. Kjems, L. Passell, H. Taub, J. G. Dash, and A. D. Novaco, *Phys. Rev. B* **13**, 1446 (1976).

³M. Bretz, J. G. Dash, D. C. Hickernell, E. O. McLean, and O. E. Vilches, *Phys. Rev. A* **8**, 1589 (1973).

⁵M. Bretz, in *Monolayer and Submonolayer Helium Films*, edited by J. G. Daunt and E. Lerner (Plenum, New York, 1973).

⁶J. A. Herb and J. G. Dash, *Phys. Rev. Lett.* **29**, 846 (1972).

⁷M. Bretz, *Phys. Rev. Lett.* **31**, 1447 (1973).

⁸To obtain an equivalent nearest-neighbor spacing in the basal plane of the 3D hcp phase of solid helium would require compression to 510 atmospheres.

⁹C. E. Campbell, F. J. Milford, A. D. Novaco, and M. Shick, *Phys. Rev. A* **6**, 1648 (1972).

¹⁰D. O. Edwards, J. R. Eckardt, and F. M. Gasparini, *Phys. Rev. A* **9**, 2070 (1974).

¹¹T. C. Padmore, *Phys. Rev. Lett.* **32**, 826 (1974).

¹²W. Götze and M. Lücke, to be published.

¹³J. H. Scholtz, E. O. McLean, and I. Rudnick, *Phys. Rev. Lett.* **32**, 147 (1974).

¹⁴M. W. Chan, A. W. Yanof, and J. D. Reppy, *Phys. Rev. Lett.* **32**, 1347 (1974).

First Observation of a Strongly Frequency-Dependent Photoconductivity

J. Schoenes

Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, Zürich Hönggerberg, Zürich, Switzerland

and

K. Keiji Kanazawa

IBM Research Laboratory, San Jose, California 95193

(Received 8 September 1976)

The observation of an ac photoconductivity $\sigma_{ph} \sim \omega^n$ is reported in the organic charge-transfer complex trinitrofluorenone:polyvinylcarbazole (TNF:PVK). The exponent n is found to increase with decreasing temperature from 0.25 at 300 K to 0.8 at 100 K and saturates at lower temperatures. This result is viewed as a strong indication for a hopping conduction mechanism for photocarriers. The temperature dependence of the exponent n suggests an increasing degree of localization of electron hopping with decreasing temperature.

It is now generally believed that conduction in extended states is associated with a frequency-independent conductivity up to infrared frequencies, while conduction due to hopping among lo-

calized states yields a frequency-dependent ac conductivity.^{1,2} Characteristic frequency and temperature dependences of dark ac conductivity have been found primarily in amorphous, glassy,