levels as well as to the ground state. The attractiveness in extending this technique to rare-earth crystalline systems is evident. In crystals, the lowest level of a multiplet generally relaxes by radiative decay or by multiphonon emission to the next lowest multiplet, and can have a homogeneous linewidth of less than 1 MHz. The limitation to the spectroscopic resolution is then the inhomogeneous width, which is generally of the order of 0.1 cm^{-1}. Since at low-enough concentrations the spectral diffusion is sufficiently arrested, a tunable coherent source, such as a dye laser or parametric oscillator, can be used to match the sharp rare-earth levels and thereby observe the FLN phenomenon. The possibility of using nonresonant excitation significantly extends the number of levels which can be studied by the FLN technique, with the additional experimental convenience that the emission is well separated in wavelength from the excitation. Application of Szabo's FLN technique to nonresonantly excited rare-earth systems should permit optical studies of a wide range of excited levels with resolutions of greater than 10^7.

It is a pleasure to thank F. D. Sinclair for his excellent technical assistance. A stimulating discussion with Dr. R. Orbach and Dr. G. F. Imbusch is gratefully acknowledged. I wish to thank Dr. M. J. Weber for his valuable comments and Dr. D. D. Buss and Dr. W. C. Holton for helpful discussions and for critically reading the manuscript.

[1]A. Szabo, Phys. Rev. Lett. 25, 924 (1970).
[2]A. Szabo, Phys. Rev. Lett. 27, 323 (1971).
[3]M. J. Weber, Phys. Rev. 157, 262 (1967), and 171, 283 (1968).
[4]L. A. Riseberg and H. W. Moos, Phys. Rev. 174, 429 (1968).
[5]L. A. Riseberg, to be published.
[6]M. M. Mann and L. G. de Shazer, J. Appl. Phys. 41, 2951 (1970).
[7]E. Cohen, L. A. Riseberg, and H. W. Moos, Phys. Rev. 175, 521 (1968).
[8]G. F. Imbusch, Phys. Rev. 153, 326 (1968).
[9]S. K. Lyo, Phys. Rev. B 3, 3331 (1971).
[10]R. J. Birgeneau, Appl. Phys. Lett. 13, 193 (1968).
[11]M. J. Weber, Phys. Rev. B 4, 2932 (1971).

Very Low-Temperature Specific Heat of Submonolayer Helium Films*

D. C. Hickernell, E. O. McLean, and O. E. Vilches
Department of Physics, University of Washington, Seattle, Washington 98105
(Received 14 February 1972)

The specific heats of He^3 and He^4 films adsorbed on exfoliated graphite have been measured between 0.04 and 4.2 K, for fractional monolayer coverages between 0.25 and 0.63. He^3 films show anomalies around 0.1 K that are absent in the He^4 results. A possible explanation is given in terms of spin ordering of the He^3 atoms.

Recent experiments have[1,2] shown that submonolayer coverage He^3 and He^4 films adsorbed on exfoliated graphite (Grafoil[3]) have substantial lateral mobility, to the extent that they behave like ideal two-dimensional (2D) gases at temperatures around 4 K. In the range between $\frac{1}{4}$ and $\frac{2}{3}$ of a monolayer, published results can be summarized in the following way.

For fractional monolayer coverages x of about $\frac{1}{4}$ of a monolayer, He^4 heat-capacity measurements show a peak around 1.2 K while He^3 measurements show no peak; both tend to $C/Nk = 1$ at 4 K. The He^4 results have been interpreted[4] as quasi-2D Bose condensation produced by a weak inhomogeneity in the substrate adsorbing potential. The He^3 experimental curves were fitted by curves for a 2D ideal Fermi gas with high degeneracy temperatures (for example, $T_F{}^{2D} \simeq 3.4$ K for $x = 0.26$) provided that a small adjustment was made in the number of particles responsible for the signal.

At higher x large heat-capacity peaks appear for both isotopes at coverages that closely correspond to the helium atoms being in registry with the graphite lattice of the substrate, the most notable being the λ-type peak occuring for He^4 at $x = 0.6$, which is equivalent to $\frac{1}{3}$ of the hexagons of the graphite lattice being occupied by helium atoms.

Substantial mobility of helium atoms adsorbed on graphite is expected theoretically.[5] The ordering transition in registry with the substrate is receiving careful treatment[6] since it resembles a 2D lattice-gas order-disorder transition.

We have extended the He^3 measurements to lower temperatures. Reference 1 showed mainly the classical gas regime and the transition towards a 2D quantum degenerate Fermi gas, suggesting a 2D analog of the 3D regime existing in dilute solutions of He^3 in He^4. Our measurements were done up to 4.2 K to compare our results with those of Refs. 1 and 2, and to provide enough data to calculate entropies up to the classical regime. A few He^4 coverages were also measured, to provide a comparison with the He^3 results. The high-temperature data for both isotopes will be mentioned only where relevant to the present Letter.

The heat-capacity measurements were done with an adsorption cell of similar construction to the one used in Refs. 1 and 2, for coverages ranging from 0.25 to 0.63 of a monolayer,[7] and between approximately 0.04 and 4.2 K. Measurements were done by electrically supplying a known amount of heat to the cell, and measuring the change in temperature. Below 1 K, 5.6 mg of cerium magnesium nitrate (CMN) was used as thermometer. A superconducting flux detector[8] measured the change of magnetic susceptibility of the CMN. Above 1 K a 56-Ω Allen-Bradley carbon resistor was used. Heat-capacity points were taken between 0.8 and 1 K using both thermometers and one coverage was taken up to 4.2 K using the CMN thermometer, with some loss of sensitivity, without appreciable difference between the data obtained with either thermometer. To cool the samples, a He^3-He^4 dilution refrigerator[9] was used. The cell was suspended from the mixing chamber by a nylon support, and a zinc heat switch[10] was used to provide thermal contact when needed. A small niobium solenoid actuated the switch. A filling line running from the cell to room temperature was used for charging the cell; in this way coverages could be increased without having to recycle the entire cryostat to room temperature.

Figure 1 shows the full range of measurement for $x = 0.252$ for both isotopes. The He^4 film shows both the lateral field anomaly[1,4] and the expected linear behavior below the peak.[4] No quantitative fitting between theory and experiment is possible, although the best fit to the data above the peak would give an inhomogeneous potential $V/k \simeq 0.8$ K, weaker than that necessary to fit the data of Ref. 1.

The curve for a 2D ideal Fermi gas has been fitted to the He^3 data. The He^3 data agree well with those of Ref. 1 where temperature overlap exists. For low temperatures they show a departure from the behavior of an ideal 2D Fermi gas beginning slightly below 1 K. At about 0.1 K a broad shoulder appears for $x = 0.25$, as seen in Fig. 1. An almost linear behavior is approached below the shoulder, but the data do not extend to low enough temperatures to verify it. Many more coverages were investigated to study the very low-temperature behavior. Results for $0.035 < T < 0.5$ K are shown in Fig. 2. As the coverage increases, the shoulder transforms into a rounded peak of reduced height that moves to lower temperature. By $x \simeq 0.6$ the peak has either vanished or gone below our range of T. The specific heat of similar coverage He^4 films shows no anomaly

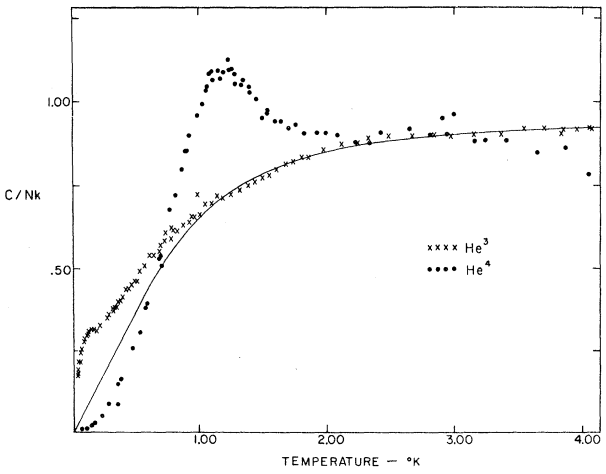

FIG. 1. $x = 0.252$ specific-heat data for both isotopes. The curve for a 2D ideal Fermi gas with $T_F^{2D} = 4.2$ K, adjusted in the number of particles, has been fitted to the He^3 data.

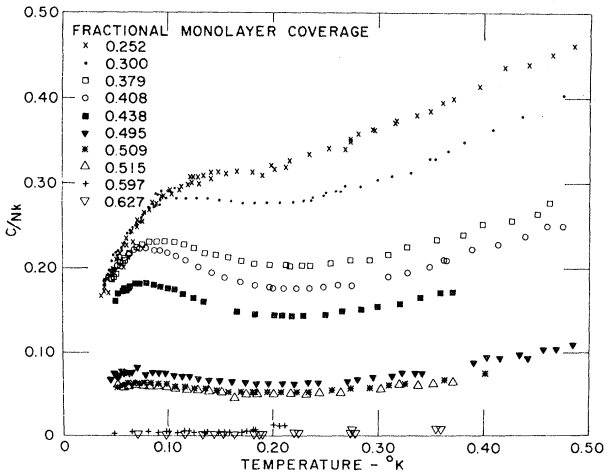

FIG. 2. The low-temperature data for ten coverages of He^3.

of any kind in this range and is extremely small: For $x = 0.25$ and $T = 0.1$ K, $(C/Nk)_{He^4} < 7\%(C/Nk)_{He^3}$.

The He^3 film behavior is similar to that of 3D He^3.[11] In liquid He^3 at saturated vapor pressure a rounded shoulder is observed near 0.1 K. The shoulder is attributed to ordering of the He^3 spins. As the density of the liquid is increased by compressing it, the shoulder moves to lower temperatures, until for solid He^3 the spin ordering occurs in the millikelvin region.

All measured specific-heat curves have been smoothly extended to $T = 0$ and the entropy for each coverage film calculated at $T = 4$ K. The graphs of entropy per particle versus temperature for two coverages are shown in Fig. 3(a), while the 4 K entropy is shown as a function of coverage in Fig. 3(b). For comparison, the entropy of an ideal 2D gas of He^4 particles, given by

$$S/Nk = 2 + \ln(2\pi mkTAg_s/h^2N) \quad (1)$$

is also shown in Fig. 3(b). In Eq. (1), $g_s = 2s + 1$ with s the spin of the particles, m their mass, and A the area of the surface where they are adsorbed. Quantitative agreement between the ideal gas behavior and He^4 films does not exist and is not expected, since the mass used in the calculation is the atomic bare mass, and the area used is the value measured with an argon isotherm. A "soft-disk model" for the helium atoms will give a better fit. But the qualitative behavior is well represented.

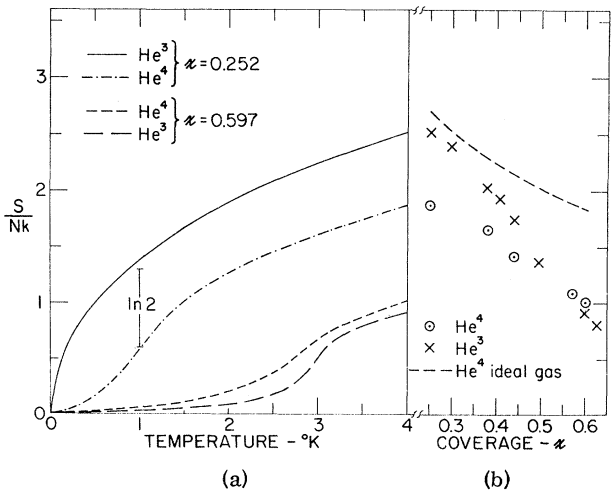

FIG. 3. (a) Entropy per particle versus temperature calculated from measured specific-heat curves for two coverages. (b) Entropy per particle at 4 K versus coverage calculated from specific-heat curves. For reference, a 2D–ideal-gas curve for He^4 particles has been included.

According to Eq. (1), He^3 should have a similar behavior, having higher entropies than He^4 at 4 K by the term $\ln\frac{3}{4} + \ln 2$. Figure 3(b) shows that for low coverages, where a specific-heat anomaly is found at low T, the He^3 entropies are higher than those of He^4 by essentially ln2. But as the coverage increases, the entropy of He^3 films falls below that of He^4 films at coverages for which an order-disorder transition has occurred for both isotopes at 3 K and no heat-capacity anomaly is present in He^3 at low T. This would be the expected behavior if the anomaly is due to spin ordering and it has now moved below our measuring range. According to Eq. (1), the He^3 entropies, neglecting the He^3 spin contribution, would lie below similar coverage He^4 entropies since $m_3 < m_4$.

Another feature of the very low-temperature measurement is that, at least for the lowest coverage He^3 films, specific-heat curves asymptotically approach linear behavior. This could be the beginning of a new 2D Fermi regime, similar to the 3D Fermi liquid. Report of this behavior has been recently given[12] for 2D He^3 films adsorbed on a solution of He^3 in He^4. From our $x = 0.25$ specific-heat curve the lowest points give an asymptotic value for the entropy per unit area per unit temperature of 0.16 ± 0.02 erg/K cm^2. The value reported in Ref. 12 is 0.15 ± 0.03 erg/K cm^2.

We wish to express our gratitude to Dr. M. Bretz and Professor M. Schick and Professor J. G. Dash for continuous encouragement and many helpful discussions during the performance of this experiment.

*Research supported by the National Science Foundation.

[1]M. Bretz and J. G. Dash, Phys. Rev. Lett. 26, 963 (1971).

[2]M. Bretz and J. G. Dash, Phys. Rev. Lett. 27, 647 (1971).

[3]Grafoil is a product manufactured by Union Carbide Carbon Products Division, 270 Park Avenue, New York.

[4]C. E. Campbell, J. G. Dash, and M. Schick, Phys. Rev. Lett. 26, 966 (1971).

[5]D. E. Hagen, A. D. Novaco, and F. J. Milford, in *Proceedings of the International Symposium on Adsorption-Desorption Phenomena, Florence, Italy, 1971* (Academic, New York, 1971).

[6]C. E. Campbell and M. Schick, to be published.

[7]The adsorbing area was determined to be approximately 284 m^2 by a nitrogen-temperature argon iso-

therm. One monolayer of He^3 is 109.3 STP cm^3 of gas. The fractional monolayer coverages for *both* isotopes throughout this Letter are fractions of this number; monolayer completion coverages are certainly not known to better than 5%.

[8]Most parts for the flux detector where obtained commercially from the SHE Manufacturing Corp., 3422 Tripp Court, La Jolla, Calif.

[9]J. C. Wheatley, O. E. Vilches, and W. R. Abel, Physics (Long Is. City, N. Y.) 4, 1 (1968).

[10]J. M. Cotignola, F. de la Cruz, M. E. de la Cruz, and R. P. Platzeck, Rev. Sci. Instrum. 38, 87 (1967).

[11]For a review of the thermodynamic properties of liquid He^3 see, for example, W. E. Keller, *Helium-3 and Helium-4* (Plenum, New York, 1969), p. 183 and following.

[12]H. M. Guo, D. O. Edwards, R. E. Sarwinski, and J. T. Tough, Phys. Rev. Lett. 27, 1259 (1971).

Dynamics of Atomic and Molecular Metastable States Produced in Electron-Bombarded Superfluid Helium*

J. W. Keto, M. Stockton, and W. A. Fitzsimmons
University of Wisconsin, Madison, Wisconsin 53706
(Received 17 January 1972)

We have studied the production, destruction, and lifetimes of the $He_2(a^3\Sigma_u^+)$ and $He(2^3S)$ metastable states of helium that are produced in electron-bombarded superfluid helium. The characteristic lifetime of a metastable molecule in the superfluid is shown to exceed 0.1 sec, while the lifetime of a metastable atom is only about 15 μsec. The production rates for the $He_2(a^3\Sigma_u^+)$ and $He(2^3S)$ metastable states are about 500 and 450 per incident 160-keV electron, respectively.

The existence of electronic metastable states of superfluid helium was established by Surko and Reif, but they were unable to identify the states involved.[1] The recent electron bombardment of superfluid helium has made it possible to observe the optical emission and absorption spectra of the excited liquid, and these experiments have shown that large concentrations of $He_2(a^3\Sigma_u^+)$ and $He(2^3S)$ metastable states of helium may be produced in the superfluid.[2-5] However, these experiments and the theory of Hickman and Lane have emphasized the steady-state nature of the excited liquid.[6]

We report the results of an experimental investigation of the production, destruction, and lifetimes of $He_2(a^3\Sigma_u^+)$ and $He(2^3S)$ metastable states produced in electron-bombarded superfluid helium. In these experiments the liquid is repetitively excited with a pulse of 160-keV electrons. The peak current could be varied between 0.1 and 4.0 μA, and the pulse duration was typically 3 msec with rise and fall times less than 10 nsec. The populations of the metastable states were monitored during and after the electron excitation by observing the absorption of a monochromated light beam focused through the excited liquid. The absorption signals were recorded using conventional signal averaging techniques. A description of the experimental apparatus has been published elsewhere, and the reader is referred to the work of Hill, Heybey, and Walters for a summary of the optical absorption spectrum of electron-bombarded superfluid helium.[3,5]

The decreasing population of the $a^3\Sigma_u^+$ state following a pulse of electrons was observed by monitoring the 2.1-μm ($b^3\Pi_g \leftarrow a^3\Sigma_u^+$) molecular absorption band.[3] As shown in Fig. 1 and insert A, the reciprocal of the concentration of $a^3\Sigma_u^+$ molecules, $1/M$, increases linearly with time for as long as 0.1 sec after the pulse of electrons, and the loss rate increases as the temperature is reduced from 2.09 to 1.62°K. In addition, the steady-state concentration of metastable molecules, M_0, increases with the square root of the peak beam current, as shown in insert B. This current dependence was noted previously by Hill, Heybey, and Walters when they suggested the bilinear collision process $a^3\Sigma_u^+ + a^3\Sigma_u^+$ as the loss mechanism for the metastable molecule.[3] This reaction implies that the concentration of metastable molecules, M, is described by the equation

$$dM/dt = -\alpha(T)M^2 \text{ or } 1/M = M_0 + \alpha(T)t, \qquad (1)$$

where $\alpha(T)$ is the bilinear reaction coefficient and t is the time after the end of the beam pulse. During the time the electron beam is on, Eq. (1) can be written as $dM/dt = KI - \alpha(T)M^2$, where the steady-state concentration of the $a^3\Sigma_u^+$ state is given by $M_0 = [KI/\alpha(T)]^{1/2}$, with K equal to the number of metastable molecules produced per