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Publication Date

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January 1989

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Heat capacity measurements of submonolayer ^4He films adsorbed on sapphire.

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Abstract

We have built a novel microcalorimeter for studies of the heat capacity of submonolayer films of ^4He adsorbed on a variety of substrates. In this report, measurements are presented of such films on optically polished, chemically cleaned sapphire. The measured heat capacity has a temperature dependent component which is the same for all coverages investigated, and a temperature independent component which increases with coverage. One interpretation is that the temperature dependent component is due to the solidification of ^4He near impurities on the surface, and that the temperature independent component is due to a dilute gas phase which occupies the rest of the surface.

PACS No : 67.70

The thermodynamics of two-dimensional helium films has been extensively investigated.^{1,2} Heat capacity measurements of two-dimensional systems are complicated by the necessary subtraction of the heat capacity of the substrate. In order to detect the fraction of the heat capacity associated with the adsorbed film, such measurements are usually carried out on insulating, porous substrates with large surface area per unit volume. The measured phase diagrams of these adsorption systems often show a variety of solid phases which are commensurate with the crystalline substrate. Such commensurate phases appear as a result of the lateral corrugation of the adsorbate-substrate potential, rather than because of adsorbate-adsorbate interactions.

The physisorption potential presented by a metallic substrate is expected to be considerably less corrugated than that from an insulator, because the electronic states near the surface of a metal are not laterally localized.^{3,4} Therefore, the thermodynamics illustrated by two-dimensional films adsorbed on metallic substrates should be more typical of fundamental two-dimensional behavior than on insulating substrates. Unfortunately, well-characterized metallic substrates with large surface area have not been available.

In an attempt to solve this problem, we have designed and constructed a novel AC microcalorimeter.⁵ The calorimeter is assembled on an optically polished sapphire substrate, with neutron transmutation doped Ge thermometers,^{6,7} and resistive heaters attached to one surface.

The other surface can be coated with any material suitable for UHV evaporation, or left as bare sapphire, as is the case in this study. The details of the design, construction and operation of this calorimeter are described elsewhere.⁴

Before exploring the heat capacity of ^4He on metallic films deposited on the front surface of the calorimeter, we undertook a study of the heat capacity of submonolayers of ^4He adsorbed on bare, optically polished sapphire. This study is of practical importance to the operation of composite infrared bolometers that are similar in construction to this calorimeter. The added heat capacity of one adsorbed monolayer on such a bolometer has never been measured directly, although reductions in bolometer sensitivity have been observed upon exposure to small amounts of ^4He .⁸

The sapphire substrates are ultrasonically cleaned in electronic grade 1,1,1-trichloroethylene, acetone and methanol prior to assembly of the calorimeter. After this treatment, the substrates are handled only on the edges with stainless steel tweezers that have been cleaned in the same manner. Bismuth films are deposited on the back surface as resistive heaters, and the substrates are then installed in an aluminum frame. Doped germanium thermometers and copper wires are attached to the back of the substrate with conductive epoxy.⁹ The entire assembly is baked in air at 100 C for several hours to complete curing of the epoxy. The calorimeters are submerged in ^4He for calibration of the thermometers and then installed in the UHV system. After several days of pumping without bakeout, the base pressure of this system is as low as 10^{-9} torr. Upon

cooling of the radiation shields to 100 K and the cold finger to 1.5 K, the pressure near the calorimeter is less than 10^{-11} torr. Before measurements the calorimeter is briefly warmed to slightly above room temperature to remove adsorbed contamination. This temperature was limited by the epoxy used to fabricate the calorimeter. No further surface preparation has been carried out for these studies. It is probable that water is present on the surface. Adsorbed hydrocarbons are also possible.

At the beginning of each experiment, the heat capacity of the bare calorimeter is measured at a series of temperatures between 1.7 and 4.2 K. Then the front surface of the calorimeter is exposed to a beam of ^4He atoms from a room temperature effusion cell. The pressure in the effusion cell is monitored with an ionization gauge. Since the geometry of the cell and the distance to the calorimeter are known, the number of incident atoms per unit time is known. Exposures of 5 atoms per square angstrom of sapphire were typical. However, an undetermined fraction of the incident ^4He atoms adsorb on the sapphire under these circumstances, so the absolute coverage is unknown. After the exposure is complete, the heat capacity of the calorimeter plus adsorbates is measured at the same temperatures as before the dose. The heat capacity of the ^4He is obtained by subtraction.

The heat capacity of several coverages of ^4He on sapphire was measured. The data for three of these coverages are shown in Fig. 1. Since the absolute coverage is unknown, the units on the vertical axis are simply J/K for the adsorbed ^4He which is spread over the 0.32 cm^2 surface area on the front of the calorimeter. The measured heat capacity can be

interpreted as a superposition of two components. One component has heat capacity independent of coverage. The heat capacity of this component increases with temperature from 1.8 to 3.3 K and then falls at higher temperatures. The second component is independent of temperature but increases with coverage. Above 3.3 K, the heat capacity of the adsorbed ^4He decreases with increasing temperature. Measurements of the heat capacity at 2 K separated by brief ramps to higher temperatures demonstrated that desorption occurs above 3.3 K. The ^4He is entirely desorbed from the sapphire at 4.2 K.

A qualitative understanding of these results is possible despite the lack of a well characterized substrate. The ^4He states with the lowest free energy are laterally bound near defects and contamination on the sapphire surface. Higher energy states with lateral mobility exist over the rest of the surface. A low coverage of ^4He would occupy the lowest energy bound states first. Higher coverages of ^4He would occupy some mobile states as well as the bound states. The heat capacity of a low coverage of ^4He would increase with temperature due to excitation of atoms within bound states and promotion from bound states to mobile states. The heat capacity of a high coverage of ^4He would have the same contribution from the bound states as the low coverage, plus an additional temperature-independent component due to the mobile states. The sudden decreases in heat capacity above 3.3 K occur due to desorption of the ^4He .

A more detailed explanation of these results would require knowledge of the distribution of binding energies presented by a partially contaminated sapphire surface. Rather than continue studies of ^4He on

sapphire, we plan to proceed to studies of ^4He on evaporated noble metal films. Studies of evaporated Ag films on sapphire have shown the surface to be exceptionally smooth¹⁰ and predominantly composed of Ag (111).¹¹ Preliminary measurements of ^4He adsorbed on evaporated Ag films in this apparatus have seen evidence for gas phase behavior over a wide range of coverages.¹²

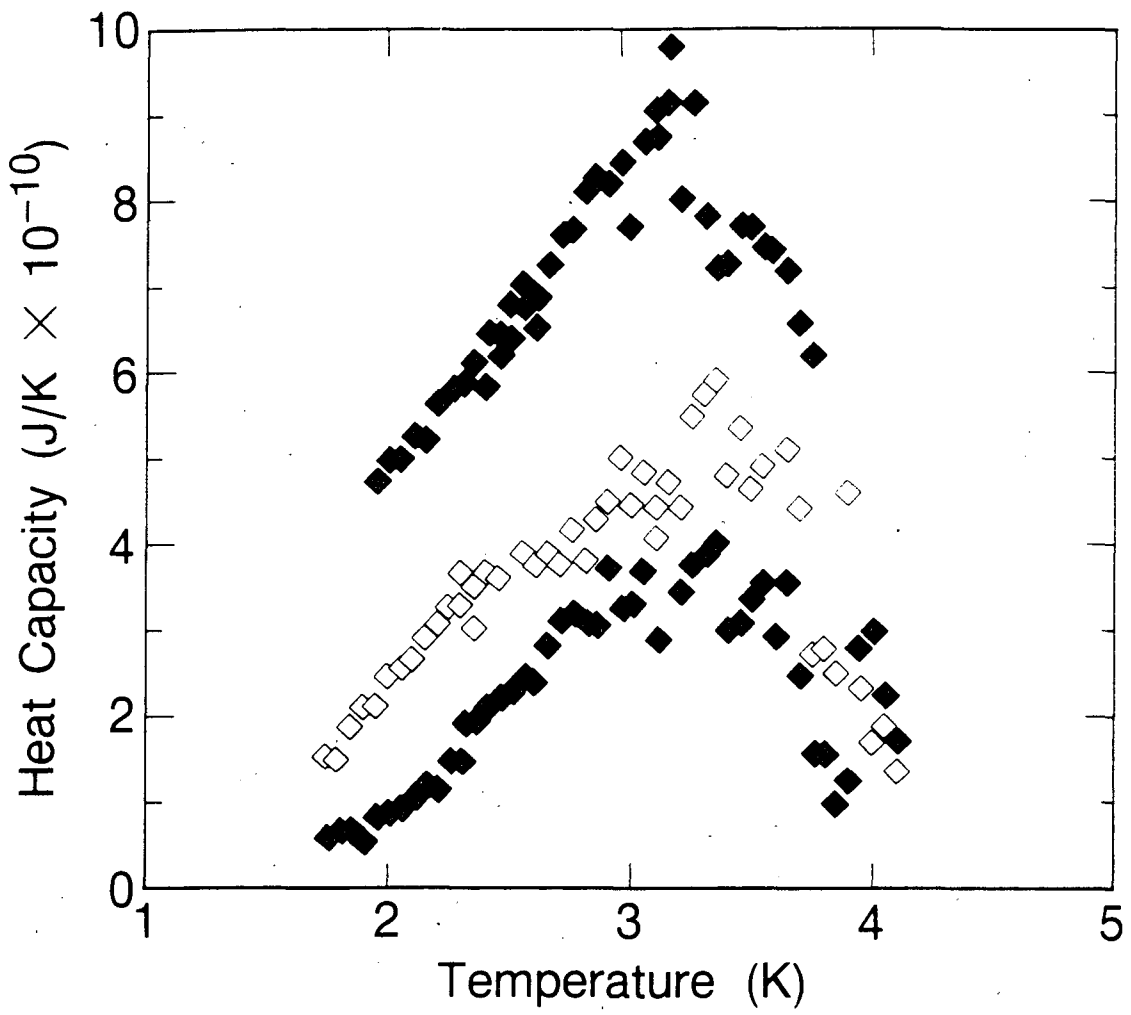
The thermometers for this experiment were provided by E.E. Haller, I.S. Park and J.W. Beeman. We have benefited from useful conversations with M.H.W. Chan, Y.P. Wang, J. Krim, A.E. Lange, R.G. Tobin, D. Miller and R.B. Phelps. T.W. Kenny gratefully acknowledges the support of an AT&T Bell Laboratories Fellowship.

This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Figure Captions

Figure 1) The heat capacity of three coverages of ^4He on sapphire. The heat capacity of the bare calorimeter has already been subtracted. The temperature dependence above 3.3 K is dominated by desorption of the adsorbed ^4He .

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XBL 8810-7666

FIGURE 1

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