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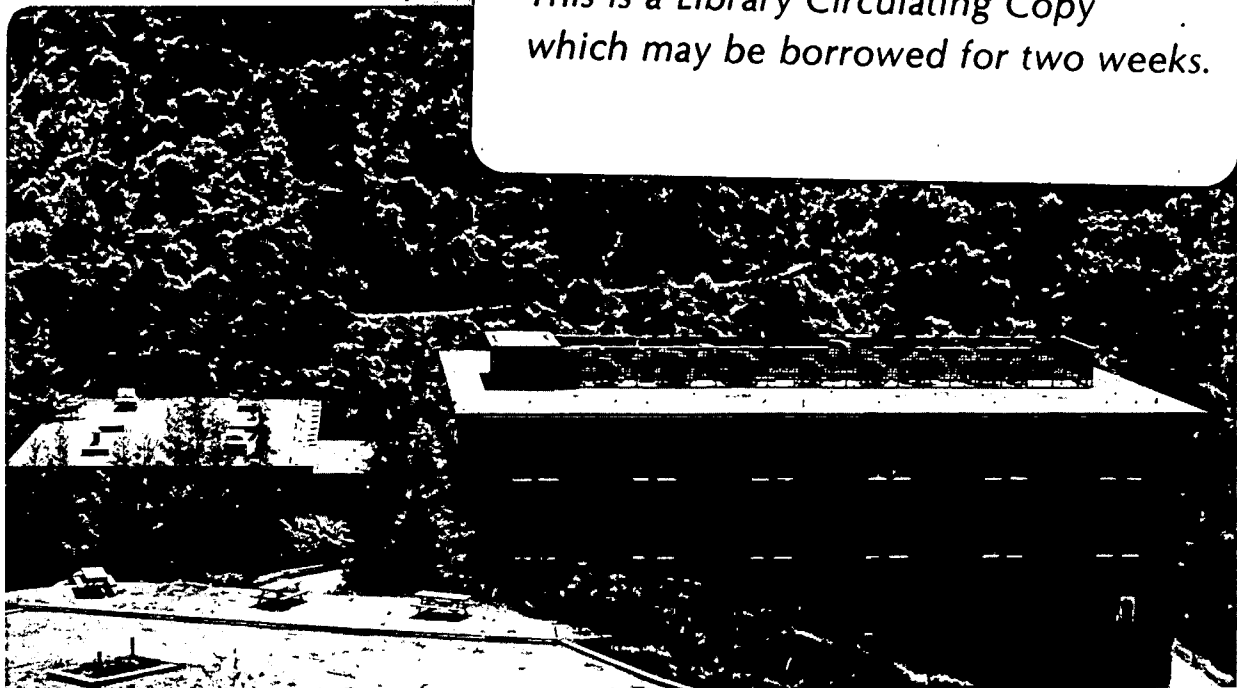
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Heat capacity and sticking probability measurements of ^4He
adsorbed on evaporated Ag films - Bose statistics in two dimensions.

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(Received

Abstract

We have measured the heat capacity of submonolayers of ^4He adsorbed on Ag films between 1.7 and 3.3 K. Good fits to the results are obtained with a model of a non-interacting two dimensional bose gas. This is the first observation of bose statistics in the thermodynamics of adsorbed monolayers. The sticking probability for room temperature ^4He atoms on cold Ag has been measured as a function of substrate temperature and ^4He coverage. The sticking probability is 3.8% at low coverage, and abruptly drops to 1.1% for coverages above 0.5 monolayers.

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There has been much interest in monolayers of physisorbed noble gases as systems suitable for testing theoretical models of thermodynamics in two dimensions.¹ Experimental measurements of the heat capacity are important for the identification of the phases and the transitions between them. These measurements are made difficult by the need to subtract the heat capacity of the physisorption substrate. This problem is usually solved by the use of insulating substrates with high specific surface area such as exfoliated graphite.

The heat capacity of > 0.8 monolayers of ^4He on graphite exhibits a rounded peak at temperatures above 2 K which arises from the melting of the incommensurable solid phase.²⁻⁶ The peak is apparently broadened by extrinsic effects, and the mechanism for the melting transition remains unidentified. The heat capacity of < 0.4 monolayers of ^4He on graphite exhibits broad anomalies at temperatures below 2 K. Above 2 K, the heat capacity approaches that of an ideal two dimensional gas. These data have been given two different interpretations. The first is that the deviation of the heat capacity from that of an ideal two dimensional gas arises from higher order terms in the virial expansion of the ideal gas law.⁷ The second interpretation ignores the He-He interactions and treats the problem of a single ^4He atom moving within a laterally varying physisorption potential.⁸ The periodic variations in the binding energy give rise to gaps in the density of states and anomalies in the heat capacity which resemble the experimental results. The success of a model which ignores the He-He interactions serves to illustrate the degree to which the He/graphite phase diagram has been influenced by the structure of the graphite surface.

Metallic substrates provide an attractive alternative to graphite for studies of adsorbed layers because the non-local nature of the electronic wave functions provides a more uniform physisorption potential.^{1,9} The large low-temperature heat capacity of most metals, however, means that the problem of sensitivity will arise even when the ratio of surface area to volume is large. Metallic powders that satisfy this criterion have a complicated assortment of surfaces and would not yield interpretable results. Evaporated films, such as Ag, that have shown a high degree of orientation are perhaps the best candidates for such measurements. Scanning tunneling microscopy (STM) has shown that Ag films deposited on room-temperature sapphire substrates are composed of (111) crystallites of about 500 Å in lateral dimension, separated by compact boundary regions.¹⁰ Scanning electron microscopy (SEM) of the films used in these studies shows 500 Å crystallites.

We have constructed a novel ac microcalorimeter with sufficient sensitivity to measure the heat capacity of ⁴He on metallic substrates. In addition, it can be used for measurements of the heat capacity of adsorbates on any surface suitable for vacuum deposition. The design of the calorimeter shown in Fig. 1 is derived from that of the composite bolometer, which is the most sensitive broadband detector of far-infrared radiation.¹¹ It is composed of a single-crystal Ge:Ga thermometer, NiCr heater films, and 25 μm Cu wires, all of which are attached with conductive epoxy to the back of a sapphire substrate. The calorimeters are mounted on the end of a liquid ⁴He-cooled cold finger in a conventional UHV system and can be operated from 1.7 - 4 K. Openings through radiation shields at 90 K can be temporarily aligned to allow deposition of

a clean Ag surface or to allow dosing of the calorimeter with a beam of ^4He atoms from an effusion cell. Because the sticking coefficient of room-temperature ^4He atoms on Ag at low temperatures is not known in advance, the final coverages are not known, except when they can be determined from the heat capacity measurements.

The very short internal time constants of this calorimeter allow us to make ac heat capacity measurements¹² at 500 Hz. An oscillation in the temperature of the calorimeter with an amplitude of ~ 1 mK is produced by application of an ac bias to one of the heaters. This oscillation in temperature is detected as an oscillation in the voltage across the dc-biased resistance thermometer. The heat capacity is then calculated from the ratio of the power oscillation to the temperature oscillation. The temperature of the calorimeter is regulated by comparison of the dc resistance of the thermometer with a reference value and application of a correction voltage to the second NiCr heater. The heat capacity of the calorimeter is measured before and after the ^4He dose at a series of temperatures between 1.7 and 4 K. Subtraction of the data for the bare calorimeter from the data for the dosed calorimeter yields the heat capacity of the adsorbed layer. Through careful control of drifts in the measured voltages, the heat capacity of less than 0.01 monolayers adsorbed on the surface of the calorimeter can be detected. A complete description of this apparatus and the measurement technique is presented elsewhere.¹³

The measured heat capacity for several coverages of ^4He adsorbed on Ag is shown in Fig. 2 as a function of temperature between 1.7 and 3.3 K. At the lowest coverages investigated, the heat capacity is independent of

the temperature. As the coverage is increased, the heat capacity is seen to decrease with decreasing temperature. The sensitivity of the measurement degrades with increasing temperature due to an increase in the heat capacity of the substrate and a reduction in the sensitivity of the thermometer. More accurate measurements at the higher temperatures have been made by increasing the amplitude of the temperature oscillation. These measurements show that the heat capacity is independent of temperature between 2.3 and 3.3 K for the five lowest coverages shown. Above 3.3 K, desorption of the ^4He occurs.

There are a number of striking differences between these data and those for similar coverages of ^4He on graphite substrates. The absence of Schottky-type anomalies is taken as evidence that the corrugation in the binding energy to the Ag substrate is weaker than for insulating substrates, as expected. There is no evidence of the increase in heat capacity with decreasing temperatures predicted from the virial expansion of the adsorbate-adsorbate interaction,⁷ or from a melting transition from the hexagonal incommensurable phase that is expected at low temperatures.¹⁴

There are reasons to expect that the adsorbate-adsorbate interaction is reduced by the electrons in the substrate. The image dipoles which appear below the metal surface partially cancel the attraction due to correlated dipole fluctuations. Also, the substrate electrons which extend beyond the top layer of Ag nuclei induce static dipole moments in the He atoms. These induced static dipole moments cause a slight repulsion between the adsorbed ^4He atoms.¹⁵ Procedures for estimating substrate-induced modifications to adsorbate-adsorbate interactions have been

published.^{16,17} At the average separations typical of the highest coverages investigated here, however, these corrections are estimated to reduce the adsorbate-adsorbate interactions by less than 5%.

The ⁴He-Ag attraction is measured to be approximately one fourth as strong as the ⁴He-graphite attraction.^{18,19} The only precise theoretical descriptions of thermodynamics in two dimensions which address the normal component of the adsorbate-substrate interaction are those which include the excited states in addition to the ground state.⁸ For ⁴He on graphite, the excited states are expected⁸ to lead to an increase in heat capacity with increasing temperatures above 10 K. The first excited state for ⁴He on Ag is calculated to be 1.9 meV above the ground state,¹⁸ compared with 5.7 meV for graphite, so this contribution should appear at temperatures above 4 K. We see no evidence of this contribution to the heat capacity, and conclude that the excited states are not thermally populated at the temperatures investigated.

Since the signatures of adsorbate-adsorbate or adsorbate-substrate interactions do not appear in the data, we compare the results with the heat capacity of two dimensional non-interacting bose gases.²⁰ The energy of the system can be written

$$U(t) = \int_{-\infty}^{\infty} \frac{E D(E) dE}{e^{[\beta(E - \mu)]} - 1}, \quad (1)$$

where $D(E)$ is the density of states, μ is the chemical potential, and $\beta = (k_B T)^{-1}$. For non-interacting particles confined to a surface of area A by a

potential with bound states E_i normal to the surface, the density of states is given by

$$D(E) = \sum_i^{\text{all bound states}} \frac{2\pi mA}{h^2} \Theta(E - E_i) \quad (2)$$

where $\Theta(E-E_i)$ is zero for $E < E_i$, and 1 for $E \geq E_i$. Since the excited states are not populated at the temperatures of interest, we consider only the ground state, for which the density of states is $D(E) = (2\pi mA/h^2)\Theta(E)$. Requiring the number of bosons in the system, N , to be constant yields an expression for the chemical potential,

$$\mu = k_B T \ln [1 - e^{-Nh^2/2\pi mA k_B T}] . \quad (3)$$

The chemical potential approaches zero at low temperatures. In this limit, the expression (1) for the energy can be evaluated exactly, and then differentiated to give $C(T) = (\pi^3 k_B mA/3h^2)T$, which is independent of the number of bosons in the system. At such low temperatures, nearly all of the bosons are in the ground state of the two dimensional system, where they do not contribute to the heat capacity. At higher temperatures, the restriction on the number of bosons in excited states of the two dimensional system due to the restriction on N becomes important, and the chemical potential takes on a finite value. As the temperatures are increased, the heat capacity eventually approaches the limit given by classical equipartition, $C(T) = N k_B$.

The expression for the energy of the two dimensional bose gas has been numerically integrated, and then differentiated to give the heat capacity as a function of temperature for several coverages. These results are shown as smooth curves in Fig. 2 for values of the coverage which were selected to fit the data. The measured deviations from the equipartition limit which occur at lower temperatures are in excellent agreement with the predictions of this model even at coverages in excess of 0.5 monolayers, as defined in terms of monolayer coverages on graphite. At higher coverages, the measured heat capacity is larger than the theoretical prediction, but the effects of adsorbate-adsorbate interactions, which are ignored in this model, may be important.

In the presence of lateral fields, which can arise due to defects on the surface, the two dimensional bose gas is susceptible to condensation, giving rise to a linear temperature dependence at low temperatures, followed by a peak at the condensation temperature.^{1,21} The lowest coverage data in this experiment may be compared directly with the calculated temperature dependence of the heat capacity for various values of the lateral field, showing that the lateral field is of order 0.1 K or smaller. For all the coverages investigated, such a lateral field is expected to induce bose condensation at temperatures below 1.8 K, giving rise to very small peaks in the heat capacity and only slight perturbations from the ordinary bose gas at the temperatures of this measurement. The occurrence of condensation cannot be excluded on the basis of the results reported here and can only be verified by measurements to below 1 K.

In order to obtain a measurement of the sticking coefficient, the change in heat capacity can be monitored while the sample is dosed at several constant temperatures. A plot of these data as a function of the exposure calculated from the properties of the effusion cell is shown for three substrate temperatures in Fig. 3. At temperatures above 2.5 K and heat capacities below 20×10^{-10} J/K, the temperature independent heat capacity is assumed to be a measure of the number of adsorbed atoms. The coverages estimated in this manner are shown on the right side of Fig. 3. The derivative of the coverage with respect to the exposure is defined as the sticking probability. At the lowest coverages, the sticking probability is 3.8 %, independent of coverage or substrate temperature. At higher coverages, the sticking probability abruptly decreases to about 1.1 %, at coverages less than 0.5 monolayers. The coverage at which the sticking probability changes decreases with increasing substrate temperatures.

During sticking, the kinetic energy of the incident atom is dissipated through the creation of a small number of excitations in the substrate. Since the energy of the incident atom is much larger than $k_B T$ of the substrate, only spontaneous emission of excitations occurs. This process should be independent of substrate temperature, as observed.

Defects or impurities on the Ag surface with greater binding energy than the rest of the surface would be expected to freeze out the first adsorbed atoms. In the measurement of the sticking coefficient, such effects would appear as a non-zero x-intercept corresponding to the adsorption of the first atoms in states with low heat capacity. The measured x-intercept is indistinguishable from zero for coverages of less

than 1% of a monolayer. The occurrence of the ideal gas phase at such low coverages is strong evidence that the physisorption potential of the Ag film is extremely uniform.

The appearance of abrupt changes in the measured sticking probability as a function of coverage usually implies either solidification in the adsorbed layer, or layer completion and promotion into the second layer. Near such structural changes, there are corresponding changes in the entropy of the adsorbate, which should appear as large anomalies in the temperature dependence of the heat capacity. The absence of such features in the measured heat capacity excludes these explanations for the changes in the sticking probability. Any explanations that would depend on inhomogeneities in the binding energy would also give rise to a finite x-intercept in the data of Fig. 3. We have no model for this complicated behavior in the sticking coefficient.

We have measured the heat capacity and sticking coefficient of ^4He on Ag films. The heat capacity measurements can be accurately fitted by calculations assuming a two dimensional non-interacting Bose gas. This is the first observation of Bose statistics in the thermodynamics of adsorbed monolayers. In contrast to similar measurements on graphite substrates, there is no evidence for the formation of solid phases at the coverages and temperatures studied. The measured sticking coefficient is independent of temperature and coverage at low coverages, but abruptly drops at coverages of about 0.5 monolayers. Because there is no evidence for the anomalies expected for solidification or layer formation, the sticking coefficient data cannot be explained by such phenomena.

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Figure Captions

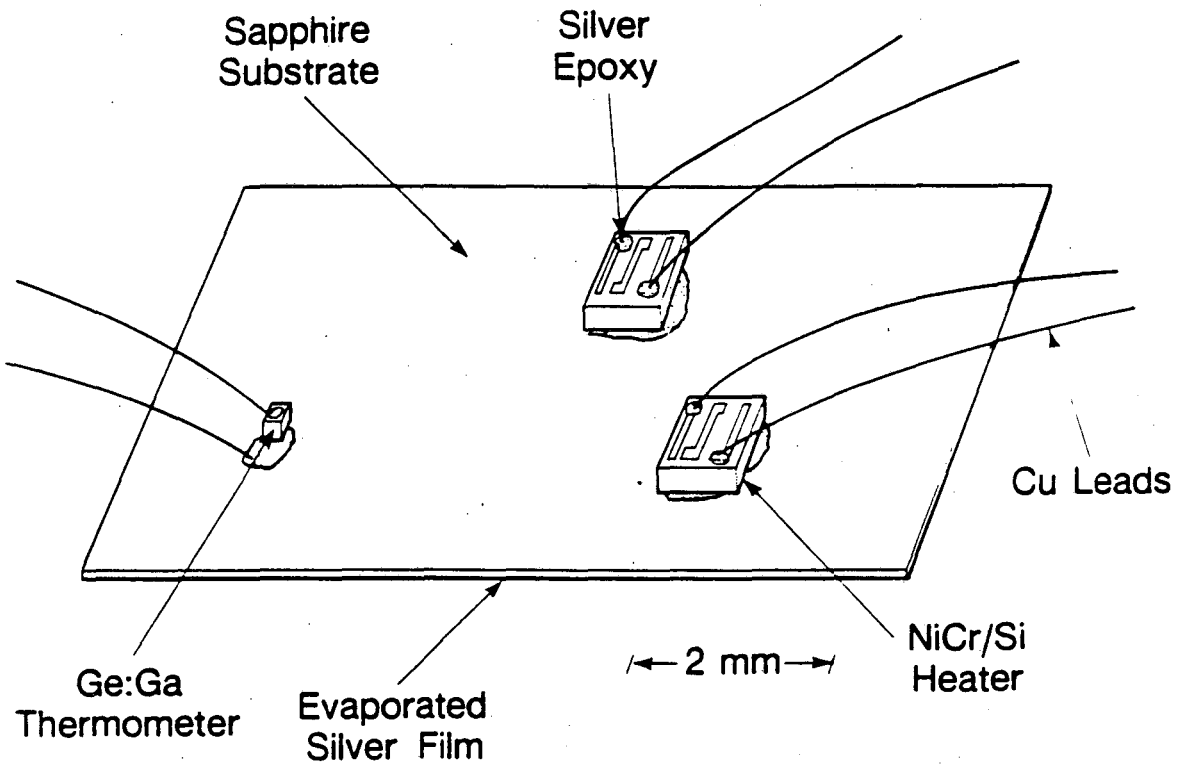
Figure 1 Schematic drawing of the calorimeter used in these studies. The Ge:Ga thermometer, NiCr heaters and Cu wires are attached to the back of the sapphire substrate with conductive epoxy. Ag films are deposited *in situ* on the front of the sapphire.

Figure 2 Measurements of the temperature dependence of the heat capacity for a series of coverages of ^4He on Ag films. The solid lines correspond to the calculated heat capacity of a two-dimensional non-interacting bose gas.

Figure 3 Measurements of the number of adsorbed atoms as a function of the number of incident atoms for ^4He on Ag at various substrate temperatures. The slope of the curves shown here is the sticking probability. The data for the lowest coverages are expanded in the inset.

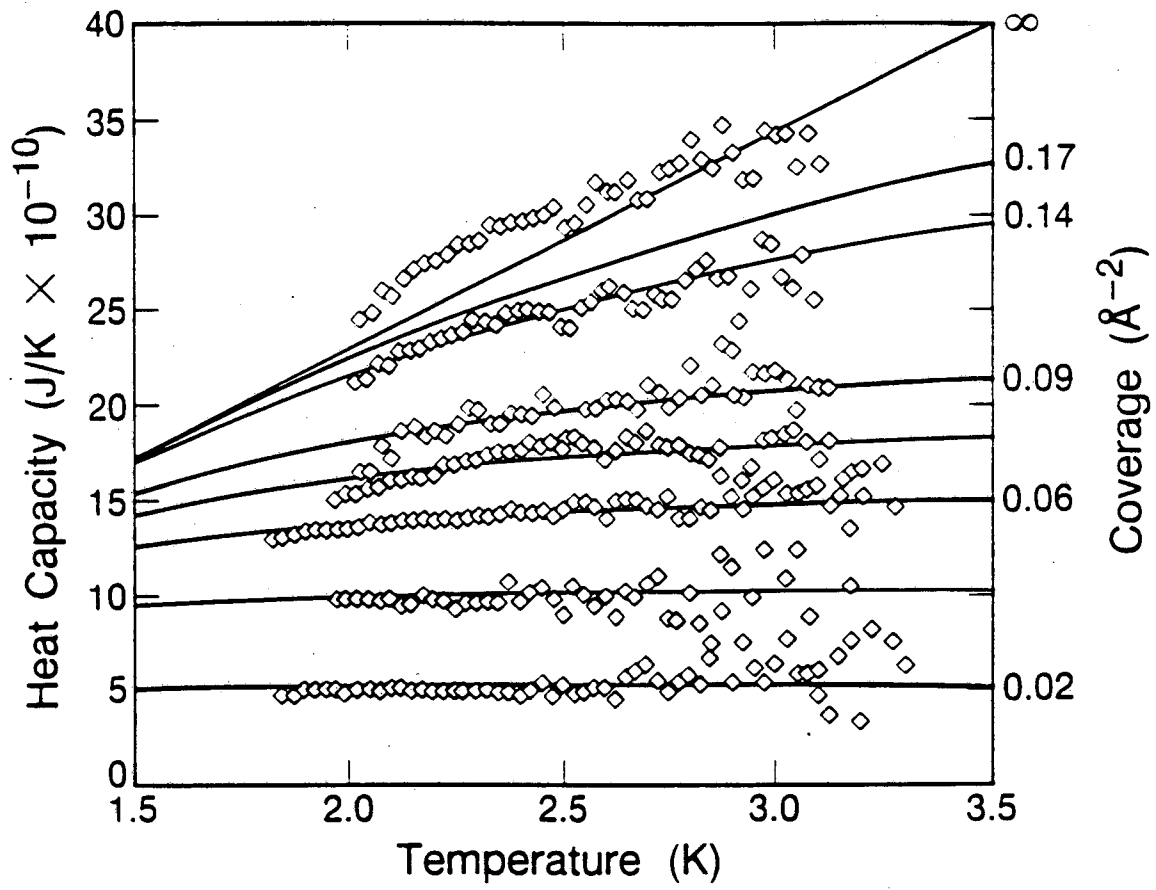
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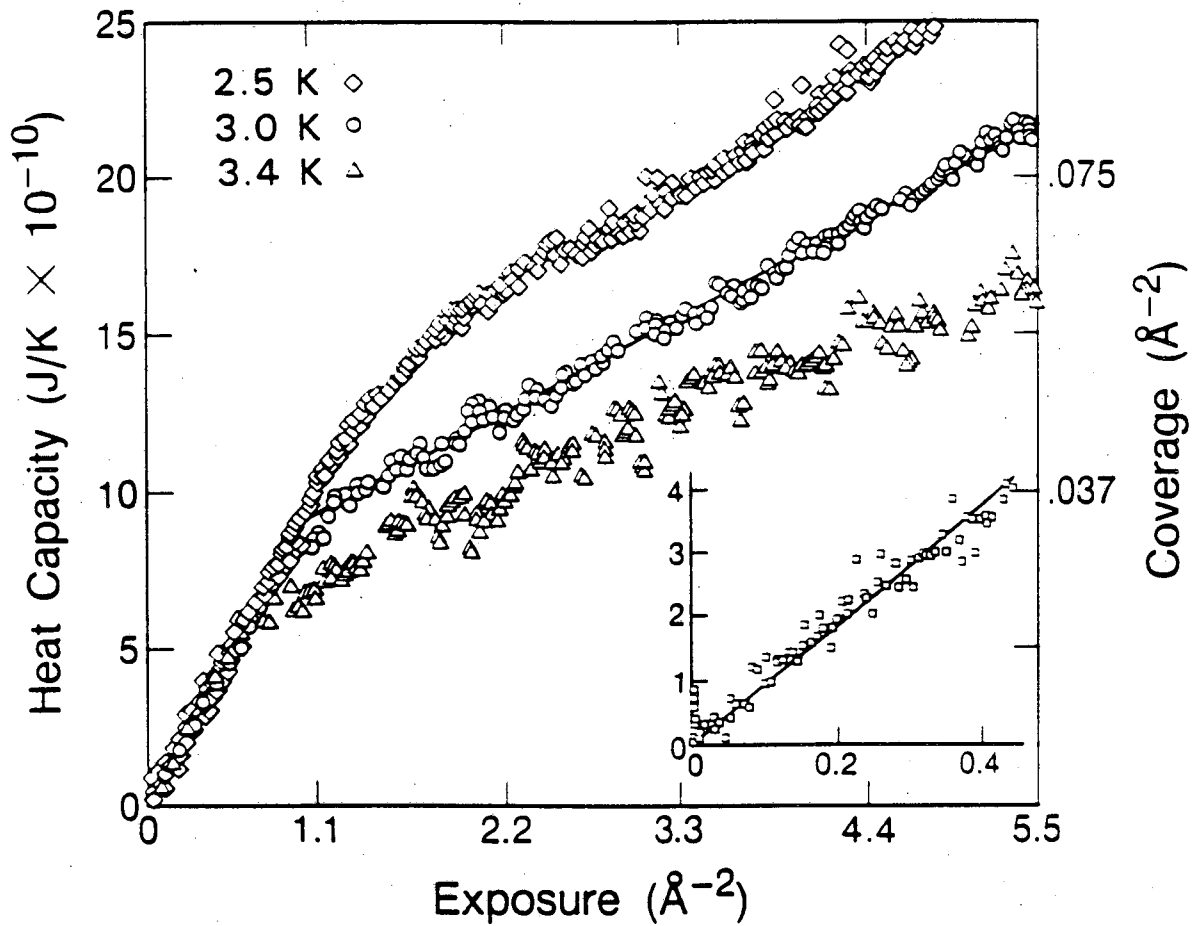
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FIGURE 1



XBL 893-5067

FIGURE 2



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FIGURE 3

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