Possible Ising Transition in a ⁴He Monolayer Adsorbed on Kr-Plated Graphite

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The specific heat of ⁴He adsorbed on Kr-plated graphite indicates the existence of an order-disorder transition from a (1×1) $[\frac{1}{2}]$ triangular structure on a honeycomb lattice of adsorption sites. The specific heat singularity is logarithmic, as predicted from universality considerations, different from the power law observed in the $(\sqrt{3} \times \sqrt{3})R30°$ order-disorder transition of ⁴He on the bare graphite.

A helium monolayer adsorbed on the basal plane of graphite orders at about 3 K into a structure in which $\frac{1}{3}$ of the graphite lattice adsorption sites are occupied with helium atoms forming an equilateral triangular lattice. This transition has been observed (indirectly) in heat capacity[1,2] and NMR[3,4] measurements and (directly) in elastic neutron scattering measurements[5] with Grafoil as the substrate. More recently, Bretz[6] has remeasured the specific heat at the critical coverage using a more uniform, relatively low-specific-area expanded graphite substrate (ZYX).[7] When the background-corrected and "merged" specific heat (C_M) was fitted by an expression of the form[8]

$$C_M = A|t|^{-\alpha} + B, \tag{1}$$

with A, B, and α being constants, and $t = (T - T_c)/T_c$, the experimental exponent found was $\alpha = 0.36 \pm 0.02$. This value of α appears to be within the most recent theoretical estimates for the three-state Potts system[9] as predicted by Alexander.[10] Domany, Schick, and Walker[11] and Domany, Schick, Walker, and Griffiths[12] have classified most of the possible order-disorder transitions for simple adsorbed systems. In particular, they confirm that the He/graphite transition belongs to the three-state Potts universality class, and predict the universality class to which a variety of order-disorder transitions should belong.

We report measurements of the specific heat of ⁴He films adsorbed on Kr-plated graphite. For a Kr plating of one monolayer, the Kr atoms are arranged in a close-packed structure. The adsorption sites now form a honeycomb lattice, Fig. 1(b), as contrasted to the bare graphite triangular lattice, Fig. 1(a). The most compact registered array of He that can be made on these substrates corresponds to either all A or all B or all C sites occupied in Fig. 1(a), or to either all A or all B in Fig. 1(b). Our Figs. 1(a) and 1(b) are equivalent to Figs. 1(c) and 1(b), respectively, of Ref. 11. In the lattice of sites described by Fig. 1(b), Domany, Schick, and Walker[11] predict

that the transition to the commensurate phase $\{(1 \times 1)[\frac{1}{2}]\}$ will belong to the Ising universality class. Our measurements confirm that ⁴He shows an order-disorder transition at about the right density (a He atom at every A site) and that $\alpha \cong 0$.

We used two different cells, one with Grafoil (cell B, Ref. 2) and one with graphite foam instead of Grafoil. Adsorption isotherms[13] show the foam to be more uniform than Grafoil, with domain sizes comparable to those of ZYX, with the added advantage that the specific area is about 30 m²/g. To characterize the bare foam cell we measured the heat capacity of various ⁴He films adsorbed on it and, in particular, surveyed very carefully the order-disorder transition. We found a maximum heat capacity peak height of $(C/N\hbar)_{\text{Max}} \cong 9$, thus suggesting that the crystallite sizes, although larger than Grafoil $[(C/N\hbar)_{\text{Max}} \cong 6]$, are not as large as those in ZYX $[(C/N\hbar)_{\text{Max}} \cong 12]$. Our data allowed us to repeat Bretz's analysis. The specific heat we measured follows a power-law behavior with $\alpha \cong 0.28 \pm 0.01$, $A^+/A^- = 1.016$, and $T_c \cong 2.9290$ K (Fig. 2). For this particular cell, the ⁴He coverage at
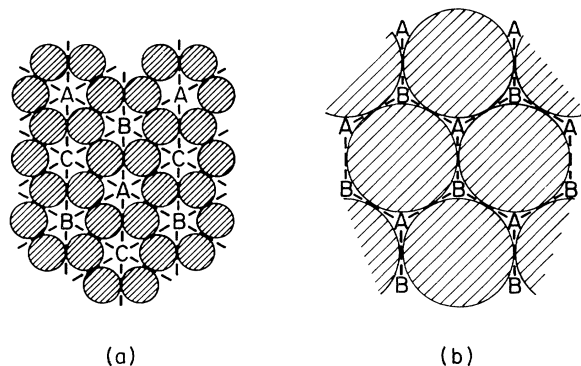

FIG. 1. (a) The graphite basal plane. A, B, and C represent equivalent absorption sites. The $(\sqrt{3} \times \sqrt{3})R30°$ structure corresponds to all of either A or B or C sites occupied. (b) The Kr plating. A and B represent equivalent adsorption sites. The (1×1) $[\frac{1}{2}]$ structure corresponds to all of either A or B sites occupied.
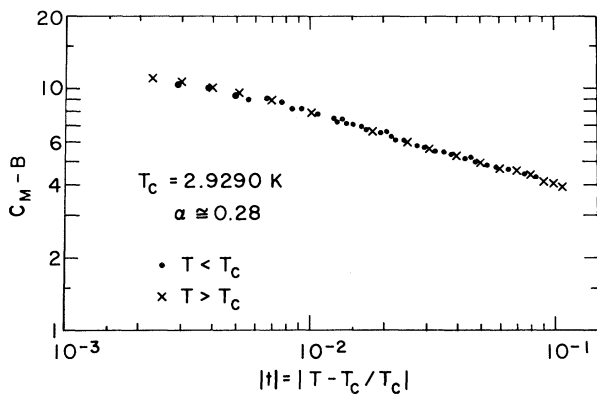

FIG. 2. The merged specific heat for ^{4}He/graphite foam at the order-disorder transition and critical coverage.

which the specific heat at T_{peak} was maximum corresponded to $(Nk)_c = 14.91$ mJ/K, where N is the number of atoms adsorbed and k is Boltzmann's constant.

For the plating study we initially surveyed the entire ^{4}He/Kr/graphite first-layer density range using cell "B". Our first Kr plating gave 27.46 mJ/K, much higher than for the registered coverage. See Table I. It was our intention to form a compact Kr layer so that we could compare the low-density He results to those on Ar-plated graphite.[14] Using Chinn and Fain's Kr lattice parameters[15] for high temperatures $(T > 47$ K), the solid Kr thermal expansion coefficient,[16] and our own Kr/Grafoil isotherms, we estimated that about 13% of the second layer was occupied, thus reducing the area available for ^{4}He adsorption by that amount. The phase diagram $(T_{peaks}$ vs $n)$ for the ^{4}He/Kr/Grafoil system showed a maximum in T_{peak} similar to the one for the ordering transition of ^{4}He/graphite but at a coverage about 3% lower than the one we estimated for the $(1 \times 1)[\frac{1}{2}]$

transition. In this case $T_c \simeq 4.29$ K. We repeated a few runs with a lower density Kr plating (second plating) and found the same features again close to the expected coverage. Details are summarized in Table I.

The quality of the ^{4}He/Kr/Grafoil data at the critical coverage is not good enough for critical exponent analysis. Part of the problem comes from the relatively small size of the uniform regions in Grafoil (~ 100 Å) and from too much Kr present on the second layer. Furthermore, for very compact Kr platings the spacing between sites is relatively small, thus forcing the transition to higher temperatures where desorption corrections complicate the analysis. To correct these shortcomings we switched to the graphite foam cell and used for plating approximately the same number of Kr atoms that gave for ^{4}He on the bare foam the tallest heat capacity peak of Fig. 2. Thus the Kr plating should have been in registry with the graphite surface, and if no surface modifications occur when helium is adsorbed, the helium order-disorder transition should occur when $N_{He} = N_{Kr}$.

We surveyed the phase diagram of He/Kr/graphite foam, and found the order-disorder transition at about the right coverage (N_{He} is 4.7% higher than N_{Kr}) for the $(1 \times 1)[\frac{1}{2}]$ transition. Figure 3(a) shows data for a coverage very close to the one that gives the maximum height at the transition. An additional feature is the appearance of a line of heat capacity peaks resembling a coexistence region, Fig. 3(b). In an effort to find if a higher value of C/Nk at the critical value could be obtained, we slightly increased the amount of the Kr gas plating, thus producing the fourth Kr plating in Table I. A survey of several high- and low-density coverages showed a 12% increase in C/Nk at the critical coverage, and the disappearance of the peaks shown as a dashed line in Fig.

TABLE I. Critical coverages $(N_c k)$ and temperatures (T_c) for ordering of a ^{4}He monolayer on bare graphite and on the four different Kr platings.

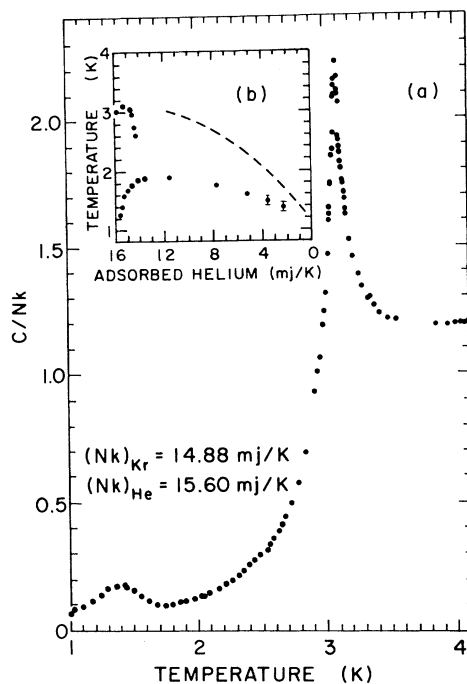| Cell | Bare graphite | | Kr plating | Kr-plated graphite | |
	$N_c k$ (mJ/K)	T_c (K)	Nk (mJ/K)	$N_c k$ (mJ/K)	T_c (K)
Grafoil	23.28	2.925	No. 1 27.46	21.4	4.29
				21.6[a]	4.98
			No. 2 25.02	21.6	3.65
Foam	14.92	2.929	No. 3 14.88	15.60	3.109
			No. 4 15.60	14.99	3.113

[a]Single ^{3}He measurement.

FIG. 3. (a) The highest specific heat peak of ^{4}He/Kr/ graphite foam for the 3rd Kr plating. Notice that at 1.4 K the system has another specific heat peak. (b) The temperature of heat capacity peaks as a function of density (phase diagram). The dashed line represents a rounded anomaly in the specific heat that is dominant at low densities and may be due to a small portion of the helium being strongly absorbed in inhomogeneous sites or as interstitials. It is absent in the 4th Kr plating.

3(b). We then measured the heat capacity at the critical coverage using very small temperature heating intervals. The numerical analysis[8] gave $T_c \cong 3.1130$ K, $\alpha \cong 0$, and $A^+/A^- \cong 0.464$. The best-fitting set of C_M vs $|t|$ is shown in Fig. 4. Only a fraction of the measured points have been pictured.

In summary, we believe that our measurements indicate the existence of a phase transition to the $(1 \times 1)[\frac{1}{2}]$ commensurate phase. Only information like that obtained by neutron scattering can determine if the structure is the one that we believe it to be. On the assumption that we are correct, the universality class to which it belongs is that expected from theoretical models. This finding should encourage the search for other structures postulated by Domany et al.,[11,12] some of them with very unusual power-law singularities, as further tests of universality. Our measurements show some discrepancy with the results of Bretz[6] for the values of α and A^+/A^-. At
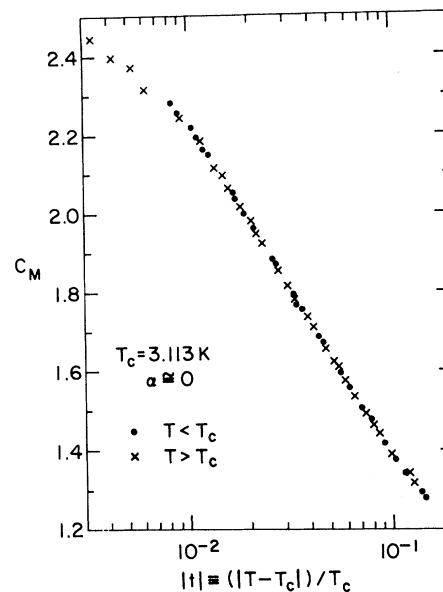

FIG. 4. The merged specific heat for ^{4}He/Kr/graphite foam for the tallest peak of the fourth Kr plating.

the moment we do not know if this discrepancy is due to our slightly smaller crystallite sizes. We applied our computer analysis to numerically generated tables of C/Nk vs T for finite-size Ising and Potts lattices[17] to determine how well the numerical analysis used for the experimental curves reproduced the theoretical value of α. In all cases we found good agreement. We will discuss the complete phase diagram, the evidence for the two-phase region, and the shifts in the low-density peaks with the various Kr platings[18] in a full article.[19]

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Site-Selective Doping of Compound Semiconductors by Ion Implantation of Radioactive Nuclei

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Sn impurity atoms have been selectively inserted on the two different substitutional lattice sites in the III-V semiconductors GaP, GaAs, GaSb, InP, InAs, and InSb. Radioactive ^{119}In$^+$ and ^{119}Sb$^+$ ions which decay to the Mössbauer state of ^{119}Sn have been implanted. From the isomer shifts determined in Mössbauer-emission experiments it is concluded that the implanted In and Sb ions selectively populate III and V sites, respectively.

Doping of semiconductors by ion-implantation techniques is widely utilized for technological as well as for research applications. Mainly ions of the desired dopant elements have been implanted. Here we report on a new method, particularly attractive for doping of compound semiconductors. The radioactive ions that are implanted decay to the desired dopant element. As shown in the present investigation, this method enables a selection of the lattice site for, e.g., amphoteric dopants like Sn in III-V semiconductors. Although technological applications might be hampered by the relatively large amounts of ra-

dioactivity needed, the method has promising aspects for microscopic investigations of dopant properties.

Radioactive ^{119}Sb$^+$ ions were implanted at room temperature at an energy of 80 keV to a dose of $\sim 10^{13}$ atoms/cm^2 with an isotope separator. The ^{119}Sb activity was obtained from a bombardment of natural tin with 20-MeV α particles by a procedure described previously.[1] The radioactive ^{119}In$^+$ ions were obtained as proton induced fission products in a uranium carbide target irradiated by 600-MeV protons from the CERN synchrocyclotron. Following on-line mass separation in