above 18.5 will be less than 25%. This interpretation also explains the larger scatter that is observed in the measured latent heat above 16 K. This scatter does not only occur between different crystals, but even for the same crystal when it is taken repeatedly through the transition. Obviously, the amount of martensite formed can vary appreciably. Below 16 K, very little scatter was observed in the measured latent heat. Only partial transformation at higher pressures incidentally also explains why Mills and Schuch[5] could find crystals showing both hcp and fcc x-ray lines so far off the transition line. It should be mentioned that another explanation for a decreased transition entropy is given by the possibility of storing elastically part of the transition energy. This would mean that measurements of the transition entropy might underestimate the amount of martensite formed. This question can obviously only be settled by crystallographic observations.

The transition entropy up to 16.0 K is in excellent agreement with the theoretical prediction of Holian $et\ al.$[8] Since it is believed that up to this temperature $(\Delta S)_{tr}$ represents a true molar quantity, one can obtain the molar volume change, $(\Delta V)_{tr}$, from the Clausius-Clapeyron equation. Its value is found near 0.3 mm³/mole, again in excellent agreement with Holian $et\ al.$ The predicted temperature dependence of ΔV, however, is not observed. The values of $(\Delta S)_{tr}$ and $(\Delta V)_{tr}$ are also in good agreement with earlier experimental determinations.[1,2]

Preliminary measurements in very close proximity to the triple point, which were referred to above, appear also to give a drastically reduced molar volume change. This effect is probably connected with premelting phenomena and at present not fully resolved.

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Phase Transition in a Dense Layer of Xenon Adsorbed on the Cleavage Face of Nickel Chloride

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A first-order phase change is observed in a dense monolayer of xenon adsorbed on the cleavage face of nickel chloride. This is the first observation of such a transition for rare gases on a surface other than the basal plane of graphite. We conjecture that it is a solid-solid transition rather than a solid-liquid one.

Numerous phase transitions in monolayers of classical rare gases adsorbed on the cleavage faces of crystals have been observed. Those occurring on the basal plane of graphite,[1] and of lamellar dihalides,[2-5] as well as the (001) plane of alkali halides,[6-10] have been particularly studied. In all these cases a 2D (two-dimensional) condensation, which is a first-order transition from a dilute to a dense monolayer, takes place. But as yet, except on graphite, there has been no evidence that additional transitions between dense phases within the monolayer could appear

as the surface density was increased. The object of this Letter is to report new data clearly showing such a phase change for xenon on the cleavage face of nickel chloride.

The sample of nickel chloride was prepared by sublimation in a rapid current of dry nitrogen according to the method previously described by one of us.[2,11] Adsorption isotherms were determined with a volumetric apparatus using a modified McLeod gauge.[2,12]

A set of isotherms of xenon on nickel chloride is represented in Fig. 1. Their general appearance is much like that of xenon on graphite, determined by Thomy and Duval.[1] Below a temperature represented by T_t, a single phase transition is observed from a dilute monolayer—a 2D gas—to a dense monolayer, which is a 2D solid. Above T_t, an intermediate dense phase appears which may be either a 2D liquid or a 2D solid. These three phases coexist at a triple point, whose temperature, $T_t = 98 \pm 0.5$ K, is very close to that for Xe on graphite, viz., 99 ± 2 K. In the latter case it has been generally accepted that the high-temperature dense monolayer was a 2D liquid. This conjecture is mainly based on the fact that potential barriers to translation of rare gases on the basal plane of graphite are low, about 40 K for Ar, Kr, and Xe (see Steele,[13] page 57). Since the triangular arrangment of the anions

of the basal plane of lamellar halides have a density about 6 times lower than that of the carbon atoms of the cleavage face of graphite, clearly one expects the former to be much less smooth than the latter to rare gas atoms. No potential energy calculations at the surface of lamellar halides have been published as yet. But results for a very similar system, Ar on a (111) plane of a xenon crystal, are known (see Ref. 13, page 37). The potential energy of an argon atom increases by 74 or 288 K when it is moved from S to SP or A (Steele's terminology is adopted to label the remarkable positions above the surface: sites S above the center of a triangle of halide ions, saddle points SP above the midpoint of two anions, and positions A above anions). An increase in the height of potential barriers will clearly favor vibrational motion to the prejudice of translational motion, so that it seemed reasonable to consider the absence of any transition between dense monolayers adsorbed on lamellar halides as evidence that no liquid layer could form.[2-5] The thermodynamic analysis of sets of adsorption isotherms supported this point of view, particularly at positive incompatibilities. A dimensional incompatibility between the adsorbate and the adsorbent is defined by $i = (a - d)/d$, where a and d are the crystalline parameters of the basal plane of the substrate and of the (111) plane
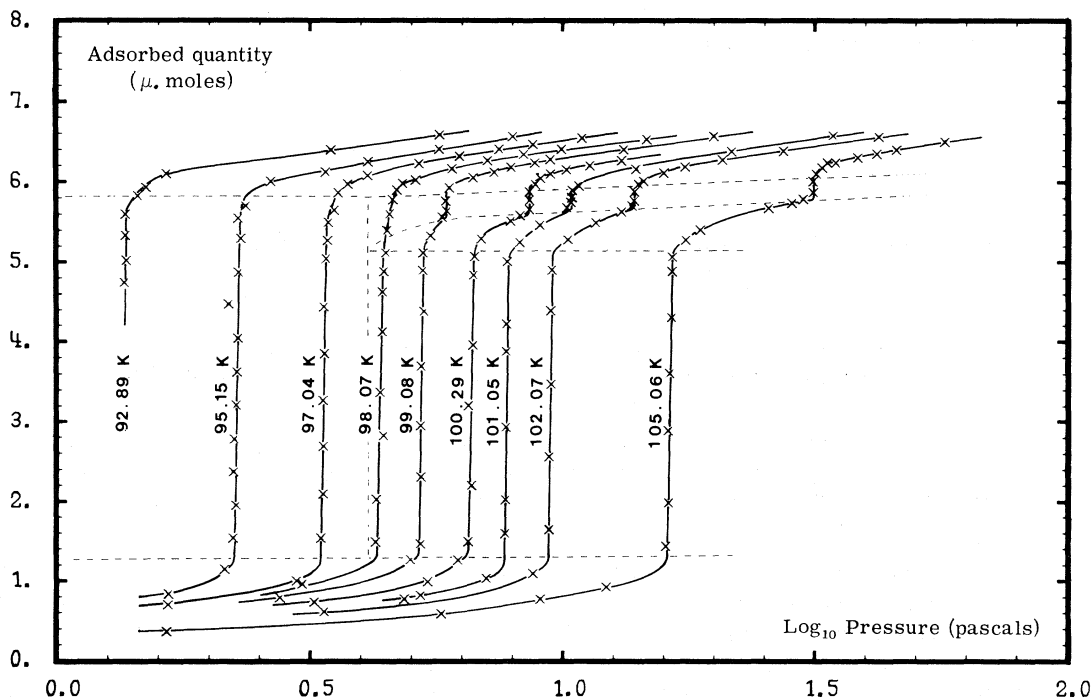

FIG. 1. Set of adsorption isotherms of xenon on the cleavage face of nickel chloride.

of the bulk f.c.c. adsorbate. Indeed for $i \geq 0$, up to about 12%, there is clear evidence that the dense layer that forms during a 2D condensation is in registry with the surface, the adatoms standing in half of its sites. It should be noted that numerous theoretical studies indicate that a critical point exists for a lattice-gas model with attractive energy, so that the existence of such a point for the 2D condensation of rare gases on the lamellar halides should not be considered as evidence that a liquid monolayer forms.

At first sight it would seem that the present observation of a dense to dense monolayer transition for Xe on $NiCl_2$ would case doubt on the previously accepted viewpoint. Among the rare-gas, lamellar-halide systems, $Xe-NiCl_2$ is the one for which the distance between the halide ions is minimum—$a(NiCl_2) = 3.485$ Å [14]—and the diameter of the adatom maximum—$d(Xe) = 4.405$ Å [15]— which suggests that it is also the system for which the surface structure should show the lowest barriers to adatom translation. It is thus the system for which the existence of a liquid monolayer is *a priori* the most probable. We have recently made semiempirical estimations of potential barriers to translation of rare gases on lamellar halides of which the details will be presented elsewhere. In essence, summations of Lennard-Jones pair potentials are carried out over the anions of the adsorbent. The results indicate that the potential energy difference between the positions A and S does not change importantly when the ratio a/d is lowered. In all cases it remains more than 6 times higher than that of the barriers to translation on graphite. Consequently we think that the existence of a 2D liquid on lamellar halides, even in the *a priori* most favorable case, remains improbable.

Of course this means that the observed transition is a 2D polymorphic phase change. The high-density solid, which is also the high-pressure phase, should correspond to a close-packed layer, whose structure would be mostly determined by the lateral interactions within the layer, in fact by the hard core of xenon, which does not exclude some relation to the structure of the substrate. [16] On the other hand, the low-density solid is expected to have a structure much more closely related to that of the substrate. As noticed earlier in this Letter, there is good evidence of a simple registry of the adlayer—(1×1) structure—at positive incompatibilities, [2-5] at least up to $i = 12\%$. At $i < 0$, we may think of a superlattice, having, for instance, a unit cell of $(n - 1)^2$ ada-

toms covering n^2 ions. [4] Taking $n = 4$ accounts for the density difference of about 10% between the two adphases of Xe on $NiCl_2$ (see Fig. 1). Such a structure makes allowance for the influence of the substrate in two ways: (i) A fraction of adatoms stand strictly above sites, and (ii) the relatively low density of the layer as compared to that of the (111) plane of bulk xenon makes possible, within the unit cell, an irregular arrangment in which the adatoms could stay away from the energetically unfavorable A positions. [5] But clearly a structural investigation by low-energy electron, x-ray, or neutron diffraction is necessary if one wants a precise answer to the question of the structure of both adlayers.

It has long been known [2-5] that for bad dimensional compatibilities between rare-gas atoms and lamellar halides, the dense monolayer which appears during the 2D condensation has a density definitely lower than that of the (111) plane of bulk adsorbate, and also that this density subsequently increases with pressure towards the latter, before an appreciable adsorption in the second layer occurs. But this is the first case in which it has been shown that a first-order transition is associated with such a change. The situation, as far as adsorption on graphite is concerned, has developed in a somewhat symmetrical manner. First-order transitions between 2D liquid and solid monolayers of Kr and Xe on that substrate have been known for a long time. On the other hand, the data at present available for the adsorption of Ar on graphite [17,18] suggest that only a higher-order transition within the dense monolayer exists. All these results show the interest of an experimental investigation of the conditions favoring first-order or any other kind of transitions in dense monolayers, at present poorly known. The family of lamellar halides offers a unique opportunity for such a study since it permits variation of the dimensional incompatibility which we suspect to be a significant parameter even for the adsorption on graphite. We will soon publish elsewhere preliminary results on this problem.

In this discussion the polymorphic phase changes observed for nitric oxide on lamellar halides have been ignored, because they are of a different nature from that reported here, being related to the very unsymmetrical shape of the admolecule, the dimer of nitric oxide. [19]

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Observations on Superfluid ³He-A in Small Cylinders: Evidence for a Textural Transition

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We report transverse and longitudinal NMR experiments on superfluid ³He-A confined within 2-μm-diam tubes at temperatures down to 1 mK. The behavior of the transverse resonance line provides evidence for a slow transition between two textures in the tubes; the shifts are smaller than in bulk for both textures. A search for longitudinal resonance was unsuccessful, and no transition to the B phase was observed.

We report the first experimental observations on superfluid ³He-A confined within cylinders whose diameter (2 μm) is sufficiently small that the bending energy associated with the spatial variation of the order parameter is greater than the dipolar energy and may be enough to stabilize textures with line singularities. We interpret our NMR results as evidence for the existence of such a texture, which seems not to be the equilibrium state (at least away from T_c), for it transforms to a different texture which we believe has no singularity in the order parameter. The observed frequency shift should determine the parameters describing the bending energy. The rate of transformation may give information on flow dissipation mechanisms.

The stable thermodynamic state of a given sample of ³He-A results from the competition between a number of small terms in the free energy which tend to orient in various ways the two vectors $\hat{l}$ and $\hat{d}$ describing the Cooper pairs.[1] The orientation of the spin space vector, $\hat{d}$, depends on a balance between the susceptibility anisotropy, orienting $\hat{d}$ perpendicular to an applied magnetic field, the dipolar interaction which tends to align $\hat{d}$ along the rotation axis $\hat{l}$ of the gap in orbit

space, and the bending- or kinetic-energy terms, which favor a uniform orientation of the $\hat{d}$ vector throughout the sample. The orientation of $\hat{l}$ depends on dipolar and bending energies and, in addition, a surface-energy term which makes it lie normal to a wall. If these requirements are not consistent with a continuous variation of the gap, an additional term arises from the loss of condensation energy at singularities.

Bending terms cannot be studied in uniform textures such as that in the 4-μm parallel-plate geometry of the NMR experiments of Ahonen, Krusius, and Paalanen,[2] although these do provide bounds on some of the other energies. Bending is present in any cylinder, for $\hat{l}$ cannot lie normal to the walls and also be uniform everywhere. In cylinders smaller than about 10 μm, the detailed configuration of the textures determines the measured NMR frequency shift, for this depends on the dipolar interaction.

The observations reported here were made by NMR on a sample of ³He contained within a large number of soda glass capillary tubes, each nominally 2 μm internal diameter, fused together into an array of overall cylindrical shape $\frac{1}{4}$ in. long and $\frac{1}{2}$ in. diam, with axis parallel to the capillar-