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Citation: The Journal of Chemical Physics **88**, 451 (1988); doi: 10.1063/1.454623 View online: http://dx.doi.org/10.1063/1.454623 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/88/1?ver=pdfcov Published by the AIP Publishing

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X-ray study of Kr and Xe adsorbed on the basal plane of nickel chloride

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(Received 20 July 1987; accepted 23 September 1987)

X-ray scattering has been used to investigate the structures and phase transitions of Xe and Kr films adsorbed on the basal plane of $NiCl_2$. The x-ray scattering measurements were carried out both as a function of temperature at fixed coverage and as a function of coverage at fixed temperature in the monolayer and bilayer coverage regimes. The results indicate that both the monolayers of Xe and Kr adsorbed on the basal plane of $NiCl_2$ form a 2D solid of the simple triangular structure incommensurate with the substrate and 2D melting is first order in the incommensurate solid of Xe but continuous in that of Kr. With the addition of the second-layer atoms the interparticle distance of the adsorbed atoms reduces and the crystallinity of the incommensurate solid improves.

I. INTRODUCTION

Monolayers of gases adsorbed on the basal plane of graphite have been studied extensively by thermodynamic and structural techniques, because they show the structures and phase transitions characteristic of two-dimensional (2D) phases. Lamellar halides have a structure and properties very similar to those of graphite, namely a high anisotropy and a low chemical reactivity of their basal plane. From the point of view of physical adsorption of rare gases, the main difference from graphite consists in the relative dimensions of the adsorbed atom and of the superficial species of the substrate. In order to characterize the mismatch between the wavelength of the substrate corrugation and the neighbor separation favored by the adsorbed atoms, Larher and collaborators¹⁻³ define the dimensional incompatibility i as i = (a - d)/d, where a is the lattice constant of the basal plane of the substrate and d is the nearest-neighbor separation in the (111) plane of the bulk fcc crystal of the adsorbed species. Thus a negative *i* corresponds to large adsorbed atoms and a positive *i* to small atoms. In the experimental systems of Ar, Kr, and Xe films on lamellar halides composed of various chemical constituents i ranged from -0.2to +0.2. From systematic thermodynamic studies of rare gas monolayers, Larher and collaborators have shown that the 2D condensation is followed by a second first-order transition within the dense layer only at the low dimensional incompatibilities below about -0.17 and conjectured that 2D melting of incommensurate monolayers is first order for i < -0.17 but continuous for -0.17 < i < -0.07. However, no structural information is currently available within the range of incompatibilities below about -0.07, except for preliminary neutron diffraction studies⁴ of CD₄-NiCl₂ and Ar-NiCl₂ systems. For i > -0.07, adsorbed gases seem to form a commensurate solid phase.³ Asada⁵ and Niskanen⁶ have discussed the nature of the transitions observed in the adsorption isotherms of rare-gas monolayers physisorbed on the lamellar halides.

In this paper we describe a set of x-ray scattering measurements on Kr and Xe on $NiCl_2$ in the monolayer and

bilayer coverage regimes. The Xe–NiCl₂ system corresponds to the lowest dimensional incompatibility (-0.21) within the class studied so far and reveals a first-order transition within a dense monolayer, while the Kr–NiCl₂ system (i = -0.14) does not show any feature at all which could indicate the existence of such a phase transition. In monolayer Xe on NiCl₂, Robert and Larher¹ had a first observation of such a transition for rare-gases on a surface other than the basal plane of graphite and conjectured that it is a solid– solid transition rather than a solid–liquid one. In a subsequent paper, however, Tessier and Larher² reached the idea that it is a first-order melting of an incommensurate solid monolayer. As we shall show, our data seem to support many of the conclusions reached in the pioneering work of Larher and collaborators.

II. EXPERIMENTAL

Powdered nickel chloride was prepared by sublimation of NiCl₂ · xH₂O (99.999% purity, Rare Metallic Co., Ltd.) in a rapid current of nitrogen gas. It has a specific surface area of $\sim 20 \text{ m}^2/\text{g}$. About 0.2 g of NiCl, thus prepared was packed in a sample holder of Cu and covered with a 0.1 mm thick sheet of Be and then evacuated at 250 °C under a vacuum of 1×10^{-5} Torr for 5 h. After that, the sample holder was attached to the cold head of a closed cycle refrigerator and sealed in a sample cell with an In O ring in a flow of nitrogen. The sample cell with a cylindrical Be window was used. The x-ray experiments have been carried out with CuK_{α} radiation ($\lambda = 1.54$ Å) in the reflection geometry. The resolution was 0.016 $Å^{-1}$ full width at half-maximum. The x-ray scattering measurements were carried out both as a function of temperature at fixed coverage and as a function of coverage at fixed temperature. The experimental apparatus is described in detail elsewhere.⁷

The temperature of the sample was measured with Si diode thermometer. Although the relative accuracy of the thermometry was rather satisfactory, $\Delta T = 0.05$ K, it was discovered during the measurements that systematic temperature errors were present. The transition pressures of gas-liquid in the vapor pressure isotherms of Xe on NiCl₂ measured in the present experiment differ from those determined by Tessier,⁴ the difference of which indicates that the

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true sample temperature should be estimated by adding ~ 1.5 K to the measured one. Throughout this paper, the measured temperature is used.

III. DATA REDUCTION

As is usual in diffraction studies of overlayers, the signal from the film was taken as the difference between counts with and without the adsorbate in the cell. In order to do this properly, it was necessary to correct the data for gas attenuation and the gradual lowering of incident x-ray intensity. This was done by scaling the observed scattering to the intensity of the (101) NiCl₂ peak, the latter being assumed to be essentially unaffected by diffraction from the adsorbed film.

The diffraction pattern of the 2D lattice was calculated according to the powder-averaged Lorentzian line shape for a completely random powder.⁸ Although this is not physical for incommensurate monolayer solids such as Kr and Xe on NiCl₂, Heiney et al.⁹ have demonstrated that the power-law line shape expected for a floating solid is well represented by a sharp powder-averaged Lorentzian convoluted with the instrumental resolution function and that the latter form is computationally more simple. Lorentzian line shape was convoluted numerically with the resolution function and corrected for a polarization factor and the absorption effect of the Be cover. The least-squares fitting was done by using the program system SALS developed by Nakagawa and Oyanagi.¹⁰ The fitting parameters were the scattering amplitude A, the peak position Q_0 , and the inverse correlation length (peak width) κ . In most of the least-squares fitting procedure, we included an additional minor parameter of a uniform background to allow for possibility of incomplete subtraction of background. This generally makes the residual sum of squares smaller but has little effect on the final result except for the inverse correlation length. The inverse correlation length tends to become smaller by the inclusion of a uniform background.



FIG. 1. Adsorption isotherms of Xe and Kr on NiCl₂.

IV. RESULTS AND DISCUSSION

A.Constant-temperature run

First, the adsorption of Xe and Kr on NiCl₂ was studied as a function of vapor pressure at constant temperatures. Figure 1 shows the adsorption isotherms which were measured coincidentally with the scattering experiments. The Xe isotherm reveals a small step due to a first-order transition within a dense monolayer, while the Kr isotherm does not show any feature at all which could indicate the existence of such a phase transition. This confirmed the results of Larher and collaborators.¹⁻³ From systematic thermodynamic studies,^{2,3} they conjectured that both the monolayers of Xe and Kr form incommensurate solids and the 2D melting is first order for the Xe monolayer and continuous for the Kr monolayer. Both the isotherms exhibit two layering transitions before the bulk vapor pressure is achieved.

At each vapor-pressure point, a x-ray scan was performed from 1.35 to 1.90 Å⁻¹ for Xe and from 1.49 to 1.97 Å⁻¹ for Kr. The diffraction profiles from these two runs are shown in Figs. 2 and 3 for Xe and Kr, respectively. The abscissa of these figures represents the magnitude of the scattering vector, $Q = 4\pi \sin \theta / \lambda$. The solid lines in these figures



FIG. 2. X-ray scattering profiles of Xe on NiCl₂ as a function of pressure at T = 106.2 K. The dashed line in the 1.323 Torr scan represents the contribution from the 2D phase to the overall profile.



FIG. 3. X-ray scattering profiles of Kr on NiCl₂ as a function of pressure at T = 78.1 K. The dashed line in the 1.769 Torr scan represents the contribution from the 2D phase to the overall profile.

are fits to a Lorentzian line shape or a composite line shape of a 2D phase and a bulk solid; the latter will be described later. When the vapor pressure of Xe is increased, the diffraction peak abruptly becomes sharper coincidentally with the appearance of the small step in the isotherm. At P = 0.435Torr, the peak is quite broad characteristic of a 2D liquid. At P = 0.46 Torr, a relatively sharp peak centered at 1.59 Å⁻¹ appears; this seems to overlap onto the former broad peak. As the pressure is increased to P = 1.30 Torr, both the peak intensity and position increases gradually. The diffraction profile of a sawtooth shape observed is typical of a 2D solid. With further increase in pressure up to the occurrence of the second layering transition, the peak centered at 1.60 $Å^{-1}$ shifts to 1.63 $Å^{-1}$, while the peak intensity of the 2D phase remains constant to within the errors. Such a behavior in intensity is compatible with the model that the second-layer atoms locate above the centers of the triangles of the firstlayer atoms.¹¹ Around the second layering transition, a broad peak of symmetrical shape appears around Q = 1.74 $Å^{-1}$, as shown in the 1.323 Torr scan. As the pressure of Xe increases, this peak grows in intensity while the 2D scattering remains constant. From the shape and position, the extra peak can be indexed as (111) reflection of solid bulk Xe. The contribution to the scattering from bulk Xe has been calculated in terms of the defect-broadening model developed by Ergun.¹² This model gives the lattice constant A and the



FIG. 4. Fitted parameters for the diffraction groups of Xe on NiCl₂ as a function of pressure at T = 106.2 K. Upper panel is the inverse correlation length and lower panel the peak position.

mean defect-free distance L. The best-fitted values of A $(6.255 \pm 0.011 \text{ Å})$ were reasonably consistent with the published value¹³ of solid bulk Xe at the same temperature. It is surprising that the bulk first appears at a vapor pressure well below the saturated vapor pressure of bulk xenon.

Similar results were obtained for the Kr isotherms, except for the liquid-solid transition region. In the transition region the diffraction peak seems to continuously become sharper with increasing pressure, although the signal-to-noise ratio is poor.

From the peak position and its variation as a function of coverage, it is almost certain that the monolayers of Xe and Kr adsorbed on the basal plane of NiCl, form a 2D solid of the simple triangular structure incommensurate with the substrate, although we have not observed higher order Bragg peaks to confirm it. All the 2D peak profiles were fitted to the powder-averaged Lorentzian scattering function as described above. Fitted values of κ and Q_0 from Lorentzian fits to the scans are shown in Figs. 4 and 5 for Xe and Kr, respectively. The inverse correlation length of Xe drops rather discontinuously from $\kappa = 0.055 \text{ Å}^{-1}$ at P = 0.43 Torrto $\kappa = 0.011$ Å⁻¹ at P = 0.46 Torr, while that of Kr decreases continuously from $\kappa = 0.07 \text{ Å}^{-1}$ at P = 0.21 Torr to $\kappa = 0.01 \text{ Å}^{-1}$ at P = 0.75 Torr. A first-order transition will manifest itself as a discontinuous change in the scattering profiles as a function of pressure; that is, a discontinuous jump in the fitted correlation length as a function of pressure is the signature of a first-order transition, while a continuous evolution of the correlation length indicates a continuous transition. However, even a first-order transition may show some rounding due to macroscopic disorder, resulting in ap-



FIG. 5. Fitted parameters for the diffraction groups of Kr on NiCl₂ as a function of pressure at T = 78.1 K. Upper panel is the inverse correlation length and lower panel the peak position.

parent two-phase coexistence. We infer that 2D melting is first order in the incommensurate solid of Xe on NiCl₂ but continuous in that of Kr on NiCl₂. In a first-order solidification transition region diffraction peaks must be described as the sums of a sharp "solid" peak and a broad "fluid" peak. However, we cannot show fits to a two-Lorentzian composite line in the transition region as a definitive model, because the quality of our x-ray data is not good enough to extract a true line shape.

When the second layer of Xe or Kr is formed, the peak position and the correlation length (inverse of κ) abruptly increases. This indicates that with the addition of the second-layer atoms the interparticle distance of the adsorbed atoms reduces and the crystallinity of the incommensurate solid improves. Such a discontinuity has not been observed for the Xe film on graphite.¹⁴ Under the assumption of the simple triangular structure, we can calculate the nearestneighbor distance in the 2D solid. It discontinuously changes from 4.51 to 4.45 Å for Xe, and from 4.15 to 4.10 Å for Kr, respectively, before and after the formation of the second layer. At the bilayer formation, the nearest-neighbor distances are still distinctly larger than those of the corresponding bulk solids under their vapor pressures,¹³ that is, 4.42 Å at 106 K for Xe and 4.06 Å at 78 K for Kr, respectively.

B. Constant-coverage run

The Xe(10) Bragg diffraction profile was measured as a function of temperature going through the melting transition for four different coverages of 0.60, 0.74, 0.89, and 0.92



FIG. 6. X-ray scattering profiles of Xe on $NiCl_2$ as a function of temperature at a coverage of 0.74.

monolayers. Figure 6 shows some of the diffraction peaks for the coverage of 0.74, which is less than the triple point value conjectured from the vapor-pressure isotherms measured by Robert and Larher.¹ At 97.0 K, one obtains pure liquid scattering. The more diffuse gas phase gives rise to a broad and weak background which is unobservable in these experiments. As the temperature is lowered through 96 K, there is a rather abrupt change in the line shape from liquid to solid form. This abrupt transition is also observed at the coverage of 0.60. Further decrease in temperature resulted in a gradual shift of the peak position to higher scattering vector and a gradual sharpening of the line shape. At 21.4 K, the peak position reached to 1.64 $Å^{-1}$ and the inverse correlation length decreased to 0.001 \AA^{-1} . At the coverages of 0.89 and 0.92, which are larger than the triple point value, the freezing transition becomes broader and shifts to higher temperature with increasing coverage. Figures 7 and 8 show the inverse correlation length and the peak position obtained from Lorentzian fits to these scans, respectively. From the published isotherms,¹ we can construct the phase diagram of submonolayer xenon on NiCl₂, which is very similar to that on graphite. The reported value of the 2D triple point is 98 ± 0.5 K and the corresponding coverage is ~0.82 in our estimation of monolayer capacity. Below T = 98 K and coverage = 1 the only possible phases are a dilute gas or a monolayer solid containing a small number of vacancies. A broad first-order coexistence region separates these two phases.



FIG. 7. Inverse correlation length as a function of temperature for submonolayer Xe on NiCl₂ at various coverages. Smooth curves are guides for the eye.

Above T = 98 K the system makes first-order transitions between a dilute gas, a dense liquid, and a monolayer solid. If we measure the diffraction peaks of this 2D system as a function of temperature at all coverages less than 0.82, we can observe a sudden change of diffraction line shape due to the 2D triple point melting. For the higher coverages, we predict a broad melting transition by crossing the solid-liquid coexistence region. The results of Fig. 7 completely coincide with these pedictions. At the coverages of 0.60 and 0.74, the inverse correlation length abruptly evolve from $\kappa = 0.006 \text{ Å}^{-1}$ at 96.2 K to $\kappa = 0.04 \text{ Å}^{-1}$ at 96.8 K. When the coverage is increased to 0.89, the phase transition becomes gradual and shifted to around 97.5 K. Further increase in coverage up to 0.92 resulted in a large increase of the transition temperature and a broadening of the transition as clearly shown in Fig. 7. These results, therefore, unambiguously confirm the exis-



FIG. 8. Peak position as a function of temperature for submonolayer Xe on NiCl₂ at various coverages. Smooth curves are guides for the eye.

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FIG. 9. Inverse correlation length and peak position as a function of temperature for submonolayer Kr on $NiCl_2$.

tence of a triple point at 96.5 \pm 0.3 K. After the correction of the estimated error of the temperature, it agrees very closely with that (98 \pm 0.5 K) obtained by the measurement of the adsorption isotherms.¹ It is evident from Fig. 8 that above the melting point the nearest-neighbor distance becomes inversely proportional to coverage indicating formation of a compressible fluid.

As Fig. 9 shows, the inverse correlation length of the 2D phase of Kr starts to continuously increase around 65 K with increasing temperature. This indicates that the Kr film un-

dergoes a continuous melting in contrast with the Xe film. The melting temperature around 65 K is comparable to that of the incommensurate Kr solid overlayer on MgO.^{15,16} It has been reported that a first-order melting transition of the Kr film on MgO is severely broadened by surface heterogeneities and the correlation length changes rather continuously through the melting point than discontinuously as expected in a first-order melting. However, it is clear that the rounding of the transition observed for the Kr film on NiCl₂ does not arise from the substrate heterogeneities, because the Xe film on NiCl₂ reveals a rather sharp transition due to a first-order melting transition.

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J. Chem. Phys., Vol. 88, No. 1, 1 January 1988