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Commensurate-incommensurate and rotational transitions of monolayer xenon on single-crystal graphite

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We have studied the structures and transitions of high-density xenon monolayers on single-crystal graphite using high-resolution synchrotron x-ray diffraction techniques. In contrast to the previous x-ray experiment, we find that at low temperatures, the xenon has a commensurate $\sqrt{3}\times\sqrt{3}R30°$ structure for a broad range of coverages. With decreasing temperature the novel reentrant sequence: aligned → rotated → aligned, occurs; this sequence is followed by a first-order incommensurate-commensurate transition.

The physics of rare gases physisorbed onto the basal planes of graphite continues to be the subject of extensive investigation.[1] A variety of novel effects occurs as a result of the competition between the absorbate-adsorbate potential and the adsorbate-substrate interaction. Furthermore, because of the simplicity of the interactions, first-principle theoretical calculations are possible.[2,3] The system xenon-on-graphite has been extensively studied experimentally because it exhibits a model two-dimensional continuous-symmetry melting transition.[4] Somewhat surprisingly, the overall monolayer phase diagram and specifically, the low-temperature phases and phase transitions remain quite controversial both experimentally[5-7] and theoretically.[2,3]

In order to clarify the overall phase diagram of xenon-on-graphite, we have carried out an extensive high-resolution synchrotron x-ray scattering study of monolayer xenon physisorbed onto high-quality single-crystal graphite. We find that for a broad range of coverages, ~0.96 to 1.16 monolayers, with decreasing temperature, the xenon exhibits the sequence of structures: aligned hexagonal incommensurate → rotated hexagonal incommensurate → aligned superlight domain-wall hexagonal incommensurate → $\sqrt{3}\times\sqrt{3}R30°$ commensurate. The rotated hexagonal phase is only reached with decreasing temperature. The incommensurate-commensurate (IC-C) transition is similar in symmetry to that exhibited by monolayer krypton-on-graphite with a $\frac{1}{3}$ power-law behavior; however, for xenon it is a first-order solid-solid transition and with no intervening fluid phase.[8,9] Detailed comparisons will be made with current theories and other recent experiments.

The experiments were carried out on the IBM-MIT beam lines X-20A and C at the National Synchrotron Light Source. We have used either double asymmetric-cut Ge(111) or double Si(111) as monochromator crystals together with a Ge(111) analyzer. The resulting resolutions are, respectively, 0.0004 and 0.0003 $Å^{-1}$ half width at half maximum (HWHM) longitudinally and <0.0001 $Å^{-1}$ in the transverse in-plane direction. The quality of the graphite sample surfaces may be assessed by diffraction from a monolayer of Kr in the commensurate $\sqrt{3}\times\sqrt{3}$ phase. The crystal discussed here exhibited only one 0.01° peak within a 2.0° range, indicating a very high-quality surface. The single-crystal sample was periodically cleaned by resistive heating to ~900 K. Coverages are controlled by a vermicular graphite ballast adjacent to the sample. The experiments have been performed in a closed-cell configuration so that the quoted coverages are best approximated at temperatures $\leq$100 K when the vapor pressure is low. Coverage $f=1$ corresponds to a filled $\sqrt{3}\times\sqrt{3}$ monolayer.

Experiments were carried out at coverages of $f=0.90$, 0.96, 1.02, and 1.16 with the most detailed data being taken for the final coverage. For $f=0.90$, the xenon overlayer is always hexagonal incommensurate although, with decreasing temperature at ~110 K, it exhibits a first-order transition from aligned to rotated $\pm 0.6°$ with respect to the graphite (110) direction. At the lowest temperature probed, 26.80 K, the structure is hexagonal incommensurate with wave vector $Q(1,0)=1.675$ $Å^{-1}$ and rotation angle 0.16°. For coverages of $f=0.96$, 1.02, and 1.16, we see with decreasing temperature two additional transitions: a second-order rotated-aligned transition followed by a first-order IC-C transition. The IC-C temperature increases with increasing coverage. The general behavior for these three densities is identical; accordingly we will present mainly our results for $f=1.16$, which are the most detailed.

We show in Fig. 1 representative transverse and longitudinal scans for $f=1.16$ through the Xe (10) peak(s) in each of the four phases. Just below the melting temperature ($T_m\sim134$ K), the physisorbed Xe layer is incommensurate but aligns orientationally with the graphite substrate [Fig. 1(a)]. On cooling, the Xe (10) wave vector (Q) increases continuously. The Xe layer remains

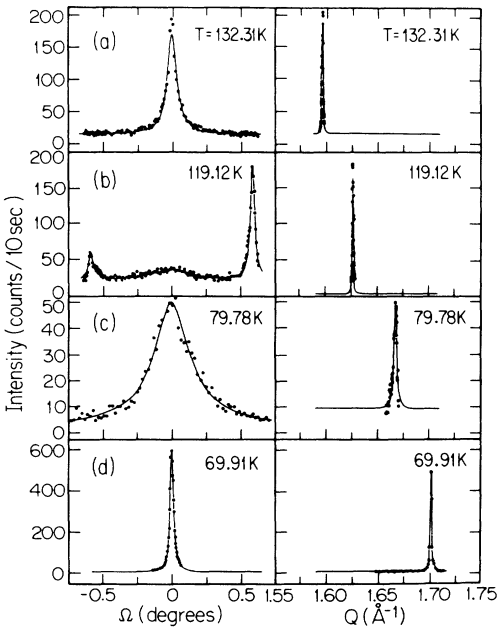

FIG. 1. Representative angular and radial scans for $f=1.16$ layers of xenon-on-graphite. The intensity is normalized to a ring current of 100 mA. Ω is the angular difference between Gr (1,1,0), i.e., commensurate Xe (10) and the scattering vector **Q**.

aligned with the substrate until at ~ 117 K where for $Q \sim 1.62$ Å^{-1}, it undergoes a discontinuous in-plane rotation of $\sim 0.6°$ [Fig. 1(b)]. The rotation angle decreases continuously with decreasing temperature, while Q increases, until for $Q=1.67$ Å^{-1} and $T \sim 80$ K the Xe domains realign with the substrate. The scans in Fig. 1(c) have been taken in the realigned phase. In the realigned phase, intense satellite peaks have been found at the positions $(Q_{\text{comm}}, \epsilon)$ and $(Q_{\text{comm}}+\epsilon, -\epsilon)$ expected for a superlight domain-wall solid.[1] Here, $\epsilon = Q_{\text{comm}} - Q$ for the primary peak $(Q,0)$ and the hexagonal basis vectors subtend an angle of 60°. We have been unable to observe any satellite peaks in the rotated phase.

At 73 K there is a discontinuous change in Q to the commensurate value of 1.701 A^{-1}. The commensurate phase persists down to the lowest temperature attainable in this experiment, 13 K. The equilibration time for the IC-C transition is remarkably long. The peak intensity for the IC phase decreases gradually over a period of hours while the intensity for the C phase increases. The tradeoff in intensity of the IC peak and C peak is complete within 0.5 K. Figure 1(d) shows a well-developed C peak at 69.91 K. The angular width of the C-phase transverse scan implies a domain size in excess of 1 μm. The results of the measurements are summarized in Figs. 2 and 3.

Before presenting our interpretation of these results, we first discuss their relationship to previous measurements. Using transmission high-energy electron diffraction (THEED) Venables and co-workers[6] have suggested that at a fixed pressure of $\sim 4\times10^{-7}$ Torr with decreasing temperature, the xenon exhibits the sequence of phases: monolayer hexagonal incommensurate → hexagonal commensurate → bilayer hexagonal incommensurate with the

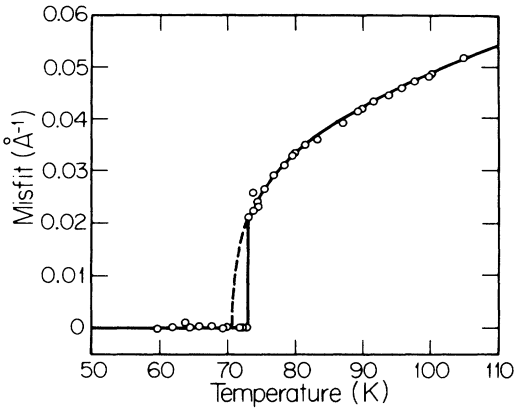

FIG. 2. Misfit vs temperature for $f=1.16$. The solid line for $T > 73$ K is the power law described in the text. The dashed curve is the extension of the power law beyond the first-order transition.

monolayer IC-C transition at 60 K. They further state that above the monolayer IC-C transition temperature the incommensurability shows an essentially linear decrease towards zero with temperature. We shall discuss this further below. Hong, Birgeneau, and Sutton,[5] on the other hand, have concluded that the limiting low-temperature phase for $f \sim 1$ is very weakly incommensurate and they further speculated that it corresponds to the superlight stripe phase. Allowing for the different paths in phase space, we have confirmed Venables's identification of the monolayer phases, although we disagree explicitly on the nature of the IC-C transition. Our single-crystal synchrotron results are inconsistent with the conclusions deduced from the vermicular graphite experiments reported in Refs. 5 and 7.

In order to elucidate the source of the disagreement, we have studied as part of this synchrotron experiment the diffraction from the vermicular graphite used to control the coverage. In brief, we find that the wave vectors for the xenon monolayers on the vermicular graphite and the single crystal agree quantitatively throughout the incom-

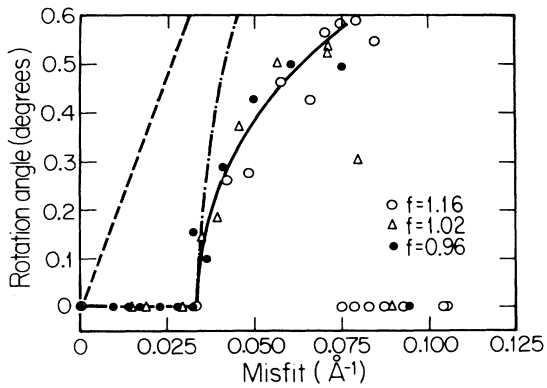

FIG. 3. Rotation angle vs temperature for various xenon layer coverages. The dashed-dotted curve is Shiba's prediction (Ref. 11) while the dashed line is the harmonic approximation (Ref. 13).

mensurate phase, thence confirming that the densities are identical. We find, however, that on the vermicular graphite the IC-C transition does not go to completion, presumably due to the very slow kinetics and pinning of the domain walls at the boundaries. Our actual data agree with those in Ref. 5 but not Ref. 7; these new results would seem to require interpretation in terms of kinetic effects rather than an equilibrium stripe phase.

We now discuss the IC-C transition. As shown in Fig. 2, for $f=1.16$ the misfit decreases smoothly towards zero but at a value of 0.021 Å^{-1}, the incommensurability jumps discontinuously to zero; thus the IC-C transition is first order. More importantly, the peak remains quite sharp; just above the transition the excess angular HWHM is $\sim 9\times 10^{-4}$ Å^{-1}. The longitudinal width is slightly larger, $\sim 2\times 10^{-3}$ Å^{-1}, but it decreases rapidly with increasing incommensurability. This longitudinal broadening is almost certainly due to substrate inhomogeneities. This IC-C transition is thus a *solid-solid transition* in contrast to the case of monolayer krypton-on-graphite where at high temperatures there is an intervening domain-wall fluid phase.[8,9] This difference presumably originates from the fact that for the xenon IC-C transition because of the low temperatures the entropic effects, which favor the weakly incommensurate domain-wall fluid phase,[8,10] are unimportant.

For krypton-on-graphite for misfits between 0.02 and 0.08 Å^{-1} the incommensurability exhibits a $\frac{1}{3}$ power law over a wide range of temperatures and pressures.[8] The solid line above 73 K is the result of a fit of the xenon misfit to a power law $Q_{\text{comm}}-Q=A(T/T_0-1)^{\beta}$. The best-fit parameters are $\beta=0.33\pm 0.08$, $T_0=70.9\pm 1.8$ K, and $A=0.065\pm 0.02$ Å^{-1}. This functional form agrees quite well with that obtained for monolayer krypton, even though for krypton at small incommensurability there is a domain-wall fluid phase. On the other hand, these results disagree with the interpretation of lower-resolution data presented in Ref. 6, which claims a second-order IC-C transition with an exponent near unity and further suggests that the krypton $\frac{1}{3}$ exponent is fortuitous.

We now discuss the superlight domain-wall structure and the rotational transitions. As noted above, we observe superlight domain-wall superlattice peaks at $(Q_{\text{comm}},\epsilon)$ and $(Q_{\text{commm}}+\epsilon,-\epsilon)$ in the aligned weakly incommensurate phase between 73 and 80 K. The relative intensity of the superlattice peaks to the primary peak at $(Q_{\text{comm}}-\epsilon,0)$ varies between 7 and 10 at different ϵ. At $T=0$ the intensity of the satellite peaks is controlled by the relative strength of the graphite corrugation $9/2V_0$ and Kr-Kr potential W. In the notation of Shiba,[11] the dimensionless wall width is $l_0=(54W/V_0)^{1/2}$. We have carried out static relaxation calculations on an array of xenon atoms for the satellite intensity for varied V_0 and thence l_0. From these calculations we find that our observed intensities correspond to $l_0\sim 41\pm 6$. The most recent theoretical estimate[12] of V_0 corresponds to $l_0=31$. We regard this agreement as satisfactory. It should be noted that in lattice units the wall $1/e$ full width is about $l_0/4$.

As discussed by Shiba,[11] at $T=0$ there should be an aligned-rotated transition at a critical value of the misfit corresponding to $0.7Qc/l_0$ (Å^{-1}) for a Cauchy solid. This transition has been studied in detail for krypton-on-graphite[9] where Shiba's theory is found to work quantitatively. For xenon-on-graphite our value $l_0=41\pm 6$ yields a critical misfit of 0.029 ± 0.004 Å^{-1}. This agrees well with our measured value of 0.033 Å^{-1} shown in Fig. 3.

The misfit dependence of the rotation angle is shown in Fig. 3 for coverages $f=0.96$, 1.02, and 1.16. These data correspond to a temperature range of ~ 60 to ~ 120 K. All of the data were taken on cooling. Surprisingly, *no rotational transition* occurs on heating from the low-temperature commensurate phase, presumably due to the difficulty in nucleating the transition at lower temperatures. The dashed line in Fig. 3 is the prediction of Novaco and McTague[13] which ignores domain-wall effects. The dashed-dotted line is Shiba's theory[11] for a Cauchy solid. The solid line is a $\frac{1}{2}$ power law. Clearly, the xenon rotation is much smaller than predicted. Most likely, both the reduced orientation and the first-order transition back to the aligned phase at a misfit of ~ 0.089 Å^{-1} are nonzero temperature effects, which are omitted in the potential calculation presented in Ref. 11. Clearly, a microscopic theory, which is applicable at high temperatures, is strongly needed.

In conclusion, these experiments have clarified the phases and phase transitions which occur for xenon-on-graphite in the monolayer coverage regime. An elaborate sequence of phases occurs including reentrant aligned $\rightarrow$ rotated $\rightarrow$ aligned transitions. As noted above, there is currently no theory for this sequence. Based on the striped-phase conjecture of Ref. 5, Halpin-Healy and Kardar[3] have predicted the sequence of phases hexagonal incommensurate $\rightarrow$ stripe $\rightarrow$ bilayer with increasing coverage at low temperature. This clearly disagrees with the results reported in this paper and in Ref. 6. However, in Ref. 3 a positive wall crossing energy of 70 K was assumed in order to generate the striped phase. Quite possibly, this assumption is incorrect. Clearly, the theory for the overall phase diagram for this and related physisorbed systems needs to be readdressed in light of the results reported in this paper.

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