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Commensurate-incommensurate transition of Kr-Xe mixtures on graphite

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We report high-resolution x-ray scattering measurements of the commensurate-incommensurate transition of Kr on graphite which has been preplated with 0.1 monolayer of Xe. The Xe raises the transition pressure and produces a 31% range of pressures over which composite line shapes are observed. These results are discussed in terms of a solubility gap between commensurate and incommensurate phases.

The commensurate-incommensurate transition of Kr on graphite has recently attracted a large amount of experimental and theoretical attention.[1-6] The Kr-Kr interaction favors an interatomic spacing 6% compressed with respect to the array of adsorption sites on the graphite surface. At low coverages, the graphite modulation dominates, and the film has a commensurate $\sqrt{3}\times\sqrt{3}R30°$ structure. As the chemical potential is increased, the film compresses, evidently by creating an array of misfit dislocations between locally commensurate regions. The shift ϵ of the diffraction peak in the incommensurate phase varies with vapor pressure P above the critical pressure P_c according to the empirical relationship[1]

$$\epsilon = A\{T\ln(P/P_c)\}^{1/3} \ , \tag{1}$$

where T is the temperature in K and $A = 0.0134\ \text{Å}^{-1}$. Recent experiments place an upper limit of $0.017\ \text{Å}^{-1}$ (1%) jump in ϵ at the transition.[2,3]

Recently, Regnier, Bockel, and Dupont-Pavlovsky have presented thermodynamic measurements showing that adding small amounts of Xe raises the commensurate-incommensurate transition pressure.[4] The larger Xe atoms apparently dissolve in the adsorbed Kr film, where they stabilize the commensurate phase by decreasing the misfit between the natural lattice constant of the Kr film and that of the graphite substrate. While the use of Xe to shift the bare length of the adsorbate is an exciting prospect for further study of the commensurate-incommensurate transition, there are significant uncertainties about the microscopic state of such an adsorbed film. In order to clarify these issues, we have undertaken an x-ray scattering study of Kr-Xe films adsorbed on graphite.

Diffraction profiles were measured with Cu $K\alpha$ radiation from a rotating anode, and at the Cornell High Energy Synchrotron Source (CHESS), using 10.95-keV x-rays from the sagitally focusing A3 monochromator. For the synchrotron radiation experiments, the longitudinal resolution was $\sim 0.0012\ \text{Å}^{-1}$ half-width at half maximum (HWHM). This high resolution, obtainable with sufficiently high intensity only from a synchrotron radiation source, was necessary for studying line shapes at small incommensurability ϵ, an important feature of this work. The sample was a sheet of *ZYX* exfoliated graphite, in a transmission scattering geometry.

The experiments discussed here were performed by dosing the sample with Xe at a temperature of 130 K, which is high enough to insure its mobility.[7] The samples were then cooled to 84.5 K. At this temperature, the vapor pressure of bulk Xe is 0.02 torr; the submonolayer phase has a much smaller vapor pressure. Consequently, we can neglect the contribution of Xe to the vapor. Based on thermodynamic evidence,[8] one expects the state of an 0.1-monolayer Xe film to be coexisting gas and solid phases, with the gas having a density less than 5% of that of the solid. We searched for, and never detected, Bragg peaks with a lattice constant characteristic of pure Xe monolayers in both the rotating anode and the synchrotron radiation experiments. The absence of Bragg peaks at low coverages has been noted previously,[9] and may be an indication that the solid Xe forms clusters of characteristic size less than 50 Å, perhaps pinned by impurities on the graphite surface.

The Kr commensurate-incommensurate transition was then studied by admitting successive increments of Kr to the sample. This dosing procedure yields a metastable distribution of atoms on the substrate surface, as demonstrated by the data taken on a rotating anode shown in Fig. 1. In the upper panel, an x-ray scan after dosing, the film is a mixture of commensurate and incommensurate phases. After the sample is cycled to 130 K, the film is completely commensurate, implying that the available Xe has been better mixed into the Kr film, stabilizing the commensurate phase.

It is clear on purely thermodynamic grounds that the Xe is mixed into the Kr film in the commensurate phase, rather than being phase separated. P_c, the Kr vapor pressure at the commensurate-incommensurate transition, continues to increase with Xe coverage to 0.15 monolayer. If the system contained separate regions of Xe at the onset of the commensurate-incommensurate transition, increasing the Xe dose would increase the area covered by the Xe clusters, but would not change the properties of the Kr film, including P_c. We may conclude that up to this coverage, the Xe is at least partially dissolved in the Kr film. This argument was also noted in Ref. 4. It is possible that some Xe is

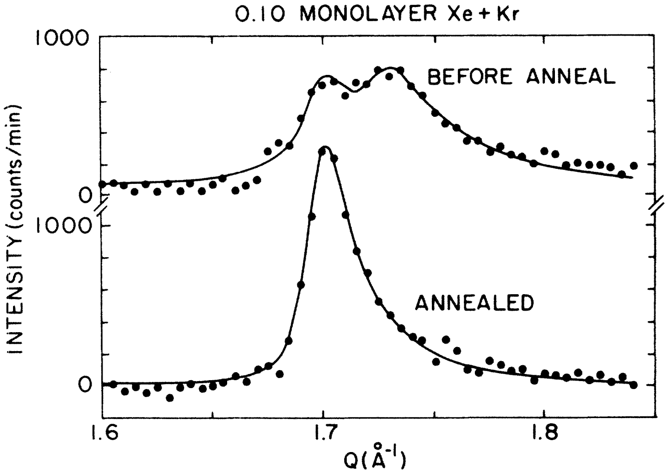

FIG. 1. Rotating-anode x-ray scans of $\sim$0.9-Kr monolayer on 0.1-Xe monolayer, before and after annealing at 130 K. $T=84.5$ K, $P=0.392$ torr (top), 0.395 torr (bottom). An empty cell background of $\sim$1500 counts/min has been subtracted. The curves show fits to powder-averaged line-shape models of commensurate (Gaussian), and mixed commensurate (Gaussian) and incommensurate (Lorentzian) phases, with 0.012-Å^{-1} HWHM resolution, as described in Ref. 2.

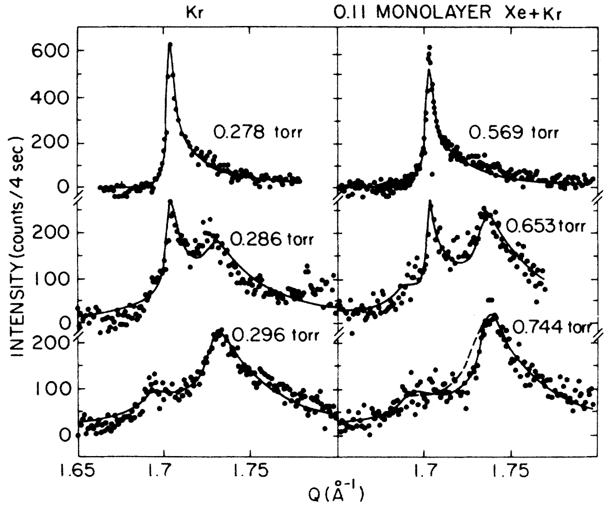

FIG. 2. X-ray scans in the immediate neighborhood of the commensurate-incommensurate transition, taken at CHESS. Empty cell background of $\sim$200 counts/4 sec has been subtracted. The commensurate-phase line-shape fits (curves in top panels) yield a correlation length of 2000 ± 500 Å. Curves through bottom panels are powder-averaged Lorentzian fits to incommensurate phase peaks with satellites, as discussed in Ref. 2. In the two center panels, the curves show a sum of the commensurate- and incommensurate-phase line-shape fits. The broken line in the 0.744-torr scan is the model of inhomogeneous broadening discussed in the text.

clustered at substrate impurities, in patches too small to produce measurable diffraction peaks.

High-resolution scans in the immediate neighborhood of the commensurate-incommensurate transition are shown in Fig. 2. These measurements were made on samples as they were dosed at 84.5 K. However, no change was detected in scans repeated after delays of a few hours, which implies that the samples were stable on the time scale of the experiment. Consider first the pure Kr scans. The diffraction line shape is that of a commensurate solid for pressures up to 0.278 torr. Between 0.278 and 0.296 torr, the diffraction scans show coexisting commensurate and incommensurate phases. For $P \geqslant 0.296$ torr, there is no trace of commensurate phase. The minimum incommensurability of a pure incommensurate phase peak is 0.0245 Å^{-1} = 1.4% for the 0.296-torr scan shown. The curve through the 0.286-torr scan is a sum of the line shapes of the 0.278- and 0.296-torr scans. The excess intensity around 1.72 Å^{-1} indicates that some of the crystallites have a smaller incommensurability than the 0.0245-Å^{-1} scan, demonstrating a degree of inhomogeneous broadening of the critical point. The same effect has been noted in previous experiments.[2] The range of pressure over which the coexisting line shapes occur is consistent with the minimum incommensurability through Eq. (1). The diffraction profiles from a sample preplated with 0.11 monolayer of Xe are similar, but the Kr pressure scale is vastly different. The transition starts at a pressure 2 times higher than the pure Kr sample, and a composite line shape is observed in the range 0.569 torr $< P <$ 0.744 torr, a 31% range of pressure. The shift of the critical point agrees with Regnier, Bockel, and Dupont-Pavlovsky,[4] but their vapor-pressure isotherm technique was insensitive to the coexistence of commensurate and incommensurate phases.

A priori it is not clear whether the large coexistence region is intrinsic to the mixed Kr-Xe film, or if some form of inhomogeneity is responsible for the effect.[10] For example, even if the substrate were perfectly uniform, inhomogeneities in the random distribution of Xe atoms on different regions of the graphite could yield a range of Kr transition pressures. Particularly in view of the 1.4% jump in lattice constant at the pure Kr commensurate-incommensurate transition, it is evident that some form of heterogeneity is playing a significant role in this experiment. The introduction of another species complicates the effect of a nonuniform substrate. For example, one might imagine that the Xe preferentially clusters about quenched impurities on the surface and influences the Kr commensurate-incommensurate transition through the length of Kr-Xe boundary.

The effect of inhomogeneity may be quantitatively modeled by using the width of the coexistence region to determine the width of the presumed distribution of critical points. At a specified vapor pressure, one can then use Eq. (1) to calculate the probability distribution of incommensurability, as in Ref. 2. The convolution of this distribution with the intrinsic line shape of pure Kr at this range of ϵ is shown as a broken line on the 0.744-torr scan. It is clearly broader than the experimental diffraction profile. If the Xe-doped sample had a distribution of substrate binding energies sufficient to account for the 31% range of transition pressure, the scan at the end of coexistence would have had this shape. Consequently, we can see that the enhanced range of coexistence between commensurate and incommensurate phases is intrinsic to the mixed system. We emphasize that the parameters in this model are determined entirely from the mixed Kr-Xe film, rather than being extrapolated from the pure Kr data. Of course, it is possible that the Xe tends to adsorb at specific sites; nevertheless, some fraction of the Xe is dissolved in the Kr, where it induces phase separation.

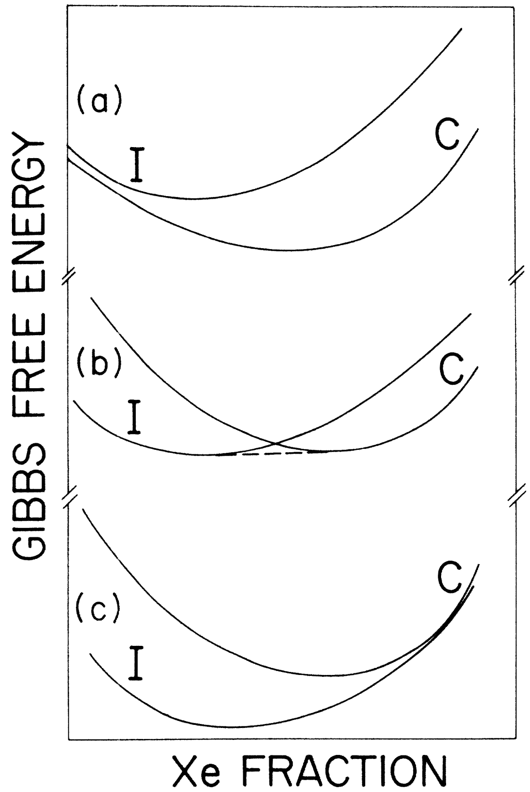

FIG. 3. Hypothesized Gibbs free-energy functions for commensurate (C) and compressed incommensurate (I) monolayers, as a function of Xe fraction. The vapor phase is neglected. Panels (a), (b), and (c) represent successively larger spreading pressure. The commensurate and incommensurate branches are different, reflecting the different symmetry of the two phases. The lattice constant is presumed to vary along each incommensurate curve. The broken line in panel (b) illustrates the fact that the minimum Gibbs free energy occurs for mixed commensurate and incommensurate phases.

This effect is easily understood in analogy with the solubility gap in binary alloys. For a range of Xe concentrations, the adsorbed Kr-Xe mixture is unstable to the formation of relatively Xe-rich and Xe-poor phases. The Gibbs free energy per particle as a function of Xe concentration for commensurate and incommensurate phases is sketched in Fig. 3, showing that coexisting commensurate and incommensurate phases can occur for a range of spreading pressure, and therefore Kr vapor pressure. According to this construction, there is not necessarily a connection between the minimum incommensurability ϵ observed in the pure and mixed systems.

It is of interest to compare the evolution of the diffraction peak shift ϵ in the incommensurate phase between pure Kr and Xe-doped systems. ϵ is plotted as a function of $\ln(P/P_c)$ in Fig. 4. For each run, we chose P_c at the center of the region of coexisting commensurate and incommensurate phases. The differences between the two sets of data are too small to be judged significant.

Previously, it has been shown that incommensurate Kr monolayers sufficiently close to the commensurate-incommensurate transition are in a disordered phase, characterized by broad diffraction peaks. The onset of this phenomenon is perhaps most clearly seen by considering the ratio of peak shift ϵ to peak HWHM κ. The inset to Fig. 4 shows this ratio as a function of ϵ for the two data sets, from which it can be seen that there is no major difference in the loss of long-range order between the pure Kr and the Xe-doped films. If the Huse-Fisher[5] description of the commensurate-incommensurate transition is correct, so that critical behavior is limited to the region where $\epsilon/\kappa \sim 1$, the expanded coexistence region precludes any statements about changes in critical properties with coadsorbed Xe.

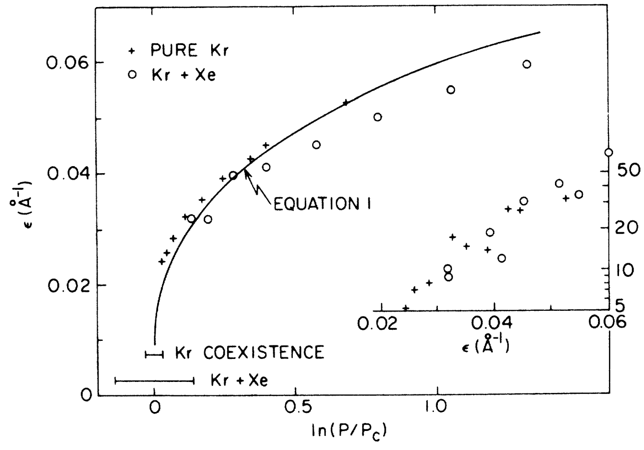

FIG. 4. Peak shift as a function of vapor pressure for pure Kr and Kr with 0.11-monolayer Xe, from line-shape fits to CHESS data. Inset shows ϵ/κ vs ϵ from the same data.

Summarizing our results, we find that addition of 0.1 monolayer of Xe shifts and broadens the commensurate-incommensurate transition of a Kr film. The large coexistence region is not due to film heterogeneity, but is an intrinsic feature of the mixed system.

We close with some remarks about a previous study of the influence of a second species on the Kr commensurate-incommensurate transition.[6] Nielsen, Als-Nielsen, Bohr, and McTague studied a Kr-D_2 mixture at a temperature of 40 K, driving the commensurate-incommensurate transition as a function of D_2 coverage. Their results were similar to those presented here, with coexisting commensurate and incommensurate phases observed for a range of D_2 pressures. In that work it was not possible to compare the transition between the mixed system and pure Kr at the same temperature as a check on the influence of phase separation on the coexisting commensurate and incommensurate line shapes. The results of the present work cast doubt on the assertion that the behavior of Kr-D_2 films may be generalized to the case of pure Kr monolayers.

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