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Synchrotron X-ray Study of Physisorbed Films of Mixtures of

Ar and Xe on Graphite

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Mixtures of Ar and Xe have been studied in most of the submonolayer region of the phase diagram (T, χ, ρ) , T = temperature, χ = chemical composition, ρ = fraction of a monolayer. The basic feature is a large tendency to form $\sqrt{3} \times \sqrt{3}$ commensurate alloys (Kr-like structures), but none of the commensurate nor of the incommensurate structures form a chemically ordered alloy at 11 K. Thus the 2D solid can be thought of as a solid consisting of particles of an average size. This allows us to study the commensurate-incommensurate phase transition driven by average particle size. The transition is indeed a sharp first order transition taking place through coexisting phases ($\tau_A = 1.64 \text{ \AA}^{-1}$ and $\tau_B = 1.703 \text{ \AA}^{-1}$), as was the case for the low temperature pure Kr-system.¹ Another interesting feature is the existence of well correlated liquid-like structures which preserve their correlation over a temperature range of 5 Kelvin or more. This unusual behavior is for chemical compositions where there is coexistence of a commensurate and an incommensurate solid at high temperature.

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The experiment was carried out at the synchrotron radiation laboratory HASYLAB/DESY in Hamburg at the storage ring DORIS running at 3.2 GeV with a typical current of 50 mA. The experimental setup and the sample cell, consisting of Union Carbide ZYX flakes, have been described earlier.² The wave vector resolution was chosen to match the coherence length of the graphite flakes, $L = 1600 \text{ \AA}$ (in a Gaussian description). The asymmetry of the Bragg diffraction was discussed by Warren.³ Tails to the Bragg scattering groups can come from algebraic long range decay.⁴ Huang scattering⁵ due to the strain field in a disordered alloy may also contribute to the tails.

The filling of the sample cell was prepared in the following way: first Xe was filled in the empty cell at $T = 132 \text{ K}$, thereafter the Ar was filled in at $T < 94 \text{ K}$, where the vapor pressure of the Xe is less than 10^{-2} torr. The Xe filling of 1 to 4 torr is therefore considered unchanged under the filling manipulation of Ar. After the filling the temperature was raised to $T = 110 \text{ K}$, allowing the film to stabilize.

Mixtures of argon and xenon have been studied earlier by isotherm measurements;⁶ they show that successive layers of xenon and argon do mix. Recent isotherm measurements⁷ on krypton, adsorbed on graphite with some pre-adsorbed xenon, report a stabilization of the commensurate phase. Our X-ray diffraction study is carried out for submonolayer coverages. Ar and Xe are well miscible, and coexistence of two incommensurate structures has not been observed. However, the $\sqrt{3} \times \sqrt{3}$ commensurate structure, one adatom per three graphite hexagons, is very common and coexistence of this structure and an incommensurate structure is one of the interesting features of this Ar-Xe two component system. Kr-Xe mixtures on graphite have these features also.⁸ The Gibbs phase rule becomes:

$$\text{"Degrees of freedom"} = 4 - \text{"Number of phases present"}.$$

Figure 1 shows a cut at $T = 11$ K in the (T, χ, ρ) phase diagram. The lines of the diagram are determined by the diffraction groups and by applying the lever rule on these. At a coverage of about $\rho = 0.6$ particles per 3 graphite hexagons, as the argon content is increased from 0% to 100%, first argon goes into solution in the xenon forming an incommensurate "Xe-like" structure whose lattice parameter changes with the argon content. Then at , about $\chi = 18\%$ Ar the film forms a coexistence of two structures, an incommensurate and a commensurate, of which the reciprocal lattice parameters are $\tau_{10} = 1.64 \text{ \AA}^{-1}$ and $1.703 \text{ \AA}^{-1}$. Their lattice parameters imply that they both are alloys with a not dissimilar composition. As the argon content is increased to about $\chi = 32\%$ only the commensurate structure is present, and for argon contents up to about 88% the alloy forms commensurate structures. The solid phases mentioned coexist with a dilute gas V in Fig. 1. In the coexistence triangle, the three phases defined by the corners coexist. It is incidental that the two upper corners are at the same coverages. The line separating the dilute gas from the coexistence regimes is only shown to illustrate the principle of the diagram, but its location is unknown. As the temperature is raised this line moves to higher densities and becomes the solid-liquid transition. There is probably no "quadruple point."

The first question raised for alloys of physisorbed films is that of the possibility of an order-disorder phase transition. The ordered structure with the smallest unit cell on the hexagonal lattice is an ABB structure: the B atoms form a honeycomb net with the A atoms in the centers. The unit cell of the structure contains two B atoms and one A atom. The first Bragg scattering is thus expected at $\tau_{\text{com.}}/\sqrt{3}$. Mixtures of Ar and Xe in the composition ratio of 2 to 1 and 1 to 2 were first studied. These form $\sqrt{3} \times \sqrt{3}$

commensurate structures, the latter with a small incommensurate coexistence. A Lennard-Jones estimate of the binding energy difference per atom between the ordered and disordered phase gives

$$\Delta E = (2E_{AB} - E_{AA} - E_{BB})/3 \approx -30 \text{ K}.^9$$

By the triangular Ising model^{10,11} the transition temperature can be estimated to be $-1.4 \times 3/4 \times \Delta E \approx 32 \text{ K}$. However, at 11 K there was no scattering peak at $1.703/\sqrt{3} \text{ \AA}^{-1}$ within the standard-deviation of our measured intensities which were an order of magnitude smaller than the expected peak height. The coexisting incommensurate alloy was also checked for ordering in a window at $\tau_{10}/\sqrt{3}$. The Lennard-Jones estimate of the binding energy difference per atom of the ordered and disordered phase when $\tau_{10} = 1.64 \text{ \AA}^{-1}$ is $\Delta E \approx -7 \text{ K}$. The films show the same lack of ordering as the commensurate films. Summarized: films with Ar contents of $\chi = 24.9\%$, 33.2% , 39.7% , 50.0% , 59.3% , 66.7% , 68.6% , 70.5% , and 76.5% were checked for ordering, but all lacked ordering at $T > 11 \text{ K}$.

Figure 2 shows the diffraction groups around (10) Bragg spot at $T = 11 \text{ K}$ as function of chemical composition, which is given on the figure as a circular disk average particle size ν , by a nearest neighbor Lennard-Jones estimate

$$\nu = (\rho_{Ar} \pi (0.56 \sigma_{Ar})^2 + \rho_{Xe} \pi (0.56 \sigma_{Xe})^2) / \rho_{tot},$$

where $0.56 = 2^{-5/6}$, $\sigma_{Ar} = 3.40 \text{ \AA}$ and $\sigma_{Xe} = 4.10 \text{ \AA}$.⁹ The respective Ar-contents in the film are 10.4% ($16.0 \text{ \AA}^2$), 25.0% , 33.2% , and 59.3% .

As the average particle size is increased the film goes from a pure commensurate state through a coexistence region to a pure incommensurate state. The structures coexist with their vapor, therefore, in the coexistence region Gibbs phase rule leaves only one degree of freedom, so that the chemical potentials are linked to the temperature. The average particle sizes of the solids in the three phase coexistence region are determined by the positions of the triangle's upper corners in the phase diagram. The numbers given by the Lennard-Jones estimate are approximately $14.70 \text{ \AA}^2$ for the commensurate and $15.84 \text{ \AA}^2$ for the incommensurate structure. The geometrical size of the commensurate structure is $14.25 \text{ \AA}^2$. A first order jump of the above $1.14 \text{ \AA}^2$ leads to a jump in the reciprocal lattice vector of $0.065 \text{ \AA}^{-1}$, which is close to the observed jump of $0.068 \text{ \AA}^{-1}$. From this we suggest that in the coexistence region the commensurate structure may have an average particle size close to the one that ideally fits the commensurate lattice. This feature may be peculiar to the two component system. It might be that the here observed first order jump in density is larger than it would be in a hypothetical one-component film, where the particle size is varied.

Note: in a one-component particle size driven commensurate-incommensurate phase transition one would not see coexistence of these two phases for a submonolayer coverage, but dilute gas coexisting with either of the two.

Figure 3 shows the melting of a commensurate alloy with 60% argon and 40% xenon; coverage $\rho = 0.81$ particle per 3 graphite hexagons. The melting is first order going through a coexistence region. It is similar to melting of commensurate submonolayer Kr-films,¹² but the correlation of the liquid is stronger. Using the same liquid droplet model which has been applied to the

liquid phase of adsorbed Xe^{13} and Ar^2 we find for the Lorentzian correlation lengths $\xi(77.21 \text{ K}) \approx 150 \text{ \AA}$, $\xi(78.34 \text{ K}) \approx 130 \text{ \AA}$ and $\xi(85.04 \text{ K}) \approx 80 \text{ \AA}$. It is interesting to note that the strong correlation of this liquid is preserved at temperatures more than 10 K above the melting point. It is possible within the phase rule to interpret the 64.15 K structure as coexistence of two commensurate structures. However, we see no mechanism to govern this in disordered commensurate alloys.

Figure 4 shows the melting of a one to one argon-xenon alloy, coverage $\rho = 0.73$ particles per 3 graphite hexagons. This particular alloy forms coexistence of a commensurate and an incommensurate structure at high temperature, and the two structures melt at the same temperature.¹⁴ This has the important consequence for the phase diagram that for argon-xenon alloys the commensurate-incommensurate phase transition stays first order all the way to the melting line. At 79.83 K the Lorentzian correlation length is about 300 $\text{\AA}$, using the same model as above.

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14. This happens only for the particular compositions (χ) and coverages (ρ) which are given by the V-points of the X+C+V coexistence region of the phase diagram (see Fig. 1).

Figure Captions

Fig. 1: A submonolayer cut at $T = 11$ K in the (T, χ, ρ) phase diagram, χ = argon content in the argon-xenon film, ρ = coverage, number of particles per 3 graphite hexagons.

A = "Argon-like"

C = $\sqrt{3} \times \sqrt{3}$ commensurate structure

V = vapor

X = "Xenon-like"

Fig. 2: The figure shows the diffraction groups from argon-xenon films at 11 K and how the commensurate-incommensurate phase transition goes through coexistence as a function of the chemical composition, given on the figure as a Lennard-Jones estimate of a circular disc average particle size.

Fig. 3: The figure shows the diffraction groups from the melting of a commensurate alloy, $\chi = 40\%$, $\rho = 81\%$. The melting takes place through coexistence of a commensurate solid and a liquid, thus it is a first order transition. The sharpness of the (10) Bragg spot from the solid is given by the experimental resolution. The correlation of the liquid at 77.21 K is about 150 Å.

Fig. 4: The figure shows the diffraction groups from the melting of an argon-xenon film, where there is coexistence of a commensurate and an incommensurate structure up to a temperature where they both melt. Argon content is $\chi = 50\%$ Ar, coverage $\rho = 73\%$. At $T = 79.83$ K the correlation of the liquid is about 300 Å.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.