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Synchrotron X-Ray Diffraction Studies of Phase Transitions in Physisorbed Monolayers of Rare Gases on Graphite

Jacob Bohr

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January 1984
SYNCHROTRON X-RAY DIFFRACTION STUDIES OF PHASE TRANSITIONS IN PHYSISORBED MONOLAYERS OF RARE GASES ON GRAPHITE

Jakob Bohr

Abstract. This study is an investigation of phase transition in monoatomic layers adsorbed on graphite. Such effects can be considered physical realizations of two-dimensional systems. The experimental technique used is synchrotron X-ray diffraction. A scattering geometry which utilizes a position-sensitive detector is developed and used for the experimental studies discussed below and carried out at the DORIS storage ring at Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany. Systems which have been investigated include the commensurate-incommensurate phase transition in krypton monolayer. By adjusting the spreading pressure in the krypton layer by means of a coadsorbent deuterium gas it has been unambiguously demonstrated that at low temperatures the phase transition is of first order. A melting study of incommensurate argon monolayers demonstrates an experimental verification of the possibility for having a continuous melting transition in two-dimensions. Mixtures of two-components have been investigated for their phases. No (chemical) order-disorder (continued on next page)
transition is seen. A discussion is given on this lack of a chemical order. This lack is utilized to study the commensurate-incommensurate phase transition driven by average particle size. Finally, a special low-temperature phase is identified in a xenon monolayer which is diluted with freon.

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1. INTRODUCTION WITH A SUMMARY OF THE X-RAY DATA FOR ARGON ON GRAPHITE

The aim of the present study is to investigate monolayers of gases adsorbed on graphite. This is motivated by considering these gases as physical realizations of two-dimensional model systems. Emphasis is given to phase transitions which are driven by fundamental topological excitations such as the unbinding of dislocation pairs, domain walls, etc. For continuous phase transitions the description of the critical behaviour usually involves only a few characteristics, e.g. some important exponents. The gain from this reduction in the description is that the critical characteristics of a system are shared with a large group of different physical systems, which have only a few fundamental properties in common such as symmetry, the number of components in the order parameter, and the dimensionality of the space where the physical interactions take place. This is the hypothesis of universality. Often distinctly different predictions have been given for the physics of two dimensions than for those of three dimensions. Moreover, theoretical models may be more easily treated in some dimensions than in others; One famous example is the exact solution of the two-dimensional Ising model given by Onsager (1944). The technology of solar cells, thin films, and coating and of catalysis rests on surface properties. There is thus a strong motivation from both fundamental and applied science for studying two-dimensional physics.

The experiment that has been carried out is a study of physisorbed films, typically of rare gases on graphite. High-intensity X-ray diffraction is used to probe the correlation of the two-dimensional matter which is constituted by the adsorbed films.

As an illustration, I shall summarize the diffraction study of a free-floating argon monolayer on graphite. The expression "free
floating" refers to translational and rotational freedom of the argon film with respect to the graphite substrate. This could be the case if the hexagonal two-dimensional lattice of the solid argon monolayer is sufficiently incommensurate with the graphite lattice. Melting studies of two-dimensional matter have been stimulated by the idea put forward by Kosterlitz and Thouless (1972), in which the melting can be continuous. Because of the lack of the possibility for having usual long-range order in two dimensions, Kosterlitz and Thouless suggested a different kind of long-range order. A system is said to have topological long-range order so long as the system can resist a shear stress (topological long-range order is now called quasi-long-range order). A melting transition into a state takes place where the system cannot resist a shear stress. It was pointed out that the existence of one free dislocation destroys any topological long-range order. Furthermore, the proposed mechanism for the melting was taken to be the unbinding of dislocation pairs. In 1967 Nobarro put forward analogous ideas for melting in three-dimensions. The theory of two-dimensional melting was refined by Halperin and Nelson; (refer to paragraph 2).

Experimentally, one measures the line profile of a Bragg spot (rod) in this study, and in most cases the technique restricts us to the first Bragg spot. In the course of time, the measurement has been performed at three different experimental set-ups. Figure 1.1 shows the (10) Bragg profiles from solid argon films of submonolayer coverages (the measure for coverage is given in paragraph 3) taken at a) the rotating anode at Risø, b) the DORIS storage ring in Hamburg, and c) the wiggler line VII-II at the SPEAR storage ring at Stanford. By eye, one can see that the synchrotrons enable us to resolve the Bragg spots in sharper detail. An account for the skewness (Warren profile) of the Bragg spots is given in paragraph 5. The experimental resolution for the three measurements allows for studies of coherence over lengths of 300 Å, 1200 Å and 10000 Å, respectively; however the graphite substrate sets an upper limits for this at about 1600 Å.

The intensity needed in this experiment is due not only to the few atoms available for scattering, and the poor X-ray scattering.
Fig. 1.1. The (10) Bragg profiles from solid argon films of submonolayer coverages $\rho < 0.93$. Top: measured at the rotating anode at Risø. Middle: measured at the DORIS storage ring in Hamburg. Bottom: measured at the SPEAR storage ring at Stanford.
properties of argon, but also to the large multiple scattering background which comes from the graphite powder. In addition, bulk graphite reflections are present in the background. Figure 1.2 shows the non-background subtracted diffraction measurement from a solid argon monolayer (\(\rho = 0.9\)) taken at Stanford. Note the height of the argon signal relative to the one of the (002) graphite reflection. Figure 1.3 (data from Hamburg) shows a series of background subtracted (10) Bragg peaks from a submonolayer argon film in the melting region. The continuous broadening of the Bragg profile shows that the transition is continuous, or
that a possible first-order jump is smaller than our sensitivity, which comes from a combination of the experimental resolution and the signal to noise ratio. The curves in Fig. 1.3 are calculated in accordance with the prediction of the Kosterlitz-Thouless-Halperin-Nelson theory (see paragraph 2). This infers that the observation is not in opposition to the KTMN theory. In order to experimentally elucidate the continuous behaviour of the melting of the argon film, melting studies of a submonolayer xenon film on graphite were carried out in the same experimental
configuration with the same graphite substrate. Rounding effects, such as those from possible substrate heterogeneities, will thus be equally important in both measurements. Figure 1.4 shows the disappearance behaviour of the (10) Bragg spot with increasing temperature. For a submonolayer xenon, the peak intensity falls to zero abruptly, within 0.02 K. In agreement with literature (Birgeneau et al. [x-ray], Thomy et al. [adsorption isotherms], and Butler et al. [heat capacity]), this is interpreted as first-order melting.

Fig. 1.4. The figures show the (10) Bragg peak disappearance with increasing temperature for adsorbed submonolayers of xenon and argon on graphite. a) and b), and d) and e) show intensities and positions of the Bragg peak, and c) and f) the widths of their left-hand sides (refer with paragraph 5).
To end this introductory discussion, the difference in the behaviour of argon and xenon films in terms of their phase diagrams is illustrated in Fig. 1.5. Xenon has a triple point where argon has a critical end point. Heiney et al. found that at higher densities of the xenon films (well above one monolayer) they also exhibit a continuous melting. It is not easy to understand why argon and xenon behave qualitatively differently. This may be the influence of the substrate-to-adsorbate size implying that the film cannot be considered completely free floating, which is in agreement with low-energy electron studies by Shaw et al. of a fluid argon monolayer which showed rotational epitaxy. Indeed Novaco and McTague have pointed out that incommensurate structures, which are not infinitely rigid, may show rotational epitaxy.

Physical systems other than the argon on graphite included in this study are the commensurate - incommensurate phase transition of a krypton layer on graphite and various two-dimensional binary alloys. For the latter a search was made to find a chemical order-disorder transition; no such transition was found. A discussion of this lack of a transition is given on the basis of the Ising model. Finally, Nelson's theory of trapped dislocations in a dilute system, which would point to the possibility for a reentrance to a hexatic phase at low temperature, has motivated investigations. A xenon monolayer diluted with freon particles was found to exhibit a distinct low-temperature phase, however it is not likely to be a hexatic phase.

First, we shall briefly outline the different kinds of order in two dimensions and of related phase transition; then we shall describe the more technical prerequisite as the substrate, its cryogenic, and the X-ray source. An account of the developed scattering geometry which is utilizing a position-sensitive detector is also given.
Fig. 1.5. The phase diagrams for xenon and argon monolayers on graphite. The symbols are: $\rho$: coverages. G: 2D gas, F: 2D fluid, L: 2D liquid. IS: Incommensurate solid, and T/TTP(3-D): the temperature in units of the triplepoint temperatures of the respective 3D solid, 84 K and 161 K for Ar and Xe. The X in the xenon diagram corresponds to the data in Fig. 1.4. The triangles in the argon diagram correspond to determined transition temperatures.
REFERENCES


2. ORDER AND PHASE TRANSITIONS IN TWO DIMENSIONS

In the thirties Peierls and Landau gave their arguments that true long range order can not exist in two dimensions, at a finite temperature a conception later refined by Mermin and others. By true long range order we mean that the pair-correlation function has an asymptotic value different from zero.

\[ \langle \rho(\mathbf{r}) \rho(\mathbf{r}') \rangle \sim \cos(\mathbf{q} \cdot \mathbf{r} + \phi) \]

\( \mathbf{r} \) position vector
\( \rho \) density function
\( \mathbf{q} \) characteristic (reciprocal) vector
\( \phi \) arbitrary phase

It is well known from calculus of limit that functions can be grouped into congruence classes, defined on the relative behaviour of two functions in the limit of the arguments going to infinity. During the early seventies the idea of the dissociation of dislocation pairs by Kosterliz and Thouless and independently by Feynman clarified the nature of the 2D correlation functions and threwed light on possible phase transitions. Although no true long range order exists, a state of two-dimensional matter, where the pair correlation function have algebraic-asymtotic behaviour, is possible, and a transition into a matter, where the pair correlation function have exponential-asymtotic behaviour must exist. It is common terminology to associate the term "quasi long range order" with the phases where the pair correlation function has algebraic decay.

Another correlation function turns out to be of high importance for the topological features of the 2D systems. That is the one, that describes the angular correlation
\[ \exp \{ i \gamma \langle \theta(\vec{r}) - \theta(\vec{r}') \rangle \} \quad (\gamma = 6, \text{ for triangular structures}) \]

\( \theta(\vec{r}) \) is the directions of bounds between nearest neighbour.

This can be derived from the four particle correlation function. 2D matter with quasi long range order has true long range angular correlation. Matter with short range positional order can have either quasi long range angular or short range angular order, the former case describe the hexatic and the latter, the isotropic fluid phase. True long range order in two dimensional systems can be induced by an applied potential. This is the case for commensurate structures, where the 2-D lattice structure is imposed by an underlying three dimensional lattice, having long range order. In Table 2.1 some different possibilities are given.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Positional order</th>
<th>Bond orientational order</th>
<th>Structure factor ( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commensurate</td>
<td>Long range</td>
<td>Long range</td>
<td>( \delta(\vec{r}-\vec{r}_1) )</td>
</tr>
<tr>
<td>Incommensurate</td>
<td>Quasi long range</td>
<td>Long range</td>
<td>(</td>
</tr>
<tr>
<td>Hexatic phase</td>
<td>Short range</td>
<td>Quasi long range</td>
<td>( 1/[1/\xi^2 + (\vec{r}-\vec{r}_1)^2] )</td>
</tr>
<tr>
<td>Isotropic fluid</td>
<td>Short range</td>
<td>Short range</td>
<td>( 1/[1/\xi^2 + (\vec{r}-\vec{r}_1)^2] )</td>
</tr>
</tbody>
</table>

The idea of The Kosterlitz-Thouless-Halperin-Nelson dislocation unbinding melting mechanism is as follows: assume a two dimensional structure with one dislocation. An example on a square net is given in Fig. 2.1a.

* For simplicity, factors which permits for comparison of intensities is omitted. Moreover, for the hexatic phase an exponent of \( 1-\eta_h/2 \) is missing.
Fig. 2.1. a) An example with one dislocation on a square net, b) with two dislocations. Note that the strain field much easily cancel in the b) than in the a) figure, when infinity is approached.

The energy of this dislocation is

$$E_{\text{dis}}(L) = \frac{\eta a^2 (1 + \nu)}{2\pi} \ln \left( \frac{L}{a} \right)$$

$L = \text{characteristic length scale for the size of the system}$

$a = \text{lattice spacing}$

$n = \text{rigidity modulus}$

$\nu = \text{Poisson's ratio}$

which diverges logarithmically with the size of the two dimensional lattice. Introduce now a dislocation with an opposite Burger's vector in the 2-d solid (see Fig. 2.1b). It then becomes clear that the strain fields in the long distance cancel. An inequality for the energy of a pair of dislocations by the distance $d$, separated can be given, because a numerical constant $K$ must exist for which
$$E_{\text{pair}}(d) \leq 2K E_{\text{dis}}(d) = \frac{Kna^2(1+\tau)}{\pi} \ln(d/a)$$

Actually the energy of a pair is proportional to the logarithm of the distance between the two dislocations. At any finite temperature there will in this way be a certain number of pairs of dislocation in the 2-d solid. Consider the entropy of a pair of dislocations, i.e. the number of configurational possibilities. This is

$$S_{\text{pair}}(d) \sim k_B \ln \frac{2\pi d}{a},$$

$k_B$ is Boltzmann's constants.

Note, that this has the same functional form as the energy, it goes as the logarithm of the above distance $d$. This allows the free energy at a certain temperature to be independent on the length scale, i.e. a phase transition from a situation with bound dislocation pairs to a situation with free dislocations must appear and there need not be a jump in the free energy.

The transition temperature $T_m$ for this higher order phase transition can as outlined be estimated to be (Kosterlitz and Thouless)

$$T_m = \frac{na^2(1+\tau)}{4\pi k_B}$$

The presence of free dislocations breaks the quasi long range order. In the high temperature phase the pair correlation function decays exponentially. The length scale of the exponential decay is predicted by the theory of Halperin and Nelson to have a unusual temperature behaviour.

$$\xi = \xi_0 \exp \left\{ \frac{b}{(T/T_m - 1)^{0.369}} \right\}, \quad b = \text{constant}$$

$\xi$ = pair-correlation length, $T_m$ = melting temperature.
Recently Greif et al. has shown that this renormalisation group calculation only hold for a narrow region above the transition. They claim the extremeness in region width of one 1/1000 of a Kelvin. However, as indicated the melting study of Ar-monolayers, and as has been found by Heiney et al. for the melting of "well completed" Xe-monolayers, there seems to be a remarkaole stability of this relation extending over several degrees. Halpern and Nelson showed that above this transition the melted 2D system is by no way isotropic. It has in fact "quasi long range" orientational order. And one transition more is needed in order to enter into an isotropic fluid. They suggest that this transition could be dissociation of the dislocations into disclinations. A disclination is a point defect where the coordination number for a particle in the 2D lattice is one too high or one too low relative to the undistorted lattice number. The intermediate state with short range positional order and "quasi long range" orientational order is conventionally called a hexatic phase.

The experimental situation is slightly different as there will always be a directional field, imposed by the substrate. Thus a phase transition between the hexatic phase and the highest temperature phase which has some substrate induced orientational order need not exist.

For some adsorbates which have an adsorption potential which minimizes at a distance close to one of those of the honeycomb lattices of the graphite surface, it may be more energetically favourable to take up a structure which is commensurate with the graphite. Such a system is krypton on graphite. Krypton makes a structure, where the atoms is located above every third of the graphite hexagons. This is the $\sqrt{3} \times \sqrt{3}$ structure, (eventually see Fig. 7.1). Adsorbates like freon can take up other commensurate structures, like the $2 \times 2$ structure. Structures which are incommensurate, but with lattice parameters still close to that of a commensurate structure, will locally rearrange their atoms to a locally (almost) commensurate situation, and thus the films will consist of domains, separated by walls, in an ordered pattern. For islands of $\sqrt{3} \times \sqrt{3}$ structure, the zero temperature domain pattern is either striped or hexagonal. Note, that there
are three commensurate sublattices corresponding to the three
equivalence sites of the $\sqrt{3} \times \sqrt{3}$ adsorbate structure, the A, B,
and C-lattice. Villain and Bak showed that the domain-wall
domain-wall interaction fall off exponentially with distance.
Thus for an almost commensurate structure the wall interaction
become unimportant. Whether or not the domain configuration is
striped or hexagonal is determined by the wall crossing energy
W. If W is negative the overlayer will form a hexagonal super­
structure with a first order transition to a commensurate struc­
ture. If it is positive the overlayer will form a striped con­
figuration, and the commensurate incommensurate phase transition
may be of higher order. At higher temperature both Villain and
Coppersmith has pointed out that the entropy related to the
hexagonal domain wall picture may be large enough to create a
system of fluid like domain walls, and these can break down the
long range order in the layer, thus introducing a new phase in
the transition region. In this way the transition takes place
through an intermediate structure and the transition can be of
either order.

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3. GRAPHITE AS A SUBSTRATE

Graphite has a hexagonal lattice structure (see Fig. 3.1) with an extremely strong inplane binding. Each carbon atom is bound by a covalent binding to the three nearest neighbour carbon atoms in the honeycomb net. The much weaker out-of-plane binding is basically due to van der Waals forces. For graphite this has the consequence that it is likely to have a large inplane surface area, the (001) surface. Therefore, graphite is a useful substrate for adsorbing studies, on which many adsorbents, rare gases, oxygen, simple molecules, will physisorb (van der Waals interactions) at temperatures below 200 K. In addition, the area available for adsorption can be many-doubled relative to the bulk volume by a chemical exfoliation. A two-stage process involving first the creation of an intercalate layer structure
compound from the graphite, then exfoliated by fast heating, creates almost only (001) surfaces. This is so for the reason that the graphite breaks along the planes of intercalation (see Fig. 3.2).

Fig. 3.2. A schematic drawing of exfoliated graphite structure.

Perfect crystals of graphite are formed very rarely and are almost exclusively derived from natural sources; some small ones are found in blast furnaces as a byproduct. Instead, the starting point is a mosaic crystal with a prepared (001) orientation (0.3 degree for ZYX graphite). This type of graphite has a specific gravity of about 2.2 g/cm³. The exfoliated product is commercially available, such as Grafoil, and ZYX, both Union Carbide Corporation products. They have specific gravities of 0.74 and 0.44 g/cm³, respectively. On comparing these specific gravities with that of graphite we conclude that the materials have 66 vol% or 80 vol% cavities, respectively. This allows easy access for the adsorbent gas to reach the small surfaces inside the material. As for the mosaic crystal the exfoliated graphite has a prepared (001) orientation (FWHM = 18°) for ZYX graphite in a Gaussian description.

Two parameters are important. These are the length scale of the graphite surfaces, and the total area available for adsorption. The larger the ideal islands of the surface area are the longer the coherence lengths in the adsorbed monolayers that can be studied, is. In addition the outer boundary condition for the
adsorbed layer itself, i.e. the actual shape of the 2D adsorbed layers, will be of lesser importance. In an adsorbing material with a large ratio of surface sites relative to its spatial extension, the small pieces of graphite giving rise to the adsorption areas must of necessity be thin. They are therefore likely to be coherent over a shorter length. GRAFOIL has an internal coherence length of about 130 Å, ZYX of about 1600 Å. But the ZYX has an area for adsorption which is a factor of about 50 lower than that of GRAFOIL (20 m²/g). This loss in adsorbed atoms to scatter can be compensated by use of a stronger X-ray source, i.e. a synchrotron source.

The adsorption surfaces have the honeycomb structure, the inplane structure of graphite. There is no rearranging of the carbon atoms in the surface layer (no reconstruction).

The sample cell is constructed as shown in Fig. 3.3.

The ZYX flake is cut into strips and stacked in the frame F. This allows the principal plane of the graphite to lie in the scattering plane, which was the geometry chosen. Because of the large number of cavities in the ZYX flakes they behave much like a marshmallow; this was utilized by constructing the frame slightly too small in the direction of exfoliation. First of all this assures good thermal contact. Secondly, this allows the frame with the graphite plate as a unit by itself to be baked in the baking oven in the metallurgy department at Risø, and in situ handled in a glove box with an Ar-atmosphere. Inside the glove box, such handling as placement of the ZYX flakes into the frame would be very difficult because of the clumsy gloves. The frame itself was made by reactor grade graphite. Later it was replaced by a stainless steel frame.

The frame with the ZYX was then placed in the main part of the sample chamber, a copper-made circular disk. On each side a beryllium window of thickness 0.2 mm was clamped with an indium seal by two stainless steel rings. It is essential that the windows are clamped at the same time from each side, as otherwise the central part of the cell, the copper part, would deform, and
the indium packing would then very likely leak. A small capillary tube, diameter 1 mm, is connected through the copper part to the valve V1, which is always kept at room temperature, sitting outside the cryostat.

Figure 3.4 shows the sample cell placed in the cryostat, which is a two-cycled Displex from Air Product Inc., the gas handling system valves, and the Baratron pressure head. The pressure head is part of a standard volume. The idea is then to fill this standard volume to a measured pressure, and then to open the valve V1 to
the sample and let gas suck into it; then valve V1 is closed and the pressure in the standard volume is then measured. This clearly controls the amount of gas in the sample cell in the ideal gas limit, and enables the filling of the cell to be measured in units of torr x standard volume. The filling of gas has to be done at a temperature for the sample cell that is high enough to avoid bulk condensation at the pressures at which we operate, always below 10 torr. It should be noted that at any time the degassing rate was negligible, and that whenever a filling was prepared the standard volume was flushed from the gas cylinder.
In measuring isotherms it is important to ensure pressure equilibrium between the sample volume and the standard volume. The pressure must be measured with the valve VI open, but the gas amount in the sample cell is with VI closed. To let this be a consistent systematic error (~ 0.01 torr) of the result, the valve VI was always opened two full turns, when the pressures were measured. The making of an isotherm measurement is a time-consuming task. For a standard isotherm (Fig. 3.5) argon was chosen over krypton due to its faster equilibrium time. This is partly due to the lighter mass of Ar, but more important because there is no commensurate-incommensurate phase transition in the argon monolayer. A temperature where the argon layer is liquid was chosen to have a reasonably short equilibrium time.

![Fig. 3.5. An argon isotherm; the circles are for increasing pressure, the triangles for decreasing pressure. Below is given the dead space subtracted isotherm, that is the one which scales proportionally with the available area for adsorption.](image-url)
Figure 3.5 shows a standard isotherm. The open circles and squares are measured for increasing and decreasing pressure, respectively. The small hysteresis is caused by the lack in attainment of the equilibrium pressure. For any 3D vapour pressure of a monolayer a certain amount of the gas in the cell will be in the 3D gas state. This is due to the "dead space". The line at the bottom of Fig. 3.5 shows the amount of gas in the dead space. The isotherm corrected for dead space is also shown in the figure. The vertical part of this isotherm corresponds to a thermodynamic situation in the film on the graphite, where its vapour pressure

![Graph](image)

**Fig. 3.6.** Helium measurement of the dead space as function of temperature. Note that the ordinate is given as dead space x temperature, this is because a simple model which divides the dead space into a sample volume and a valve volume will give a straight line.
changes very slowly with filling, i.e. the number of atoms in the film, which means that the chemical potential \((T \times \ln P)\), ideal gas limit) is not changing. This occurs when the film builds up the first and the second monolayer. The strong increase in vapour pressure happens when a layer begins to be complete. The spreading pressure in that layer is increased strongly by adding more atoms.

The dead space was determined by a helium isotherm measurement. At this temperature there is no adsorption of He on the graphite, and all the gas is in the gas phase. The dead space can be measured for a number of temperatures. In Fig. 3.6 the "dead space" vs temperature versus temperature is plotted. A simple model is to consider the dead space to be divided into a volume at room temperature (the valve volume), and a volume at sample temperature. The points on the figure should then lie on a straight line. This is used to interpolate the dead space measurements.

The absolute calibration of filling scale relative to one completed monolayer was made by a diffraction measurement of Kr monolayers. At submonolayers coverage, Kr monolayers take up the \(\sqrt{3} \times \sqrt{3}\) structure. This corresponds to one krypton atom per 6 surface carbon atoms. As the coverage is increased further the krypton undergoes a transition to a denser monolayer. At low temperatures this transition is first order with a jump in the lattice constant. Over a range of coverages, therefore, coexistence of the two structures is present, and a lever rule applies between these. The onset of this coexistence regime is used for defining one completed monolayer on the monolayer scale for all of the diffraction experiments involved in this work. The actual krypton measurements are shown in Fig. 3.7. Figure 3.8 shows the peak intensity of the commensurate structure, the kink on the curve thus defines the filling equal to filled monolayer.

Note that this does not necessarily mean that this definition of a monolayer corresponds to a number of atoms in the just completed monolayer defined equal to 1 per 6 graphite atoms. There
Fig. 3.7. Diffraction groups of the krypton commensurate-incommensurate phase transition given as function of coverage in units of torr x standard volume (torr units). In this way the monolayer scale can be defined.
Fig. 3.8. The scattered intensity at $Q = 1.703 \text{ Å}^{-1}$ (the commensurate position) as function of coverage. The kink at the curve is taken to correspond to one filled monolayer.

may be a number of vacancies in the krypton monolayer, or there may be a number of interstitials. There may also be a few particles in the second layer. The study of the nitrogen phase diagram showed that its commensurate-incommensurate phase transition from a $\sqrt{3} \times \sqrt{3}$ commensurate nitrogen monolayer to a uniaxial compressed phase, at low temperatures, takes place at a filling 20% larger than that of the krypton.

The density scale for the argon measurements and the freon measurements also has some discrepancies. For the argon measurements we found that a completed monolayer of argon would have 9% vacancies compared with krypton. For the freon study a phase transition took place at a coverage 76% of a completed 2x2 structure when this is taken to be 3/4 of the number given by the Krypton standard. Both of these numbers may be incorrect, as we
later found that the dead space of this cell with a graphite frame around the ZYX flakes behaved peculiarly with temperature, as seen in Fig. 3.9. Suppose that the graphite frame did cause some adsorption by itself. Such an adsorption would probably be both gas and temperature dependent, thereby making systematic errors on the constant density lines in the phase diagrams. When the graphite frame was replaced by one of stainless steel, and the ZYX graphite flakes were rebaked, the dead space as function of temperature behaved as in Fig. 3.6. The nitrogen density scale was remeasured and the onset of the commensurate-incommensurate transition indeed decreased - from 1.4 to 1.2 of completed

Fig. 3.9. The dead space behaviour with the graphite frame surrounding the ZYX graphite. Compare with Fig. 3.6 where a stainless steel frame was installed.
(krypton) monolayers. The argon and the freon scales still have to be remeasured. The fact that the (01) diffraction peak, from both a commensurate Kr and an incommensurate Xe monolayer, showed no deterioration in their sharpness when either frame was in use, assured us that no surface contamination of the ZYX flakes had occurred. Apart from the uncertainties in the absolute filling, relative fillings could be determined with an accuracy better than 2%.

REFERENCES


4. THE SYNCHROTRON AS A SOURCE OF X-RAYS

In this section I shall briefly refer to the type of X-ray sources that are important in this diffraction study. The work was initiated on the rotating anode at Risø and continued at the storage ring DORIS (\(R = 12.12\) m, \(E = 3.65\) GeV) in Hamburg.

In conventional X-ray generators the photons are created in a metal target which is bombarded by accelerated electrons. The emitted X-ray spectrum has two components: (a) bremsstrahlung, a continuous spectrum principally created by scattering of the electrons in the Coulomb field of the nuclei, and (b) characteristic line spectra (discrete energy). The latter is of primary importance in diffraction work. The desired spectral line (most
probably the Kα1) can be selected by a monochromator. As only a few elements are useful as anodes in X-ray generators, only a small number of X-ray energies are available.

The generated X-rays are emitted into a solid angle of 2\(^\pi\). The greatest flux available is determined by the maximum heating power that the anode can absorb without deteriorating. To increase this maximum, the anode is cooled by an internal stream of water. Moreover, the photon flux can be raised by use of a rotating anode instead of a stationary one. In this way the effective target area for emission of X-rays becomes only a fraction of the actual area that is heated by the electron beam.

Berman reported on an alternative idea: The cathode beam is revolved in a circle on the target by a magnetic field while the entire tube is synchronously gyrated so that the focal spot is stationary in laboratory space; water cooling can then be used without rotating joints. In both cases the excess heat is thus radiated away during most of the cycle. A 12-kW Regaku rotating anode X-ray generator with a projected source size of 1 mm x 1 mm is available at Risø. Similar machines with up to approximately 5 times its output power are produced commercially.

Synchrotron radiation appears as a radiation loss from accelerated charged particles. A storage ring or a synchrotron, where the particles moves in a closed orbit, compensate for this energy loss by means of microwave cavities inserted into the ring which are capable of delivering small kick accelerations. Thus for practical purpose the energy of a particle is considered constant doing its evolution and the following considerations is based on the impact of the centripetal acceleration. A strongly relativistic particle (\(v \approx c\)) with charge \(e\) and restmass \(m_0\) which is accelerated to the energy \(E\) in an orbit of radius \(R\) emits radiation of power

\[
\dot{\mathbf{E}} = \frac{2}{3} \frac{c e^2}{R^2} \left( \frac{E}{m_0 c^2} \right)^4
\]

where \(c\) is the speed of light in vacuo.
The expression for $W$ explains the strong dependence upon the mass of the particles of the radiation losses. This demonstrates the necessity for the very large constructions of electron/positron synchrotrons at high-energy physics research centres. The expression also shows why only electron or positron rings are conceived as electromagnetic sources. Furthermore, the radiated power is very sensitive to the energy of the particle. In a reference system $S^*$, which I define by the property that at one point $P$ of a circulation of the electron, the electron is at rest in $S^*$, the radiation losses at $P$ are emitted in a classical Larmor distribution. It has a $\sin^2 \psi$ (dipole) dependence, where $\psi$ is the angle to the direction of the (centripetal) acceleration of the electron. Let $\phi^*$ be the angle (in $S^*$) of emission for one such photon measured relative to a direction parallel to the electron velocity $\vec{v}_e$ in a reference system $S$, which is fixed relative to the machine. In accordance with the Lorentz transformation, the transformed angle $\phi$ in the $S$-system is given by

$$\tan \phi = \frac{(1 - v^2_e/c^2)^{1/2}}{1 + v_e/c \cos \phi^*} \tan \phi^*$$

This phenomenon is identical to that known as the aberration of light. As the first factor in the equation is $<< 1$ it follows that synchrotron radiation is confined to within a narrow angle to the plane of the electron's trajectory. In radians the spread away from this orbital plane is limited to about the magnitude of half the relativistic factor $1/\gamma = 1.4 \cdot 10^{-4}$ (DORIS); thus, the radiation is by origin very well collimated. Actually the angular spread $\phi$ is a decreasing function of increasing photon energies. In contrast to the radiation pattern from a rotating anode, for a synchrotron all the radiation is emitted into a spatial angle of $2\phi \cdot 2\pi$.

To account for the frequency distribution it is not enough to include the doppler shift associated with the above transformation from $S^*$ to $S$. Due to the high speed of the electron its trajectory in retarded space-time is not sinusoidal in either $S^*$ or $S$. This has the consequence that in both systems a large number of higher harmonics to the fundamental frequency $\omega_0$ are
present. As the trajectory is least complicated in S I shall refer to this system. Following Feynman, assume for a moment that the electron moves with the speed of light; then its trajectory in retarded space-time \( (ct_{\text{observer}}, r) \), seen from an observer at a large distance, is a cycloid. The synchrotron is "rolling" on the \( ct_{\text{OB}} \)-axis. At \( x_0 = p \times 2\pi R \) \( (p, \text{integer}) \) we have the infinitely sharp cusps of the cycloid. For \( v_e < c \) the apparent motion becomes a prolate cycloid. Let \( (x, y, z) = (R \cos \omega_0 t, 0, - R \sin \omega_0 t) \) be the parameterization of the electron orbit with respect to the time \( t \), and let the observer be looking in the direction of the \( z \)-axis, then the prolate cycloid has the form

\[
(ct_{\text{OB}}, x) = (ct - R \sin \omega_0 t, R \cos \omega t)
\]

It is the "cusps" which give rise to the high-frequency Fourier component. We will roughly estimate the magnitude of an frequency \( \omega_a \) for which the Fourier component must have appreciable intensity. Half of the corresponding wavelength \( \lambda_a \) is the width of the "cusps", i.e. the distance between the point with zero curvature of the prolate cycloid. These points are found by

\[
\begin{vmatrix}
  x_0' & x_1' \\
  x_0'' & x_1'' \\
\end{vmatrix} = 0
\]

which gives \( \cos \omega t = v_e / c \). By series expansion we then find

\[
\lambda_a = 4 \sqrt{2} R (1 - v_e / c)^{3/2} = 16 R \gamma^{-3}
\]

For DORIS \( \lambda_a = 5.3 \text{ Å} \) (the X-ray region) but the fundamental frequency \( \omega_0 \) corresponds to \( \lambda_o = 2\pi R = 75 \text{ m} \). Fluctuations in

\*

This \( \lambda_a \) must not be confused with the in literature frequently referred to characteristic wavelength \( \lambda_c = 4\pi \gamma^{-3}/3 \), sometimes also called the critical wavelength. However, \( \lambda_a \) and \( \lambda_c \) differ only by a proportionality constant of \( \pi/12 \), so \( \lambda_c = 1.4 \text{ Å} \).
the orbit length in size of $\lambda_0$ would completely smooth out the frequency spectrum at $\omega_0$. It can be rigorously found that for a relativistic particle the energy radiated per unit frequency and per unit solid angle is (see, for example, Jackson)

$$\frac{d^2I}{d\omega d\Omega} = \frac{e^2}{3\pi c} \left(\frac{\omega R}{c}\right)^2 \left[\left(\frac{1}{\gamma^2} + a^2\right)^2 K_{2/3}^2(\xi) + \left(\frac{a^2}{\gamma^2} + a^4\right) K_{1/3}^2(\xi)\right]$$

where

$$\xi = \frac{\omega R}{3c} \left(\frac{1}{\gamma^2} + a^2\right)^{3/2}$$

$a = \text{angle to orbit plane}$

$K_{1/3}$ and $K_{2/3}$ are modified Bessel functions of the second kind.

The first term in the parenthesis is the part of the radiation which is horizontally polarized (polarized in the orbit plane). The second term accounts for the vertically polarized part of the radiation. Consequently, for $a = 0$ the polarization is linear. Some departure from this linearity must be expected due to the final extension of the source in a real machine. Integration over all angles reaches a ratio of 7 to 1 of the intensities of the two polarizations. For X-ray scattering this has the consequence that when scattering is performed in the orbital plane (horizontally), then a polarization factor of $\cos^2(2\theta)$ contributes to the cross section, i.e. in any scattering event little intensity can be seen at $2\theta = 90^\circ$. On the contrary, the polarization factor for a vertical scattering experiment is unity. All the scattering experiments to be described are done in the horizontal plane at an angle below $30^\circ$, where the polarization factor is of little hindrance. Machine parameters in the non-ideal synchrotron such as the size of the electron bunches and the electron divergences influence the brightness and may also enter into the resolution of the experiment. It is possible to place intersection elements such as wigglers and undulators in a storage ring, thereby increasing the radiation intensity magnitudes and/or cause a shift in wavelength. In that way the
spectra is changed without redesigning the machine to any great extent (see, for example, Bonse).

Figure 4.1 gives the wavevector distribution of spatially integrated intensities from a bending magnet in DORIS and that from the proposed Wiggler-line (see Gürtler et al.)

Fig. 4.1. The wavevector distribution of spatially integrated intensities from a bending magnet and the proposed Wiggler line in DORIS for electron energies of 3.5 GeV and 5 GeV, respectively, at a machine current of 1 mA (reproduced from Gürtler et al.).

REFERENCES

  X-ray sources, DESY SR79/29
5. LINE SHAPES

The profile of Bragg reflections from a monolayer has several characteristics. In paragraph 1 we saw that it has characteristic asymmetry. Four various inceptions of a line shape are given below:

i. The resolution of the experimental configuration.

ii. The final size of the crystallites under study.

iii. The Warren line shape. For a sample confined to a plane the Fourier-transformation of the spatial electron pair correlation function leaves complete translational symmetry in one direction of the reciprocal space. For the special case of true long-range order the reciprocal space is determined by only two Laue conditions, thus allowing for Bragg rods, in contrast to the Bragg spots found from 3-dimensional crystals. A misorientation of a 2D-crystallite can thus lead to a momentum transfer at a Q vector
larger than the distance between Bragg rods. For a sample with an angular distribution of the normal vectors of the 2D-crystallites, averaging over the crystallites will lead to a sawtooth line-profile.

iv The specific nature of the structure under study (its correlation function). A commensurate structure with true long-range order has delta function rods. An incommensurate structure with quasi-long-range order leads to a scattered intensity proportional to

\[ \frac{1}{(q^2 - \eta)}, \quad 0 < \eta < 1/3 \]  

(1)

where \( q \) is the distance to a rod. Equation (1) diverge at the Bragg rods while tails extend into the Brillouin zone. A liquid droplet model for a fluid structure gives rise to Lorenzian distributed scattered intensity around the Bragg rods. Point ii may be thought of as a special case of iv.

To state the intensity at a given \( Q \)-setting in a diffraction experiment from a sample of powder nature involves calculation of the structure factor from each crystallite. I shall here assume that each individual feature as i.e. final size, algebraic decay etc. is a sufficiently small perturbation on each other so that a convolution principle is valid.

The intensity from crystallite \( p \), \( I_p(Q) \) has to be summed over the sample distribution of crystallites

\[ I(Q) = \sum I_p(Q, n, \alpha) \]  

(2)

where \( (n, \alpha) \) describes the orientation of the reciprocal lattice of a crystallite \( p \). \( n \) is the direction vector of the rods and \( \alpha \) the angular orientation measured in a plane perpendicular to the rods. In the following I assume that for all crystallites \( I_p \) is identical except from a transformation in \( (n, \alpha) \), that is using an average structure factor for each crystallite.
In the case of final square lattice we have

\[ I_p(q) = \pi \sin^2((N_p-1)q, a/2)/\sin^2(q, a/2) \quad \gamma = 1, 2 \]  

where \( I_p \) is the number of lattice sites along a side, \( q \) is a lattice distance, \( q = (q_1, q_2) \) connect the Bragg rod with \( Q \).

As an average for \( I_p \) the large \( N_p \) result may be applicable, that is

\[ I(q) = \exp\{-q^2/(2\sqrt{N_p}L)^2\} \]  

where \( L = Na \) is a measure of the average length of the crystallites. In this way the average \( I(Q) \) reflects the stochastic \( I_p(Q) \) distribution, rather than assume uniformity. Equation (2) reduces to

\[ I(Q) \propto \frac{2\pi}{4\pi} \int \int I(Q, \mathbf{n}, \phi) P(\mathbf{n}, \phi) d\mathbf{n} d\phi \]  

where \( P(\mathbf{n}, \phi) \) is a density (or probability) distribution in the orientation space \( (\mathbf{n}, \phi) \). An assumption that I prefer is that around any given chosen direction the crystallite distribution is isotropic:

\[ p(\mathbf{n}, \phi) = p(\mathbf{n}) \]  

Moreover, \( P(\mathbf{n}) \) is assumed to peak around a specific direction again in an isotropic way such that

\[ P(\mathbf{n}) = P(\beta) \sin \beta \]  

where \( \beta \) is the angle between \( \mathbf{n} \) and a characteristic \( \mathbf{n}_0 \). \( P(\beta) \) is the probability of finding the angle \( \beta \) between \( \mathbf{n} \) and \( \mathbf{n}_0 \) when \( \mathbf{n} \) is restricted to lie in a fixed plane. The sample is aligned so that \( \mathbf{n}_0 \) is perpendicular to the scattering plane. Later a Gaussian distribution shall be assumed.
\[ P(\phi) = \exp\left(-\frac{\phi^2}{\kappa^2}\right) \]  

(8)

where \( \kappa = \Delta / 2\sqrt{\ln 2} \) if \( \Delta \) is the FWHM, full-width-at-half-maximum, of the Gaussian distribution. Equation (6) then reduces to

\[ I(Q) = \int_{4\pi} P(\phi) I_a(Q, n) d\Omega \]  

(9)

where \( I_a(Q, n) \) is an "inplane powder average scattering function"

\[ I_a(Q, n) = \int_0^{2\pi} I(Q, n, \phi) d\phi \]  

(10)

Finally, to compare the measured diffraction profiles involves a convolution with the resolution function in 3D. However, as we shall see later the mathematics turns out to be sensitive principally in one direction.

**Fig. 5.1.** Illustrates the transformation from coordinate \((x, y, z)\) to \((x', y', z')\).
For the creation of computer routines it is useful to coordinate the previous considerations. To describe the distribution $(\mathbf{n}, \alpha)$ of the crystallites in the sample, I shall introduce the Cartesian coordinate transformation from $(x'', y'', z'')$ to $(x, y, z)$ such that in the coordinate system '$\mathbf{n}$ will be parallel to the $z''$-axis, and $\alpha$ then measured in the $x'', y''$plane will be found as 0 when measured away from the $y''$ axis. The non-primed coordinate system is defined by the property that the $z$-direction is parallel to the $\mathbf{n}_0$. This transformation can be parametricized in several (canonical) ways. One could utilize an assumption for the crystallite distribution such that integration over this becomes easy. I will take another approach where integration over the crystallites, which causes the same scattering amplitude, reduces somewhat. The angular coordinates are defined as follows: First, we rotate by $\omega$ around the $x$-axis and arrive at the coordinate system $(x', y', z')$ (see Fig. 5.1). Then following a $\psi$ rotation around the (old) $y$-axis, we arrive at the coordinate system $(x'', y'', z'')$, and finally a $\phi$ rotation around $z''$-axis (see Figure 5.2). In this way the $x'', y'',$ and $z''$ are defined by an orien-
tation of the crystallite. Let the y-axis be in the direction of the momentum transfer $Q$. Because the direction of $Q$ changes with its length due to the scattering geometry, this produces a general set-back, namely, that the orientation probability function $P(n_\phi)$ in the most general case will be a function of $Q$. However, this does not apply when the $P$ distribution is isotropic around the $z$-axis. Combining the three transformations given above we, arrive directly or inversely at (11)

$$
\begin{pmatrix}
    x' \\
    y' \\
    z'
\end{pmatrix} =
\begin{pmatrix}
    \sin \phi \sin \psi \cos \phi \cos \psi + \cos \phi \sin \psi - \sin \phi \cos \psi \cos \omega \sin \psi \\
    \sin \phi \cos \omega \\
    \cos \phi \sin \psi + \sin \phi \cos \psi \cos \omega \sin \psi
\end{pmatrix}
\begin{pmatrix}
    x \\
    y \\
    z
\end{pmatrix}
$$

(11)

The language of Bragg rods can be extended to non-ideal 2D situations, or to 3D symmetry by the introduction of a scattering amplitude along the Bragg rod. Let $P_0$ be a point on the Bragg rod in the principal plane (see Fig. 5.3), that is

$$
P_0 = (0, Q_0, 0)'' = Q_0(-\sin \phi \cos \psi + \cos \phi \sin \psi \cos \omega, \cos \phi \sin \omega, \sin \psi \cos \phi \sin \omega \cos \psi)
$$

(12)

**Fig. 5.3.** Gives the geometry necessary to calculate $q_\perp$. Note $P_0 = (0, Q_0, 0)''$ and $P = (0, Q, 0)$. 
The distance \( q_{\parallel} \) from the point \( P = (0,Q,0) \) to the Bragg rod which has the normal vector \( \mathbf{n} = (\cos \omega \sin \psi, -\sin \omega, \cos \omega \cos \psi) \) is

\[
q_{\parallel} = |\mathbf{P} \times \mathbf{n}| \quad (13)
\]

that is

\[
q_{\parallel}^2 = Q^2 \cos^2 \omega + Q_0^2 - 2Q_0 \cos \psi \cos \omega \quad (14)
\]

For all cases which will be considered, the \( q_{\parallel} \) is all that goes into the inplane powder average scattering function (10), which can arise from a Gaussian, Lorentzian or algebraic distribution. In the cases of true long range order the condition is that \( q_{\parallel} = 0 \). However, then a simpler geometric viewpoint will prove useful.

For non-ideal 2D situations one will need the momentum transfer along the rod which can be found as \( \mathbf{P} \times \mathbf{n} \)

\[
q_{\perp} = -Q \sin \omega \quad (15)
\]

To exemplify a line calculation I will go through that of a Lorentzian scattering function. This is the calculation which led to calculated line profiles of Fig. 1.3 for the melting study of a submonolayer argon film. Equation (1) becomes

\[
I = \frac{\xi^2}{1 + q_{\parallel}^2} \quad (16)
\]

where \( \xi \) is the correlation length. The inplane powder averaging (10) then becomes (a multiplicity factor of 6 has been omitted).

\[
I_a = 2\int_0^\pi \frac{\xi^2}{\left[1 + \xi^2 Q^2 \cos^2 \omega + \xi^2 Q_0^2 - 2\xi^2 Q_0 \cos \psi \cos \omega \right]} d\psi
\]

\[
= 4\xi^2 (1 + \xi^2 Q^2 \cos^2 \omega + \xi^2 Q_0^2 - 2\xi^2 Q_0 \cos \omega)^{-1/2} \times
(1 + \xi^2 Q^2 \cos^2 \omega + \xi^2 Q_0^2 + 2\xi^2 Q_0 \cos \omega)^{-1/2} \quad (17)
\]
The first term in (17) is the frequently used approximation for the inplane powder average Lorentzian; a square rod of a Lorentzian

$$I_a \sim \xi^2 (1 + \xi^2 q_0^2)^{-1/2}$$  \hspace{1cm} (18)

when $q_0$ is the shortest distance to the rod. This result (18) arises naturally from approximating the integrating path by a straight line (see Fig. 5.4). This was used in the actual line calculation. That is reasonable, because for $\omega$ small ($q_0$ small) the first term in (19) is the dominant one in the $\omega$ dependence. The distribution of the crystallite orientation does favour small values of $\omega$.

The crystallite orientational distribution is assumed Gaussian as (9). A line shape calculation for the commensurate structure in a Gaussian description indicates a FWHM value of 18° for the crystallite distribution for our sample. Equation (9) then becomes

$$I = \int \int I_a(\omega, \psi) P(\beta) \cos \omega d\psi d\omega$$  \hspace{1cm} (19)

$\beta$ is given by $\cos \beta = \vec{n} \cdot \vec{z}$

$$\cos \beta = \cos \omega \cos \psi$$  \hspace{1cm} (20)

Summarizing: In this parameter description we have

$$I = 8 \int_0^{\pi/2} \int_0^{\pi/2} \xi^2 (1 + \xi^2 |Q_0 - Q \cos \omega|^2)^{-1/2} \times$$

$$\exp \left\{ - (\arccos(\cos \omega \cos \psi))^2 / \kappa^2 \right\} \times \cos \omega d\psi d\omega$$  \hspace{1cm} (21)

This integral can be evaluated numerically directly or after a coordinate transformation utilizing the variable $\beta$. I found that the Lorentzian (or square-root Lorentzian) in combination with standard integration routines using a Gaussian integration or a Chebyshev polynomial method creates artificial oscillations in the numerically calculated line shape. However, although
Fig. 5.4. Shows the approximate path for the calculation of the inplane powder average.

long-winded, Simson's rule may be applied in the sensitive area of integration. This calculation has led to the curves on Fig.
1.3. They were carried out on a VAX at the Department of Chemical Physics at University of California, Los Angeles. The calculation could also have been carried out on a PDP 11/03. The
spherical geometry expressed in equation (20) may be approximated to a plane; that is,

\[ \beta^2 = \omega^2 + \gamma^2 \]  

(22)

and then the equation (21) becomes

\[ I = \int_0^{\pi/2} \xi^2 (1 + \xi^2 |Q_0 - Q \cos \omega|^2)^{-1/2} \exp \{-\omega^2/\kappa^2\} \cos \omega \mathrm{d} \omega \]  

(23)

This calculation with an FWHM of 18° for the P(\beta) reproduces the line shapes of Fig. 1.3 calculated from Equation (21). Similar line shape calculations have been performed with a Gaussian basic scattering function as given in (4). An example of calculated curves is given in Fig. 7.3. When carrying out the inplane powder average integral (11) the result naturally factorizes in a product of a Gaussian term and one with a much weaker \( \omega \) dependence. Similar to the Lorentzian case, the term with the strong \( \omega \) dependence (the Gaussian term) is obtained solely by approximating the integration part by the straight line in Fig. 5.4.

For a general scattering amplitude, e.g. one that arises after convolution with final size, the inplane powder averaging can be calculated numerically. An analytic approach to this is given by Dutta et al., who have developed an expression with use of confluent hypergeometric functions.

Not surprisingly, a powder-averaged Lorentzian has tails extending much longer than from a Gaussian. The low-Q side of a Bragg reflection is, in principle, determined by a combination of the experimental resolution and of the nature of the crystallites, i.e. their correlation length. The high Q side in respect to this reflects also be distribution of misaligned crystallites. For a quick characterization of a Bragg reflection two measures of its width is useful: The FWHM, full-width-at-half-maximum, (see Fig. 5.5) and a WLS, width-of-left-side. The latter is defined as the width between a footpoint and the position of maximum intensity (see Fig. 5.6). The footpoint is defined by the intersection with the line through the points, where the Bragg peak has obtained 20% and 90% of the maximum intensity.
Figure 5.5 gives the FWHM measured from calculated curves for Gaussian and Lorentzian cases and Fig. 5.6 gives the WLS.

An upper limit for the influence of the resolution function out of the scattering plane can be given by assuming that all the crystallites' \( \mathbf{n} \) vectors lie in the \( y, z \) plane. To allow for \( Q \) components along a vertical line, the detector opening, corresponds in our calculation to an ensemble of \( P(\mathbf{n}, \phi) \) with their \( \mathbf{n}_0 \), distributed with some misalignment in respect to the \( z \)-axis. In our experimental configuration this vertical collection of

\[ \begin{align*}
\text{FULL WIDTH HALF MAXIMUM (Å⁻¹)} & = 10^{-1} \\
\text{COHERENCE LENGTH (Å)} & = 10^2
\end{align*} \]
Figure 5.6. The WLS for calculated Gaussian and Lorentzian line-shapes. The WLS, width-of-left-side, is defined as the width between a footpoint and the position of maximum intensity. The left side footpoint is obtained by use of the points of 20% and 90% of the maximum intensity.

Photons has a maximum out of plane angle $\alpha$ of the magnitude of $1^\circ$. This corresponds to a $\Delta Q = (1 - \cos \alpha)Q_0$ of 0.0003 Å⁻¹ or in direct space to length-scales above 20,000 Å. The final size of the crystallites is of magnitude 1600 Å. I shall therefore assume that it is important to fold only with a resolution function along the $Q$-axis. If one assumes a Gaussian resolution function and the scattering function is Gaussian, then the con-
volution becomes trivial (again a Gaussian); otherwise this integral has to be performed numerically.

I would like to comment briefly on some primary results obtained in collaboration with Peter Stephens. As mentioned in paragraph 1, the argon experiment has gone to a phase 3 performed at Stanford. The data obtained here have a much better signal-to-noise ratio and are allowing for a rigorous line-shape analysis. Peter Stephens has developed a least-square fit program invoking convolution with resolution as well as final size. The results so far show that for solid argon one cannot distinguish between a Lorentzian and an algebraic lineshape. A sample that is less powdery is needed for this test. This is in agreement with what was found by Heiney et al. in the analyse of their melting study of xenon on ZYX graphite.

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HEINEY, P.A., BIRGENEAU, R.S., BROWN, G.S., HORN, P.M.,

6. SCATTERING GEOMETRY AND EXPERIMENTAL RESOLUTION

The powder of the sample nature, and the existence of the Bragg rods which is a consequence of the two dimensional nature of the monolayers imply that the diffraction groups depend on the instrumental resolution principally in one direction in Q-space.
We may assume that the resolution is infinitely broad in energy which means that we are integrating over all energies.

Initially, the experiments were carried out at the existing Danish triple-axis spectrometer at DORIS in Hamburg; The commensurate-incommensurate phase transition of Kr induced by a pusher gas was studied. The measurement showed that a commensurate Kr monolayer on the graphite flakes has a coherence length in a Gaussian description of about 1600 Å.

At a triple-axis spectrometer with Ge-crystals in the monochromator and analyser the resolution allows study of coherences as large as 10000 Å. A lack in the resolution relative to that of the triple-axis spectrometer could be tolerated without any loss in the physical information obtainable with the existing sample ZYX, and this would give us much needed intensity.

However, the resolution can be relaxed only by replacing the Ge-crystals with others and our choices are limited. In particular, the semiconductor crystals (Si, Ge and InSb) give resolutions that are too fine and pyrolytic graphite, too coarse. Therefore, we developed a new technique. This involves the application of a position-sensitive detector (PSD) and a slit configuration (see Fig. 6.1, top view). The white beam of the synchrotron is monochromitized in the double-monochromator system, M1 and M2. The monochromators are perfect germanium crystals cut for the (111) reflection. For this the second-order reflection is forbidden, but higher-order contamination of the monochromatic beam exists. Besides giving a small contribution to the background in the experiment, such higher-order contaminations and particularly the third-order is a serious obstacle to performing the experiment. The graphite (110) reflection in the sample has a momentum transfer which is exactly three times that of the (10) reflection from a commensurate $\sqrt{3} \times \sqrt{3}$ overlayer. Any third-order contamination of the monochromatic beam thereby gives a false reflection overlapping those from a commensurate overlayer.

However, this is overcome by setting the second monochromator crystal at a slight angle to the reflection. As the Darwin width
Fig. 6.1. Top view of the configuration used at the storage ring DORIS in the HASYLAB, DESY, Hamburg. A1: Slit, $w_1 = 4\,\text{mm}$, at $L_1 = 20\,\text{m}$ from the source point in the electron storage ring DORIS. M1 and M2: Ge(111) perfect crystal double monochromator. IC: Ionization chamber monitoring the monochromatic beam intensity. C: Displex refrigerator, providing temperatures down to 10 K. S: Exfoliated graphite sample, (001) axis vertical. A2: Slit $w_2 = 1\,\text{mm}$, typically. PSD: Position sensitive detector (Braun), typically at $L_2 = 550\,\text{mm}$ from the A2 slit. Also shown are evacuated flight tubes and the gas-handling system.

is much smaller for the third-order than the first-order reflection of the monochromatic crystals such a missetting can effectively eliminate the higher-order components in the beam while the fundamental component is decreased by a factor of less than two. The width $W$ of a rocking curve given by the Darwin treatment for perfect crystals is (Warren)

$$W = 2.80\, r_e \frac{N\lambda d |F| |\cos\theta|}{\left(\frac{r_e}{\cos\theta}\right)}$$

$r_e$ classical electron radius (2.818 fm)
N reciprocal of cell volume
$F$ Structure factor
$\lambda$ wavelength, $d$ distance between reflection planes.
At a wavelength of $\lambda = 1.76$ Å the third-order component is of $\lambda = 0.59$ Å and the calculated widths are:

\[
\begin{align*}
W(111) &= 0.007^\circ & \lambda &= 1.76$ Å
W(333) &= 0.0005^\circ & \lambda &= 0.59$ Å
\end{align*}
\]

This agrees well with the experimentally measured rocking curves for the two reflections (see Fig. 6.2). Principally, first-order reflection is measured using an ionization chamber as a detector. The chamber is very transparent, thus working in the linear regime. It is even more transparent for the higher orders, but in principle measures weighted contributions from all wavelengths. The third order is measured by a scintillation detector, which is covered in front by 13.6 mm aluminium, thereby highly amplifying the third-order relative to the first order in the

**Fig. 6.2.** The rocking curves for the first and third order photons of the double Ge(111) monochromator system. The first order ($\lambda = 1.76$ Å) is measured by an ionisation chamber (I.C.) and the third order by a scintillation detector (Sci).
beam. When using the scintillation detector it is also possible to discriminate electronically between first- and third-order photons. In our measurements we used symmetrically cut Ge(111) perfect crystals. However, asymmetrically cut monocromator: where at least one of crystals surfaces are not parallel to the diffraction planes, can offset the rocking curve of the third-order so that it falls outside that of the first-order photons.

The analyzer part of the spectrometer configuration consists of a position-sensitive detector looking at the sample from distance $L_2$ (typically 550 mm). A slit $W_2$ (typically 1 mm) is installed close to the sample which determines the width of the scattered beam from the sample. The resolution of this experimental set-up thus has three contributions - at first considered separately.

1. The angular diversions of the white beam reaching the monochromator. This is determined by the slit width $W_1$, the distance to the source $L_1$, and the source size $W_0$.

$$\Delta \theta / \theta = (W_0 + W_1) / (2L_1) = (4\text{ mm} + 4\text{ mm}) / (2.20000 \text{ mm}) = 4 \times 10^{-4}$$

2. The band width of the monochromator crystal. Due to the perfectness of these crystals, this is determined by the width $W$. $\theta_M$ is the monochromator angle.

$$\Delta \lambda / \lambda = W \cot \theta_M = 1.20 \times 10^{-4} \times 3.56 = 4.3 \times 10^{-4}$$

3. The angular resolution in the analyzer part.

$$\Delta Q / Q = (W_2 + W_3) / (2L_2) \cot \theta = 4 \times 10^{-3}$$

where $W_3$ is the resolution of the PSD. We have measured the intrinsic resolution of the PSD to better than 0.1 mm. Another contribution to the width of a measured Bragg reflection arises from the finite effective height $(h)$ of the detector. The photons scattered with a constant momentum in the sample come out in a cone with the wave vector of the incoming photons as axis (the Debye-Scherrer cone). In a
given counter channel we collected the photons along the vertical lines perpendicular to to the counting wire of the PSD and the curvature of the Debye-Scherrer cone at the position of the PSD; this gives the following combination to the effective resolution of the PSD

\[ \frac{h^2}{8L^2 \sin \theta} = 30 \mu m, \]

h is the effective height of the detector.

By means of Bragg's law the contribution to the resolution from 1. and 2. which together gives the bandwidth that hits the sample was given by Nielsen and Møller. However, with the present choice of Ge(111) for monochromator crystal the analyser effectively determines the resolution. This enables us to measure roughly coherence properties of the set-up over \(4(\pi \ln 2)^{1/2}/\Delta Q = 870 \) Å. The angular diffraction measurements of a commensurate krypton structure with this spectrometer set-up compared to the Warren line shape calculators described in paragraph 5 show that the experimentally determined resolution allows studies of coherences of a length of ~ 1200 Å in the Gaussian description.

The monochromator system and the analyzer configuration may look like they are unbalanced in respect to their resolutions. But this is misleading, because with the exception of the divergence due to the final source distance the monochromators contribution to the resolution comes from the reciprocal space. In retrospect to this, the analyzer system's resolution is direct-space dictated. So the geometric property which should match the resolution of the monochromometer system is the thickness of the sample. With these simplifications this thickness can be arbitrarily thick in principle. Indeed the experimental configuration to some extent makes use of this, as the thickness (3 mm) is three times that of the slit's width \(W_2\). The thickness is constructed to correspond to a 1/e length for the adsorption in the graphite substrate*. This somewhat makes up for the gain

* This thickness was actually chosen to match an other diffraction geometry used at the rotating anode.
in intensity, which could be derived from use of a more broad band monochromator as eventually the thickness of the sample then has to be match to the width W₂. The intensity which anyhow could be gained would not be at the cost of much deterioration in the overall resolution. However, this cannot be done by a mosaic crystals, because then 'he third order can no longer be eliminated by a double monochromator crystal system. The higher order could be eliminated by an X-ray mirror and a more broad-banded monochrometer could be achieved by use of a mosaic crystal.

One modification of the above spectroscrometer configurations is to replace one of the monochromator crystals by an X-ray mirror, e.g. a gold-plated optic glass utilizing the cut off angle for total reflection which is given when the refractive index exceeds unity,

$$\theta_c = \frac{36'}{1.5 \lambda} \text{ (gold)}$$

Thus the mirror angle has to be in the range of about 0.5°. The reflectivity of the mirror was measured at the rotating anode copper Kβ to 82%. It was thought that this would be a more powerful technique to minimize or even exclude all higher-order contributions to the monochromized beam, thus allowing measurement also when the white spectrum of the synchrotron is shifted to harder radiation, i.e. higher electron's energy. At 5.3 GeV operation of the storage ring there were no bulk graphite replication at the third-order positions when this mirror geometry was used. In addition we found that at 5.3 GeV and a typical machine current of 20 mA, the counting rate is on a par with that of the 3.6 GeV dedicated runs of the storage ring with a typical machine current of 60 mA. Thus scattering experiments are possible in the high-energy runs of DORIS, particularly if strong scatterers like xenon are subjects of study. An important limitation in the non-dedicated runs of DORIS is the lack in stability of the source position.
Some spectrometer configurations may discriminate the higher-order photons in the analyzer as is the case with a scintillation detector where higher-order photons can be discriminated in the electronics. The PSD (Braun) used in the above experimental configurations is a gasflow delay line counter. The delay line is a quartz string covered with a thin layer of carbon. The resistance over the length of 4.25 cm is approximately 0.5 megaohm with a slight variation from one counterwire to another. This wire is placed in the counter-house. Thus there will be a RC time constant of the system (~ 1 usec). Counter-gas consisting of 90% argon and 10% methane flows through the wire-house at a pressure of 11.5 atmosphere. The adsorption power for first order (\(\lambda = 1.76\) Å) and third (\(\lambda = 0.59\) Å) is insufficient to allow discrimination. Typical spectra from the position sensitive detector are shown in Fig. 6.3.

![Fig. 6.3. A typical spectrum from the position sensitive detector. This one with three features: (a) commensurate Kr (10) reflection, (b) bulk graphite C (002), and (c) the huge background mainly due to multiple scattering. The spectrum is taken with \(\lambda = 1.5\) Å.](image-url)
The spectra consists of the signal from a commensurate krypton monolayer, the (002) bulk peak from the graphite ZYX sample and of a large very broad background. The measurements of the signal from an adsorbed monolayer consist therefore of the diffraction of a spectrum taken with adsorbed monolayers on the graphite and a spectrum taken with an empty sample cell. The broad background is due mainly to multiple, diffuse and defect scattering in the sample (cell). The cross section for X-rays is of the order of \( \sim 10^{-6} \, \text{Å}^2 \). Multiple- or two-scattering processes may well be of the same magnitude as scattering from a surface layer. For a multiple scattering process there is a cut-off in the wave vectors for which a certain combined momentum transfer \( Q_c = Q_1 + Q_2 \) is possible.

Figure 6.4 shows the peak intensity from a commensurate overlayer of krypton, relative to the intensity of the broad background at the commensurate position as function of the wave vector which was chosen in the monochromator. It is relatively easy to change the wave vector by varying the angle of the monochromator. This can be done continuously due to the white nature of the beam from a synchrotron source. It is seen that coming from about 3.5 Å\(^{-1}\) the signal-to-background ratio stays approximately constant up to slightly above 4 Å\(^{-1}\), where the ratio gets dramatically more unfavorable by a factor of 3, and as the k-vector is increased further the ratio continues being this unfavorable. The scattered point at the top of the figure is due to third-order reflection from the (110) bulk graphite. This has been discussed in connection with the double monochromator design.

In order that a two-scattering process come out with the same final momentum transfer as that of the commensurate \( \sqrt{3} \times \sqrt{3} \) structures (10) reflection, the two reciprocal lattice vectors \( Q_1 \) and \( Q_2 \) describing the two scattering processes in the multiple scattering must be able to combine with that of the reciprocal lattice vector \( Q_c \) of the commensurate structure (10). This gives rise to the triangular inequality between the three momentum transfers.
Fig. 6.4. The ratio of the peak intensity from a 0.74 monolayer commensurate krypton film to the background scattering as function of monochromatic wave-vector. The scattered points at the top of the Figure is due to third-order reflection from the (110) bulk graphite and not the Krypton.

\[ |Q_2 - Q_1| \leq Q_c \]

and

\[ Q_2 + Q_1 \geq Q_c \]

In order that the two processes as well as the diffraction from the commensurate overlayer is elastic the triangle combined by the three reciprocal lattice vectors \( Q_1, Q_2 \) and \( Q_c \) must have its corners on the surface of a sphere which has the wave vector \( k \) as the radius. As the wave vector goes to infinity the sphere becomes a plane, and this condition is always satisfied. In contrast as the \( k \)-vector is decreased from infinity towards 0 the plane with the three reciprocal lattice vectors will divide the
sphere into two parts which will become more even, a sphere with a smaller $k$-vector cannot be able to reach the three points of the triangle. That is the cut-off wave vector for the multiple scattering process, which is then given as the radius of the sphere, when the triangles lie on a great-circle. The cut-off wave vector is therefore given by the radius in the circumcircle of the triangle $Q_1$, $Q_2$ and $Q_c$ which has the well-known geometrical solution,

$$k_{\text{cutoff}} = \frac{Q_c Q_1 Q_2}{4A}$$

$$A = \sqrt{S(S-Q_c)(S-Q_1)(S-Q_2)} \cdot \text{the area}$$

$$S = \frac{Q_c + Q_1 + Q_2}{2}$$

In the sample cell multiple scattering is possible both in the bulk graphite and in the beryllium windows of the cell. The calculated cut-off vectors for scattering involving the lowest index reflection in the graphite and the beryllium is given in Table 6.a.

The multiple-scattering process in graphite (002) and beryllium (002) has a cut-off wave vector of 3.996 Å⁻¹, which in connection with the absence of cut-off wave vectors in the neighbourhood of this number for other multiple processes explains the experimental results (Fig. 6.4). It is also satisfactory for this explanation that it is low index reflections. Multiple scattering processes involving higher index reflection is reduced due to the Debye-Waller-factor, which also would lead to a much stronger temperature dependence on the background than has been observed.

The $k_{\text{cutoff}}$ of 3.996 Å⁻¹ is most unfortunate for the rotating anode set-up which utilizes the copper $K\alpha$-line as it has a $k = 4.079$ Å⁻¹ $K\alpha_1$(Cu). In order to avoid this an iron wheel was prepared for the rotating anode at Risø, and was used for the measurements there.
Table 6.a. Calculated cut-off wave vectors [Å⁻¹] for multiple scattering in graphite and beryllium.

<table>
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<tr>
<th></th>
<th>C(002)</th>
<th>C(010)</th>
<th>C(012)</th>
<th>C(004)</th>
<th>C(014)</th>
<th>C(1-20)</th>
<th>Be(010)</th>
<th>Be(002)</th>
<th>Be(011)</th>
<th>Be(012)</th>
<th>Be(110)</th>
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<td></td>
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<td>C(010)</td>
<td>1.589</td>
<td>1.547</td>
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<tr>
<td>C(012)</td>
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<td>1.810</td>
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<tr>
<td>C(004)</td>
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<td>1.892</td>
<td>1.935</td>
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<tr>
<td>C(014)</td>
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<tr>
<td>C(1-20)</td>
<td>-</td>
<td>-</td>
<td>6.899</td>
<td>3.688</td>
<td>2.567</td>
<td>2.602</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Be(010)</td>
<td>1.974</td>
<td>1.615</td>
<td>1.760</td>
<td>1.894</td>
<td>5.668</td>
<td>-</td>
<td>1.658</td>
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<tr>
<td>Be(002)</td>
<td>3.996</td>
<td>1.751</td>
<td>1.806</td>
<td>1.890</td>
<td>3.191</td>
<td>7.577</td>
<td>1.754</td>
<td>1.802</td>
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<tr>
<td>Be(011)</td>
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<td>1.846</td>
<td>1.909</td>
<td>2.867</td>
<td>4.464</td>
<td>1.822</td>
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<tr>
<td>Be(012)</td>
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<td>-</td>
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<td>2.604</td>
<td>2.423</td>
<td>2.570</td>
<td>4.588</td>
<td>3.002</td>
<td>2.745</td>
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<td></td>
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<tr>
<td>Be(110)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.895</td>
<td>2.778</td>
<td>-</td>
<td>-</td>
<td>2.932</td>
<td>2.802</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
\[ \lambda_{K-\text{Fe}} = 1.9383 \text{ Å} : k = 3.2433 \text{ Å}^{-1} \]

The spectroscometer was controlled by a PDP 11 Digital Computer interfaced to a Carmac system with stepping motor module controls for the Huber tables of the instruments. The mechanical design of the spectromter allows all angles to be set to a thousand of a degree or better, programs was developed to control the spectroscometer. During measurements the control was actually reduced to transfer data from a multichannel analyzer (Canberra) to the PDP 11 computer. In addition to this, tracks including averaging of files, and background subtraction of files, and online plotting on a Graphics Decwriter II were created.

REFERENCES

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7. KRYPTON

At low temperatures krypton forms the $\sqrt{3} \times \sqrt{3}$ commensurate structure (Thomy et al.) i.e. there is one krypton atom for each 6 carbon atom (see Fig. 7.1a). For any adsorbate the question of whether a solid have a commensurate or an incommensurate structure is a matter of the competition between the adsorbate-adsorbate interaction and the adsorbate-substrate interactions. The controlling factor is thus the natural lattice distance in a hypothetical isolated adsorbate-adsorbate system and the compressibility of this lattice. The natural lattice distance is a function of temperature and spreading pressure in the monolayer. Spreading pressure in a truly monolayer film may be defined as (Dash or Kensington).
The spreading pressure is directly related to the chemical potential (from the Gibbs-Duhem equation).

\[ d\phi = \frac{N_A}{A} d\mu_A + \frac{N_B}{A} d\mu_B + \ldots \]

\( \phi \) = spreading pressure
\( F \) = the Helmholtz free energy of the monolayer particles
\( A \) = the area of the film

\( N_i \) = number of (i) particles
\( \mu_i \) = chemical potential of the (i) particles.

The commensurate-incommensurate phase transition of krypton was studied at low temperature as a function of filling (Bohr et al.). As long as the commensurate krypton monolayer coexists with a two-dimensional dilute gas, there is (in constant \( T \)) no change in the spreading pressure of the commensurate layer. However, when the layer fills the whole area available for adsorption, there is no coexistence of dilute gas. The chemical potential must therefore increase rapidly if extra atoms are added. The spreading pressure will increase in the layer, and a phase transition to an incommensurate hexagonal solid occurs (Thorny and others). At low temperature the transition takes place through a coexistent regime with a \( \sqrt{3} \times \sqrt{3} \) commensurate and an incommensurate solid (Bohr et al. and Nielsen et al.). The incommensurate solid is mass density-modulated due to the substrate. The modulation produces a super-hexagonal domain structure, thus giving rise to additional diffraction peaks. The phase diagram found is shown in Fig. 7.2 (rotating-anode study).

This is the transition which is used to set the absolute monolayer density scale. For a series of krypton diffraction patterns references to Fig. 3.7. At higher temperatures, Chinn et al. have studied the transition by LEED (low energy electron
Fig. 7.2. The phase diagram covering the commensurate-incommensurate phase transition at low temperature mapped out in a rotating anode study. Circles indicate the observation of commensurate structure, squares of coexistence of commensurate and incommensurate structure, and triangles of incommensurate structure.

diffraction), Moncton et al. by synchrotron radiation. In both cases the 3D vapour pressure in equilibrium with of the krypton monolayer was used as independent experimental variable. In their interpretation of the data the commensurate-incommensurate transition is continuous and give a critical exponent $\beta$ of $1/3$. Theoretical explanations of this exponent have been suggested later by Baxter. The aim of the experiment now to be discussed is to induce the transition by controlling the spreading pressure of a sub-monolayer krypton film at low temperature. This is done by controlling the vapour pressure of a co-adsorbed deu-
terium twodimensional dilute fluid film. The deuterium fluid is phase separated from the krypton layer. (Refer to the later discussion of mixability and solubility of different gases in two dimensions, paragraph 8). The transition can now be driven in an open sample cell configuration by changing the 3D vapour pressure of the deuterium. In a close sample cell configuration the transition can be driven by changing the temperature. It should be noted that the vapour pressure of krypton at 40 K is below 10⁻⁷ torr (Price and Venables).

Figure 7.3 shows three typical diffraction scans in the transition region. They are interpreted to originate from coexistence of a commensurate and an incommensurate phase. At 33.24 K the structure is purely incommensurate. To the right of the figure is shown the calculated Warren line shape in a Gaussian description having a hexagonal domain wall super structure. The intensity ratio of the two peaks belonging to the incommensurate structure 2:7 is chosen to fit the experimental data. As the temperature is raised coexistence of this structure and a commensurate \( \sqrt{3} \times \sqrt{3} \) structure at \( Q = 1.703 \) Å⁻¹ appears. At 33.81 K the diffraction pattern is interpreted to constitute an admixture of the 33.24 K pattern and that from a commensurate structure. In a lever rule interpretation this corresponds to 38% commensurate phase.

The transition showed a clear hysteresis (see Fig. 7.4). Although the transition region could be searched in a time scale of half an hour, there was no indication within ten hours of any change in the diffraction pattern at a point in the hysteresis loop. This clearly illustrates that the hysteresis is due to the first-order nature of the transition and not to a thermodynamical non-equilibrium situation. The top section of Fig. 7.4 shows the hysteresis loop measured when the transition is induced by changing the pressure of the deuterium. This was also checked for thermodynamical equilibrium. The hysteresis in pressure is much larger than that of inversed temperature, in relative numbers a factor of ten. By a simple argument this factor can be thermodynamically understood. The controlling factor of the width is the difference in spreading pressure \( \Delta \gamma \) across
Fig. 7.3. Diffraction groups in the transition region at constant $D_2$ filling. With increasing temperature $D_2$ is evaporated from the film and the two-dimensional pressure decreases. The line profiles at the right are calculated by using fixed values of the ratio between the intensities of the $+\epsilon$ and $-\epsilon/2$ peaks (7:2), the coherence length $L = 250 \text{ Å}$, and $\epsilon = 0.33$. The only varying parameter is the relative intensity of the commensurate phase, given in percent in the figure and with a line profile as shown by the dotted line. At 34.04 K the commensurate and the incommensurate phases thus coexist in approximately even proportions.
Fig. 7.4. Hysteresis loops of the commensurate-incommensurate transition. In the top part the vapour pressure of D₂ is varied at constant temperature; in the bottom part the temperature is varied at constant filling. The full lines are guides to the eye.
the loop, assuming this to equal or be proportional to \( \Delta \psi_1 = \Delta \psi \),
the overall Gibbs pressure, thereby neglecting nonlinearity due to the eventual presence of a few D\(_2\) molecules in the second layer.

We shall need the logarithmic derivatives

\[
\left( \frac{\partial \phi}{\partial \ln P} \right)_T \quad \text{and} \quad \left( \frac{\partial \phi}{\partial \ln T} \right)_D, \quad \text{fill}.
\]

The chemical potential can be estimated in the ideal gas limit, that is

\[
\mu = - k_B T \ln \left( \frac{kT}{\rho \lambda^3} \right), \quad \lambda = \hbar (2 \pi m kT)^{1/2}
\]

- \( P \) bulk vap. pressure
- \( \lambda \) mean free path
- \( m \) mass of ad-particle
- \( \mu \) chemical potential
- \( k_B \) Boltzman constant

and in accordance

\[
d\mu = \frac{k_B T}{P} dP.
\]

Applying the Gibbs-Duhem equation, when the chemical potential of the film is equalized to that of the vapour gives

\[
d\phi = \frac{1}{A} d\mu = \frac{k_B T}{AP} dP
\]

\( A \) is the specific area of ad-particle

or

\[
\left( \frac{\partial \phi}{\partial \ln P} \right)_T = \frac{kT}{A}
\]

\[
\left( \frac{\partial \phi}{\partial \ln T} \right)_D, \quad \text{fill}
\]
can be estimated by use of the Clausius-Clapeyron relation, which reduces to
\[ \left( \frac{3 \phi}{3T} \right) = \left( \frac{q_{eq}}{AT} \right) \quad \text{or} \quad \left( \frac{3 \phi}{3 \ln T} \right) = \frac{q_{eq}}{A} \]

where the equilibrium heat of adsorption \( q_{eq} = T(S_{\text{film}} - S_{\text{gas}}) \). The term \( q_{eq} \) is related to the isosteric heat of adsorption \( q_{st} \) by \( q_{eq} = q_{st} - \phi A \). The isosteric heat of adsorption can be estimated by extrapolating the isothermal measurement:

\[ q_{st} = k_B T^2 \left( \frac{3 \ln P}{3T} \right) \]

Our isothermal measurement gives a value of approximately \( q_{st} = -390 \) Kelvin \( (k_B) \). By making a rough estimate of the commensuration energy to \( 70 T \) (refer to paragraph 11), we may take \( q_{eq} = -320 \) Kelvin. At \( T = 40 \) Kelvin we find

\[ \left( \frac{3 \phi}{3 \ln P} \right) = \frac{kT}{q_{eq}} = -1.8 \]

This agrees with the relative width of the two hysteresis curves. However, the finite slope in the pressure plot requires some heterogeneity.

The experiment was repeated at several temperatures in the 30-40 K range. Both the first-order behaviour of the phase transition and the hysteresis were again observed. At lower temperatures \( 25 \) K a D\(_2\) submonolayer becomes unable to increase the spreading pressure in the submonolayer of krypton sufficiently to drive the transition. This might be caused by the approaching solidification of the D\(_2\)-liquid layer. The experiment has been repeated with neon as a pusher gas, increasing the transition temperature obtainable by the technique to \( 46 \) K. The results of the diffraction patterns are shown in Fig. 7.5 and hysteresis loop in 7.6. They can be interpreted in the same manner by applying the lever rule. The first-order jump is on the order of \( 0.035 \) A. This is the same number as the data for the D\(_2\)-krypton and the pure krypton system.
Fig. 7.5. Diffraction groups in the transition region when utilizing neon as a pusher gas, the pressures required are rather high but the qualitative behaviour is the same as for the deuterium-krypton system.
Fig. 7.6. Hysteresis loop of the C-I transition when Ne is applied as a pusher gas. The transition shows the same qualitative behaviour as for the D$_2$-Kr system, but the peak intensity of the incommensurate structure had a slight time evolution, maybe indicating low solubility.

REFERENCES


8. MIXTURES. ORDER-DISORDER

Lennard-Jones Potential. Ordered Structure

The first question that arises for films of two substances is that of the possibility of producing chemically ordered alloys, in analogy to the 3-dimensional ordering of Cu and Zn atoms in beta brass. Conceivable order-disorder phase transitions also involve the questions related to phase separation and solubility.

For the rare gas atoms the interatomic forces are well described by the Lennard-Jones potential

\[ E(r) = 4\varepsilon \left( \frac{\sigma^12}{r^6} - \frac{\sigma^6}{r^6} \right) \]

Experimental values for \( \varepsilon \) and \( \sigma \) are given in Table 8.a. For mixtures, a useful approximation for the interatomic forces is to
take $\sigma$ and $\varepsilon$ as the arithmetric and geometric means, respectively:

$$
\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) \quad \text{and} \quad \varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B}
$$

Table 8.a shows $(\sigma_A + \sigma_B)/2$ and $(\varepsilon_A \varepsilon_B)^{1/2}$ for Xe-Ne and Xe-Ar. These values are within 2% of the experimental values. In the following I shall therefore use calculated mean values. Of course the Lennard-Jones potential is not as good as an approximation when used to describe the nonisotopic molecules.

<table>
<thead>
<tr>
<th></th>
<th>$\varepsilon$</th>
<th>$\sigma$</th>
<th>$(\varepsilon_A \varepsilon_B)^{1/2}$</th>
<th>$(\sigma_A + \sigma_B)/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
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<td></td>
</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
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<td></td>
</tr>
<tr>
<td>Kr</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Xe</td>
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<td>4.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>95</td>
<td>3.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>148</td>
<td>3.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>243</td>
<td>3.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe-Ne</td>
<td>89.6</td>
<td>3.40</td>
<td>87.9</td>
<td>3.44</td>
</tr>
<tr>
<td>Xe-Ar</td>
<td>164.1</td>
<td>3.74</td>
<td>162.9</td>
<td>3.75</td>
</tr>
</tbody>
</table>

For specific features other potentials than the Lennard-Jones may be a better descriptor, also three-body-interaction is of importance (for a list of references see Klein and Venables).

On a two-dimensional hexagonal lattice, if a chemical ordering is favoured, the energetically favoured configuration for atoms of two kinds which are close to each other in size is the one fulfilled by a 1:2 in composition ratio (see Fig. 8.1).

For this configuration on the hexagonal lattice, there is 1 A atom for every 2 B atoms. In the approximation of only nearest
Fig. 8.1. A 1:2 ordered configuration on the two dimensional hexagonal lattice. Note that every A particle (open circle) is completely encircled by B particles (hatched circles).

neighbour interaction, the mean energy per atom of the ordered state is

$$E_{\text{ord}} = 2E_{AB} + E_{BB}$$

By considering all possible occupations of the sites in a near-neighbour bond with the appropriate probabilities and by associating 3 bonds per atom, the mean energy per atom of a completely disordered state is

$$E_{\text{dis}} = \frac{1}{3}(E_{AA} + 4E_{AB} + 4E_{BB})$$

The mean energy per atom if a phase separation occurs is

$$E_{\text{sep}} = E_{AA} + 2E_{BB}$$

Therefore, whether or not the two-component film will phase-separate at 0 K is determined by the sign of $w_1 = E_{\text{ord}} - E_{\text{dis}} = (E_{\text{dis}} - E_{\text{sep}})/2 = (E_{\text{ord}} - E_{\text{sep}})/3$

$$w_1 = (2E_{AB} - E_{AA} - E_{BB})/3$$
If $w_i$ is positive a phase separation should be expected. If $w_i$ is negative a chemical ordering should be expected. For a $\sqrt{3} \times \sqrt{3}$ commensurate argon and xenon film, the difference between the energy per atom of the ordered film and that of a chemically disordered film is $w_1 = -29.3$ K.

**Further Interaction Range**

Any number of distant neighbour interactions can easily be taken into account, and the following formula yields the mean energy per atom:

$$E = \sum_{p} \sum_{q} M_{pq} E_{pq}(u)$$

where the distance $u$ is given by

$$u = \frac{a}{2} \left[ (2p-q)^2 + 3q^2 \right]^{1/2}$$

$p,q$ are integer coordinates describing the position of a distant atom in units of lattice vectors (see Fig. 8.2).

$p > 0$ and $0 \leq q \leq p/2$

$M_{pq}$ is half the number of equivalent sites; each bond is shared by two atoms.

$$M_{pq} = 3 \text{ if } q = 0 \text{ or } q = p/2$$

$$6 \text{ otherwise}$$

For the chemically ordered structure

$$E_{pq}(u) = \frac{1}{3} \left[ E_{AA}(u) + 2E_{BB}(u) \right] \text{ if } (p+q) \mod 3 = 0$$

$$E_{pq}(u) = \frac{1}{3} \left[ 2E_{AB}(u) + E_{BB}(u) \right] \text{ if } (p+q) \mod 3 \neq 0$$

For the chemically disordered structure
Fig. 8.2. The triangular lattice where it is indicated how further interactions are counted by coordinates p,q.

\[ E_{pq}(u) = \frac{1}{2} E_{AA}(u) + \frac{1}{3} E_{AB}(u) + \frac{1}{3} E_{BB}(u) \]

For an argon-xenon film the result of including up to the third hexagons of distant neighbour interaction changes the energy difference from \( w_1 = -29.3 \) K to \( w_3 = -28.7 \) K. Furthermore, including up to the 20th hexagon of distant neighbour interaction gives \( w_{20} = -28.7 \) K. In all of the above calculations the experimentally observed lattice distance for the commensurate argon-xenon film, that of the \( \sqrt{3} \times \sqrt{3} \) structure, 4.260 Å has been
used. I conclude from this exercise on the 1:2 composition that further neighbour van der Waal interactions are insignificant for the discussion of possible ordering energies. I will assume that this conclusion is independent of composition ratio.

**Ising Model. Phase Diagram**

For an arbitrary composition ratio $N_A:N_B$, in the approximation where the size of the A and B atoms are equal there will be no dependence on the lattice parameters upon the composition of the film, and there will be no local elastic deformations of the lattice. Thus, it is useful to use the language of spin variables. Assign the spin variable $S_i$ to each lattice position on a rigid lattice as

$$S_i = \begin{cases} 
1 & \text{if lattice position } i \text{ is occupied by an A atom} \\
-1 & \text{if lattice position } i \text{ is occupied by a B atom}
\end{cases}$$

The energy $E_{ij}$ of a nearest neighbour binding is thus given by

$$E_{ij} = E_{AA}(S_i+1)(S_j+1)/4 + E_{BB}(S_i-1)(S_j-1)/4 - E_{AB}[(S_i+1)(S_j-1) + (S_i-1)(S_j+1)]/4$$

and the total energy of the lattice with the spin variable $S_i$ is given by

$$E = \sum_{ij} E_{ij} \quad [ij] \text{ denotes summations over all nearest neighbour pairs}$$

which reduces to

$$E = -\frac{3w}{4} \sum S_i S_j + \frac{1}{2} (E_{AA} - E_{BB})(N_A - N_B) + \frac{1}{4} (E_{AA} + 2E_{BB} + 2E_{AB})(N_A + N_B)$$

$$w = (2E_{AB} - E_{AA} - E_{BB})/3 \quad (\text{as defined previously})$$

where each lattice position is assumed to have the same number $\gamma$ of nearest neighbours (the coordination number). $N_A$ and $N_B$ are the number of A and B atoms, respectively. Note that $\sum S_i = N_A - N_B$. 


Apart from a constant $E$ is that of the Ising model with an applied field (Ising 1925).

$$E_{\text{Ising}} = - \zeta \langle S_i S_j \rangle - m_H \langle S_i \rangle$$

With spin exchange coupling constant $\zeta = \frac{3|\psi|}{4}$ and $m_H = - \gamma \frac{(E_{AA} - E_{BB})}{2}$. Note that $\zeta$ is independent of both the lattice dimensions and of the coordination number.

Before adopting the phase diagram of the Ising model on a 2D-triangular lattice to the monolayer system, note that in the partition function the spin system involves summing over all possible spin configurations, where the monolayer system involves only summing over configurations with the same net magnetisation since $N_A - N_B$ is assumed constant. The summation reaches

$$F_{\text{Is}} = \frac{1}{1} e^{-\frac{1}{\beta} \sum_{\text{all}} \langle S_i S_j \rangle - m_H \langle S_i \rangle}$$

$$F_{\text{Mo}} = \frac{1}{1} e^{-\frac{1}{\beta} \sum_{\langle S_i S_i \rangle = \text{const.}} \langle S_i S_j \rangle - m \Lambda \langle S_i \rangle} = F_{\text{Is}}$$

where a $k_B T$ divisor is left out and a multiplier $\Lambda$ has been applied in the $F_{\text{Mo}}$. Upon differentiating, we obtain

$$\frac{dF_{\text{Mo}}}{d\Lambda} = (-m \langle S_i \rangle) F_{\text{Is}}$$

From this we conclude that the phase diagram for the monolayer system can be mapped out when that of the Ising system is known, implying that constant composition in the monolayer system corresponds to an applied field $\Lambda$ in the spin system with the complication that $\Lambda$ can be a function of temperature and that in coexistence regions several compositions may correspond to the same $\Lambda$. For the further discussion it is necessary to distinguish between the ferromagnetic (phase separation) and the antiferromagnetic case.
For a positive coupling constant ($\xi > 0$) the film will phase separate. The spinsystem is ferromagnetic and has a Curie point at a temperature 1.8 times the coupling constant, see Wannier.

The zero field line from the Curie point to zero temperature corresponds to the coexistence area in the monolayer phase diagram, see Fig. 8.3. The phase boundary is horizontal at a composition one-to-one, this is inferred by a usually critical behaviour with a critical exponent.

\[ \text{Ferromagnetic} \]
\[ \text{Spin system} \]
\[ \text{Monolayer system} \]
\[ W_1 > 0 \]

Figure 8.3. a) shows the phase diagram of the ferromagnetic triangular Ising model as given by Wannier. The Curie point is at 1.8 times the coupling constant. b) gives the corresponding diagram for the monolayer system.

For a negative coupling constant ($\xi < 0$) the film form ordered status. The spinsystem is antiferromagnetic. In a study of the phase diagram of the triangular lattice gas as function of coverage Schick et al. accounted for the before discussed link to the Ising system by computing the magnetization along the phase boundaries. The lattice gas system is isomorphic to the one of order-disorder in binary monolayers. Based on Schick et al. we then have the phase diagram given in Fig. 8.4. In the first half of the diagram $x < \frac{1}{2}$ where the composition ratio is less
than one-to-one, we have long range order of the ordered structure of Fig. 8.1 anywhere under the curve C. Above the temperature given by the curve C there is only short-range order. At the composition one-to-one the transition temperature has gone to 0, this is a consequence of the frustration of the system at this composition where it has a final entropy per particle at zero temperature as was demonstrated by Wannier. The argument

\[ \text{Figure 8.4. The phase diagram of the chemically order-disorder transition for a binary monolayer with only nearest neighbour interaction. Composition means } x \text{ A for every } 1-x \text{ B particles. The diagram is based on and redrawn from Schick et al.} \]

is easily repeated: For structures which favour noneven neighbours, no arrangement can have lower energy than one which satisfies that for every near-neighbour triangle either two spins are up and one down or two are down and one up. The triangular lattice can be divided into three intertwining sublattices \( \alpha, \beta, \) and \( \gamma, \) of which the lattice distance is \( \sqrt{3} \) times larger than that of the principle lattice. In this way all the near-neighbour triangles have their three lattice points distri-
buted with one on each of the three sublattices. By choosing one of the sublattices to have spin down and one to have spin up we have ensured that the energy is at minimum, however we have the degeneracy of being able to choose the spins on the third sublattice by random (the degeneracy is even larger). The energy of this state is

\[
\frac{E_{BB} + 2E_{AB}}{2} + \frac{E_{AA} + 2E_{AB}}{2} = 2E_{AB} + \frac{E_{AA} + E_{BB}}{2}
\]

The maximum transition temperature occurs at a composition \( \chi = 0.337 \) that is slightly offset from the \( T = 0 \) energetically most favourable composition of 1:2 or \( \chi = 1/3 \). Metcalf showed by a Monte Carlo study that this temperature is 1.4 times the exchange constant. At a composition smaller than about 24% no ordered phase exists. The phase diagram is symmetric around \( \chi = \frac{1}{2} \).

**Larger Unit Cells**

Nowhere in the phase diagram of Fig. 8.4 does the film have long-range order for greater unit cells commensurate or incommensurate to the 1:2 ordering such as 1:3, 1:8, 1:11, etc. This is easily understood in an only nearest-neighbour interaction model. For composition ratios where there is less than one A atom per two B atoms, any configuration in which no pair of A atoms are nearest neighbours has the lowest energy. Due to this frustration, ordering in unit cells larger than the 1:2 will not form. However, if any number of second or eventually more distant neighbour interactions are introduced, then ordering in larger unit cells will appear and a series of phase diagrams would evolve as illustrated phenomenologically in Figure 8.5 where only the 1:3 ordering has been introduced. The case chosen is that which favours the longest possible distance between the A-particles.

den Nijs et al. introduced (ferromagnetic) second-neighbour spin interaction with the opposite sign of the nearest neighbour interaction just considered and arrived at the phase diagram of Figure 8.6 (redrawn). At 0 Kelvin there will be coexistence of solids with \( \chi = 0 \) and 1/3, or 1/3 and 2/3 or 2/3 and 1.
Fig. 8.5. The modified phase diagram of that for only nearest neighbour interactions (see Figure 8.4). A sufficient number of next nearest neighbour interactions has been included to stabilize the 3:1 structure, in this way the composition at which the ordered regions begins has lessened. The actual drawing should not be taken to be numerical, but if anything phenomenological.

Fig. 8.6. A redrawing of the phase diagram with ferromagnetic second-neighbour interaction as given by den Nijs et al.
Substrate Potential Periodicity and Different Size Particles

So far we have assumed that A and B atoms are of equal size and we have also assumed the substrate to be ideally smooth. The world of adsorbed mixtures is not this idealized. For some mean lattice distances, in the adsorbed layer, close to those of the substrate, it might be energetically favourable to construct a commensurate structure. Assume now that A and B atoms are different in size, and further, that the size of a lattice consisting of only A atoms is incommensurate and denser than that of the nearest commensurate lattice. Let conversely, the B-lattice form an incommensurate structure that has a larger lattice distance than that of the same commensurate lattice. Then, in a mixed structure the lattice mean distances will approach that of the commensurate structure. Thus even for systems which naturally does phase separate, that is, has a positive spin-exchange coupling, a well-mixed commensurate film may be energetically stable and chemical ordering is again possible as illustrated in Fig. 8.7.

![Phase Diagram](image)

**Fig. 8.7.** A phenomenological suggestion for a combination of the nearest neighbour phase diagram given by Schick et al. on a commensurate lattice combined with the "ferromagnetic" phase diagram given in Figure 8.3b for a smooth substrate.
The influence of the different sizes of atoms as well as of the periodic substrate potential, shows the limitations of the Ising considerations. We must take into account the different lattice vectors for binary mixtures of different composition. To estimate the lattice parameters and the average particle size in a binary mixture, a crude approximation is to consider the particles as two-dimensional sacks. Then a nearest-neighbour Lennard-Jones estimate of the average particle size, when the average size is defined to be equal to that of a hard disc which makes a hexagonal close packing becomes (see Fig. 8.8a)

\[ v = \pi \langle R^2 \rangle \]

![2d Sacks](image1.png)  ![1d Hard spheres](image2.png)

*Fig. 8.8. a) shows a net of two-dimensional sacks.*  
*b) shows a chain of hard spheres.*

Another conjecture of \( v \) arises from considering the particles to pack randomly as they would do in a one-dimensional chain of hard spheres; this is identical to Vegard's law (see Fig. 8.8b)

\[ v = \pi \langle R \rangle^2 \]

The energy of a random binary mixture, an ordered binary mixture and a phase separated film, depends on the structural variation in lattice distance. A consistent calculation, using the Lennard-Jones potential and involving only nearest-neighbour interactions
must therefore use those lattice distances which minimize the energy of the configuration under study. For phase separation this means that the two phase-separated films must have each their lattice distance, which is

\[ a^{1/6} \sigma_a \] and \[ a^{1/6} \sigma_b \]

To find the lattice distance in an ordered mixture, it is necessary to differentiate the energy of the film with respect to the lattice distance, as for a one-component film. The energy in an ordered 1:2 film is given by

\[ E_{\text{ord}} = 2E_{AB} + E_{BB} \]

Differentiating \( E_{\text{ord}} \) and finding its minimum, reaches a natural LJ lattice distance,

\[ d_{\text{ord}} = \left( \frac{2 \frac{E_{AB} \sigma_{AB}^{12} + E_{BB} \sigma_{BB}^{12}}{2 E_{AB} \sigma_{AB}^{6} + E_{BB} \sigma_{BB}^{6}}} \right)^{1/6} \]

To find the natural LJ lattice distance of a one-to-two randomly binary film, we shall similarly differentiate

\[ E_{\text{dis}} = \frac{1}{3} \left( E_{AA} + 4E_{AB} + 4E_{BB} \right) \]

and get

\[ d_{\text{dis}} = \left( \frac{E_{AA} \sigma_{AA}^{12} + 4E_{AB} \sigma_{AB}^{12} + 4E_{BB} \sigma_{BB}^{12}}{E_{AA} \sigma_{AA}^{5} + 4E_{BB} \sigma_{BB}^{5}} \right)^{1/6} \]

Note that a binary mixture of ratio 1:2 has a natural LJ lattice distance which depends upon the degree of local order in the film. This means that a binary film has the local degree of ordering as an adjustable parameter to adjust to a certain lattice distance. This may lead to a softer "potential" than that of a one-component film, which also relates to the compressibility of the film. If the film is forced to take up a certain lattice distance by, for instance, a commensuration or by apply-
ing a spreading pressure to the film, such a lock-in lattice distance may influence the degree of local ordering.

For the constituents for which the Lennard-Jones parameters are given in Table 8.a, the lattice distance of binary mixtures of A- and B-particles in the ratio of infinity-to-one, two-to-one in an ordered configuration, two-to-one in a disordered configuration, one-to-two in an ordered configuration, and one-to-two in a disordered configuration, and one-to-infinity are given in Table 8.b. In Table 8.c the reciprocal lattice distances corresponding to the lattice distance given in Table 8.b are found. It should be added that for a pure one-component film the effect of taking into account three, or any number up to twenty, distant neighbouring hexagonal rings changes the lattice distance from the nearest-neighbour estimate by less than one per cent (namely 0.4%). A cal-

Table 8.b. The optimal near neighbour distance for a nearest-neighbour Lennard-Jones alloy.

<table>
<thead>
<tr>
<th>A</th>
<th>AAA order</th>
<th>AAA disorder</th>
<th>AAB order</th>
<th>AAB disorder</th>
<th>ABB order</th>
<th>ABB disorder</th>
<th>BBB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne-Ar</td>
<td>3.120</td>
<td>3.434</td>
<td>3.594</td>
<td>3.703</td>
<td>3.742</td>
<td>3.816</td>
<td></td>
</tr>
<tr>
<td>Ne-Kr</td>
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<td>3.927</td>
<td>3.971</td>
<td>4.041</td>
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</tr>
<tr>
<td>Ne-CH₄</td>
<td>3.120</td>
<td>3.672</td>
<td>4.037</td>
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<tr>
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<td>4.434</td>
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<tr>
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<td>4.170</td>
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### Table 8.c. The reciprocal (10) lattice vector for a nearest-neighbour Lennard-Jones alloy.

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<th>A⁻¹</th>
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<th>AAB disorder</th>
<th>ABB order</th>
<th>ABB disorder</th>
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<td>Ne-Ar</td>
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<td>1.723</td>
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<td>1.733</td>
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<td>1.660</td>
<td>1.652</td>
<td>1.650</td>
<td>1.636</td>
</tr>
<tr>
<td>CH₄-Xe</td>
<td>1.692</td>
<td>1.646</td>
<td>1.638</td>
<td>1.607</td>
<td>1.602</td>
<td>1.576</td>
</tr>
<tr>
<td>C₂H₆-Xe</td>
<td>1.536</td>
<td>1.615</td>
<td>1.614</td>
<td>1.595</td>
<td>1.595</td>
<td>1.576</td>
</tr>
</tbody>
</table>

Calculation for the binary mixtures of argon and xenon showed that by including sufficiently many distant neighbour hexagonal rings, both the lattice distance of the ordered one-to-two and that of the random one-to-two binary mixtures reduce by very nearly the same factor; this reduction factor is, not surprisingly, the same as that found for a single-component Lennard-Jones film. For the lighter gases, zero point motion, effectively, increases the particle size. In 3D this gives rise to an expansion from the "Lennard-Jones lattice" of 4.7% for neon, 1.1% for argon, and ~ 0.3% for krypton (see, for example, Ashcroft and Meimin, and Singh and Neb).

The energy calculated by using the numbers of Table 8.b is given in Table 8.d. For all combinations in the table it is most ener-
getically favourable to phase separate*. However, there is a large spread in the energy differences and particularly the energy difference relative to that of the mixture. Systems like neon-krypton, neon-xenon - the neon parameters are approximately valid for hydrogen and deuterium - are among those that most strongly try to phase separate. Systems as argon-krypton, krypton-methane, and ethane-xenon have almost the same energy in the three states.

In the Ising model, the system will phase separate if the spin coupling is positive, and order if the spin coupling is negative - there is never competition between ordering and phase separation - it is either way. In this way Table 8.d is interesting, most of the systems have competition between ordering and phase separation, both being more favourable than the disordered structure. The only systems which behave Ising-like in this sense are those with Ne as one of the components, and the methane-ethane system.

Some systems may form commensurate alloys. Taking the native lattice distance from Tables 8.b and 8.c, several systems are good candidates. These are Ne-CH₄, Ne-Xe, Ar-CH₄, Ar-C₂H₆, Ar-Xe, Kr-CH₄, Kr-C₂H₆, and Kr-Xe where the argon-xenon and krypton-xenon have been investigated experimentally by this study, and they have indeed been found to have a commensurate \( \sqrt{3} \times \sqrt{3} \) structure for some composition ratios. By the same procedure as before, a nearest-neighbour Lennard-Jones estimate of the energy in the ordered, disordered and phase-separated situation can be made. Here it is interesting to calculate the mean energy, both as if

---

* When the parameters for the unlike pair potentials are derived as mean values of those for the like pairs the energy difference becomes a well defined function of \((E_B/E_A, \sigma_B/\sigma_A, E_A, \sigma_A)\) and it is easy by means of double differentiating to show that it is positive definite in a vicinity of \((E_B/E_A, \sigma_B/\sigma_A) = (1,1)\).
Table 8.d. Binding energy per particle in a binary film estimated for a nearest-neighbour Lennard-Jones alloy.

<table>
<thead>
<tr>
<th>Kelvin</th>
<th>$E_{\text{ord}}$</th>
<th>$E_{\text{dis}}$</th>
<th>$E_{\text{sep}}$</th>
<th>$E_{\text{ord}}-E_{\text{sep}}$</th>
<th>$E_{\text{ord}}$</th>
<th>$E_{\text{dis}}$</th>
<th>$E_{\text{sep}}$</th>
<th>$E_{\text{ord}}-E_{\text{sep}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AAB order</td>
<td>AAB disorder</td>
<td>AAB phase</td>
<td>AAB sep</td>
<td>AAB order</td>
<td>AAB disorder</td>
<td>AAB phase</td>
<td>AAB sep</td>
</tr>
<tr>
<td>Ne-Ar</td>
<td>-157</td>
<td>-147</td>
<td>-190</td>
<td>33</td>
<td>-231</td>
<td>-239</td>
<td>-275</td>
<td>44</td>
</tr>
<tr>
<td>Ne-Kr</td>
<td>-179</td>
<td>-164</td>
<td>-241</td>
<td>62</td>
<td>-292</td>
<td>-311</td>
<td>-377</td>
<td>85</td>
</tr>
<tr>
<td>Ne-CH$_4$</td>
<td>-165</td>
<td>-138</td>
<td>-218</td>
<td>53</td>
<td>-250</td>
<td>-277</td>
<td>-331</td>
<td>81</td>
</tr>
<tr>
<td>Ne-C$_2$H$_6$</td>
<td>-203</td>
<td>-179</td>
<td>-313</td>
<td>110</td>
<td>-364</td>
<td>-405</td>
<td>-521</td>
<td>157</td>
</tr>
<tr>
<td>Ar-Kr</td>
<td>-404</td>
<td>-402</td>
<td>-411</td>
<td>7</td>
<td>-454</td>
<td>-454</td>
<td>-462</td>
<td>8</td>
</tr>
<tr>
<td>Ar-CH$_4$</td>
<td>-378</td>
<td>-364</td>
<td>-388</td>
<td>10</td>
<td>-403</td>
<td>-397</td>
<td>-416</td>
<td>13</td>
</tr>
<tr>
<td>Ar-C$_2$H$_6$</td>
<td>-447</td>
<td>-425</td>
<td>-483</td>
<td>36</td>
<td>-558</td>
<td>-558</td>
<td>-606</td>
<td>48</td>
</tr>
<tr>
<td>Ar-Xe</td>
<td>-424</td>
<td>-387</td>
<td>-461</td>
<td>37</td>
<td>-510</td>
<td>-506</td>
<td>-562</td>
<td>52</td>
</tr>
<tr>
<td>Kr-CH$_4$</td>
<td>-486</td>
<td>-482</td>
<td>-490</td>
<td>4</td>
<td>-463</td>
<td>-460</td>
<td>-467</td>
<td>4</td>
</tr>
<tr>
<td>Kr-C$_2$H$_6$</td>
<td>-570</td>
<td>-559</td>
<td>-585</td>
<td>15</td>
<td>-639</td>
<td>-635</td>
<td>-657</td>
<td>28</td>
</tr>
<tr>
<td>Kr-Xe</td>
<td>-544</td>
<td>-520</td>
<td>-563</td>
<td>17</td>
<td>-589</td>
<td>-580</td>
<td>-613</td>
<td>24</td>
</tr>
<tr>
<td>CH$_4$-C$_2$H$_6$</td>
<td>-526</td>
<td>-529</td>
<td>-539</td>
<td>13</td>
<td>-621</td>
<td>-624</td>
<td>-634</td>
<td>13</td>
</tr>
<tr>
<td>CH$_4$-Xe</td>
<td>-505</td>
<td>-501</td>
<td>-517</td>
<td>12</td>
<td>-577</td>
<td>-576</td>
<td>-590</td>
<td>13</td>
</tr>
<tr>
<td>C$_2$H$_6$-Xe</td>
<td>-705</td>
<td>-703</td>
<td>-707</td>
<td>2</td>
<td>-683</td>
<td>-681</td>
<td>-685</td>
<td>2</td>
</tr>
</tbody>
</table>
Table 8.e. Binding energy per particle in a $\sqrt{3} \times \sqrt{3} \ R^{30^\circ}$ commensurate binary film estimated by a nearest neighbour Lennard-Jones consideration. Order corresponds to a $3 \times 3 \ R^{0^\circ}$ structure.

<table>
<thead>
<tr>
<th>Kelvin</th>
<th>$E_{\text{ord}}$</th>
<th>$E_{\text{dis}}$</th>
<th>$E_{\text{com.sep}}$</th>
<th>$E_{\text{sep}}$</th>
<th>$E_{\text{ord}}$</th>
<th>$E_{\text{dis}}$</th>
<th>$E_{\text{com.sep}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne-CH$_4$</td>
<td>-108</td>
<td>-128</td>
<td>-168</td>
<td>-218</td>
<td>-245</td>
<td>-265</td>
<td>-306</td>
</tr>
<tr>
<td>Ar-CH$_4$</td>
<td>-341</td>
<td>-338</td>
<td>-332</td>
<td>-388</td>
<td>-396</td>
<td>-393</td>
<td>-388</td>
</tr>
<tr>
<td>Ar-C$_2$H$_6$</td>
<td>-423</td>
<td>-418</td>
<td>-409</td>
<td>-483</td>
<td>-556</td>
<td>-551</td>
<td>-542</td>
</tr>
<tr>
<td>Ar-Xe</td>
<td>-416</td>
<td>-387</td>
<td>-328</td>
<td>-461</td>
<td>-468</td>
<td>-439</td>
<td>-380</td>
</tr>
<tr>
<td>Kr-CH$_4$</td>
<td>-471</td>
<td>-469</td>
<td>-465</td>
<td>-490</td>
<td>-461</td>
<td>-458</td>
<td>-454</td>
</tr>
<tr>
<td>Kr-C$_2$H$_6$</td>
<td>-566</td>
<td>-558</td>
<td>-542</td>
<td>-585</td>
<td>-632</td>
<td>-625</td>
<td>-609</td>
</tr>
<tr>
<td>Kr-Xe</td>
<td>-544</td>
<td>-516</td>
<td>-461</td>
<td>-563</td>
<td>-530</td>
<td>-502</td>
<td>-447</td>
</tr>
</tbody>
</table>
the film phase separates into two commensurate pure films, and into two incommensurate pure films. The energies are given in Table 8.e.

All these films will, of course, have their most energetically favourable configuration in the situation with phase-separation into two incommensurate films. This is caused by tendency of the alloys to phase separate beforehand; changing the lattice parameters to a less favourable value for the ordered structure cannot make the ordering more favourable. The point here is that in addition to this energy of the ordered structure, the energy gain in the commensuration per particle has to be added. Comparing the energies on the commensurate lattice, several of the systems are in favour of ordering, and their ordering temperature can be estimated by the Ising model results.

Table 8.f. Estimate of the order-disorder transition temperature for some possible \( \sqrt{3} \times \sqrt{3} \) commensurate binary films, using the Ising model result.

<table>
<thead>
<tr>
<th></th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-CH₄</td>
<td>3</td>
</tr>
<tr>
<td>Ar-C₂H₆</td>
<td>5</td>
</tr>
<tr>
<td>Ar-Xe</td>
<td>30</td>
</tr>
<tr>
<td>Kr-CH₄</td>
<td>2</td>
</tr>
<tr>
<td>Kr-C₂H₆</td>
<td>8</td>
</tr>
<tr>
<td>Kr-Xe</td>
<td>30</td>
</tr>
</tbody>
</table>

In the above given tables the numbers for mixtures of nitrogen have been left out. They do not differ from the average numbers given in the table, but due to the large anisotropy of the \( \text{N}_2 \) molecule, which to some extent may also apply for \( \text{CH}_4 \) and \( \text{C}_2\text{H}_6 \), the physical picture given above is too simplified. Any ordering of the film would also involve orientational ordering of the nitrogen molecules. Diehl et al. showed that a pure nitrogen film
exibits orientational ordering at low temperature, a herring-bone structure. Diluting the system with another component one would have to take into account the competition between herring bone, mill-wheel, and other structures.

Super Lattice Reflections

In a scattering experiment the distinction between the ordered and disordered structures appears in the presence or absence of super lattice reflections. The fully ordered one-to-two mono­layer has a unit cell involving three particles, contrary to the disordered monolayer, in which the unit cell involves a single particle. In reciprocal space the ordered structure allows for a momentum transfer at a length of \( \sqrt{3} \) times that of the disordered structure. The intensity of the different diffraction peaks depends upon their structure factor. For super structures the structure factor is a function of the difference in (atomic) scattering factor of the two components, therefore experimental difficulties are present when the A and B particles have an almost equal scattering amplitude, i.e. an almost equal number of electrons. With the notation of the super reflections by third part indices \((h,k)\) eg. \((1/3, 1/3)\), the structure factor becomes

\[
P = f_A + 2f_B \cos 2\pi k
\]

To estimate the expected intensity of a super lattice reflection involves the squared ratios of these structure factors. For a one-argon to two-xenon film this reaches an intensity ratio of 1 to 13.3 between the \((1/3, 1/3)\) and \((1, 0)\) reflection. In addition a Debye-Waller and a Lorentz factor enter in this ratio, the multiplicity factor is 6 for both reflections. The Lorentz factor relevant for this work gives the dependence for the integrated intensities \(1/(4 \sin^2 \theta \cos \theta)\). This arises both from the final width in crystallite orientation for which there will be appreciable intensity reflected and from the relative length of the Debye-Scherrer cone which the final detector-height selects. Moreover the geometry of the analyser gives rise to a resolution
determined peak intensity, which in the limit of relaxed resolution is proportional to \( \Delta Q = Q^2 w^2 \cot \theta / (2L_2) \propto \cos \theta \) (see paragraph 6). Furthermore for the synchrotron beam a polarization factor approximately of \( \cos^2 \theta \) enter, and we arrive at \( \cos^2 \theta / 4 \sin^2 \theta \). For \( \theta = 7.92 \) and 13.80 which are the relevant values for a commensurate film studied with a monochromatic beam with \( \lambda = 1.76 \) Å, the above accounted for ratio between peak intensities is 3.5 in favor of the super-peak. The Debye-Waller factor is also in odds of observing the \((1/3, 1/3)\) reflection.

Of the commensurate structures given in Table 8.f, argon and xenon, and krypton and xenon, have been examined for ordering. However, they both lack ordering (see Fig. 8.9 for argon-xenon in the ratio 1:2). There is no Bragg-scattering at the position \( Q = 0.983 \) Å\(^{-1}\) as expected if superstructure occurred due to a chemical ordering in the film. The Poisson statistics in the diffraction experiment allow observation of intensities one order of magnitude less than expected for a fully ordered film. In addition to this, a double-layered film of xenon and methane which in a ratio of 1:2 is \( \sqrt{3} \times \sqrt{3} \) commensurate also showed the absence of a superstructure peak at at least to one order of magnitude less than the expected peak height.

Although the main results of the above given Lennard-Jones consideration indicate a major tendency for the incommensurate structures to phase separate, some mixtures do show experimentally first a residual content of the one component in the other. It cannot be denied that a small fraction of the adsorbant sites have a different nature than that of the "honeycomb" plane of graphite. Therefore one has to be careful in counting small fractions of a monolayer, the origin of which can be caused by other things than residual content of the one component in the other. It is an open question whether a possible quenching of the films, which were typically cooled over a time scale of 5 hours from their melting point to 11 K occurs, or whether the films are somewhat miscible. As expounded above the miscibility in the range 0% to 24% is dependent upon the long range character of the interactions. Some films showed well-mixed incommensurate structures like xenon-argon up to 18% argon, or more dramatically
Fig. 8.9. The diffraction signal around the (1/3,1/3) reflection (0.983 Å⁻¹) for a commensurate monolayer of argon and xenon in the composition 1:2. 2000 denotes the expected peak height for a fully chemically ordered film. It is estimated on the basis of (10) peak intensity. 200 denotes an approximate expected peak height in diffraction from short-range order of 200 Å in a Lorentzian description. The Debye-Waller factor has been omitted.
xenon-methane in the ratio of two-to-one. Within an order of magnitude above the Poisson statistics these films show no evidence for chemical ordering.

Summarized: films which lack ordering at 11 K are given in Table 8.h.

Table 8.h. Binary films with Xe as one of the components which were checked for chemical ordering at 11 K. All lacked ordering. The numbers in the table are the (mol.) percentage of the second component and the total coverage.

Second component.

Argon : (25%;0.65) (33%;0.73) (33%;1.00)*) (40%;0.81) (50%;0.97) (59%;0.65) (67%;0.79) (69%;0.84) (71%;0.89) (76%;1.12)

Krypton : (50%;0.85) (67%;0.80)

Methane : (33%;0.91) (67%;0.75) (68%;1.91) (75%;1.00) (89%;0.78)

Argon and Krypton : (33%;33%;0.99)

*) Data Figure 8.9.

A commensurate completed monolayer consisting of argon, krypton and xenon in an equal composition also lacks ordering. The energy difference between the ordered and disordered structure is 28 K, which is very close to that of argon-xenon and krypton xenon mixtures. However, a sub-ordering between some of the components would reduce this energy difference considerably.
Atomic Displacement

In a disordered binary mixture of components of different size, local elastic deformations as shown in Fig. 8.10 give rise to a displacement field of the atomic positions in the lattice. In a two-dimensional continuous elastic medium the fall-off of the displacement field goes as 1/r. By adjusting to such a local strain field the film will have lowered its configurational energy. A rough estimate of the energy change is attempted in Fig. 8.11 where the smaller particles are argon and the larger one in the middle xenon. The outermost hexagon is considered to be fixed in space at a lattice distance d, taken as that which minimizes the total Lennard-Jones energy of a non relaxed configuration. The relaxing atoms are indicated by hatching in Fig. 8.11. Adjusting the distortion parameter δ given in Fig. 8.11 to yield the minimum total Lennard-Jones energy is lowering the average energy per particle by 16 K.

Although this is far from the situation in a one-to-two disordered film, it does indicate that the energy gained by relaxing the atoms in response to strain fields can lower the transition temperature considerably. A Monte Carlo calculation on the displacement field of the individual atoms would provide an improved estimate on this question. If the two-component film is commensurate, similar considerations apply, however, the gain in configurational energy due to strain field relaxation in a disordered alloy is partly off-set by a loss in commensuration en-

Fig. 8.10. An illustration of an elastic deformation of a regular lattice when the centre site is occupied by a different size atom.
Fig. 8.11. The smaller circles are argon and the bigger circle is a xenon atom, the open circles denote the regular lattice sites of the inner argon hexagon. The hatched ones are the relaxed positions, \( \delta \) is the distortion parameter. Summing the nearest neighbour Lennard-Jones energies reaches a difference of 16 K between the regular lattice and the relaxed.

Energy. This potential is relatively soft because of the ability of the particles to individually adjust their height above the graphite surface.

In order to permit the particles in the two-dimensional film to relax their interparticle distance by small displacements from their lattice positions out of the binary mixture plane, a change of configurational energy must take place. This change should occur both for the ordered structure A to 2B, as well as for a disordered structure which relaxes elastically to a strain field. For the ordered structure in a two-dimensional film, in which the presence of the substrate is neglected, the relaxations out of plane would lead to all of the B-particles lying in one plane and all of the A particles in two adjunct planes. If the A par-
ticles are smaller than the B particles then the A planes will coincide with the B planes. The lattice distance and energy per particle is as given above. If the A particles are larger than the B particles then the planes will not coincide and the lattice distances and the energy per particle are

\[ d_{B-B} = 2^{1/6} \sigma_B, \quad d_{A-B} = 2^{1/6} (\sigma_A + \sigma_B) \]

\[ E = -\epsilon_B - 2^1/6 \epsilon_A \epsilon_B \]

Taking the numbers for a one-xenon to two-argon film, for an incommensurate film this energy reaches -446 K, which is a reduction of 22 K compared to the previous estimate. For a commensurate film taking the assumption that the argon-argon distance is that of the commensurate distance, and allowing the argon-xenon distance to be slightly larger, we arrive at an estimated energy per particle of -418 K, which is almost identical to the -416 K estimated for a plane commensurate structure. This is of course so, because an argon-xenon bond tends to have a distance close to that of commensuration. Both for incommensurate and commensurate films, in order to get a sensible estimate of these energies, it is necessary to take the structure of the graphite substrate into account, and both for the disordered and ordered structure a Monte Carlo calculation could produce an answer as to how this affects the transition temperature.

**Growth Mechanism for Ordering**

It is of interest to try to consider the formation mechanism growth of the chemical ordering in an A-2B mixture, arising from a high-temperature state where there is complete disorder (for a general discussion see Lipson).

As earlier discussed, the overall lattice for the film can be divided into three intertwining sublattices, of which the lattice distance is \( \sqrt{3} \) times that of the principal lattice. An ordered structure means that all of the A particles lie on one of the three sublattices, either \( \alpha \), \( \beta \), or \( \gamma \), and all of the B particles
on the remaining two. There is no symmetry difference of the environment seen from a site of a \( \alpha \), \( \beta \), or \( \gamma \)-lattice. Therefore, when the ordering formation begins, we cannot know which sublattice is to become the \( \Lambda \)-lattice. Locally, the particles will start to order; this means that in one region the \( A \) particles will be on the \( \alpha \)-lattice, but in another region the \( a \) particles will have chosen the \( \beta \)-lattice. The monolayer will then consist of strangely shaped domains where each has the \( A \) particles on one of the sublattices. The excess energy of this configuration, relative to the completely ordered film, is thus connected with the walls between the domains. A few types of walls can exist, but I assume that they will relax to the type of wall, which has the lowest excess energy. Therefore, the excess energy of the whole film is equal to the wall length. So, by locally interchanging two atoms or interchanging a group of three atoms forming a super structure unit cell, the domain walls may be straightened out, thereby decreasing the total domain wall length. By this procedure, where atoms are interchanging continuously only on a local scale at the walls, a domain wall configuration can be reached, like that of Fig. 8.12, where all of the domains are unevenly shaped hexagons, some large and others small. The question arises: Can the large ones grow bigger at the expense of the smaller? Unfortunately the answer is no; this is due to an argument similar to that of Villain for the entropy in a superhexagonal domain structure for almost commensurate single particle structures. The argument is that fluctuations in such a hexagon net do not change the total domain wall length. This is a simple consequence of the \( 120^\circ \) angles in a hexagon which is twice those of an equilateral triangle (see Fig. 8.13). Assume that there are no domain-wall domain-wall interactions, which is the case when only a nearest-neighbour interaction is accounted. There is thus no mechanism for such local wall fluctuations to produce a more ordered state of the film. Fluctuations which will lead to larger ordered domains thus finally leading to long-range ordering of the mixture, must thus involve particles in an area that is larger than the typical size of the hexagon domains. The above given consideration is on line with Bragg who suggested an explanation for the lack of ordering in fcc Au$_3$Cu.
Fig. 8.12. A possible domain wall configuration with 1:2 order on different sublattices in the area between the walls. All angles are 120° and fluctuation in the domain wall net does not change the total domain wall length.

a 1A to 3B system in 3 dimensions. In such a system locking of the domain walls would take place and necessary fluctuations, in order to produce long-range order, are impossible, however this lack of ordering is the exception from the rule in fcc A:3B systems, which well can order, fx as AuCu3. But in 2D we also have the freedom due to possible domain-wall configurations.

There will be no Bragg scattering, delta function, at the superposition from an α, β, and γ domain structure. That is because, although the different domains are ordered in respect to the
Fig. 8.13. The fluctuation of the hexagon net which is described by a movement of the corner $P$ to the corner $P'$ creates no excess domain wall length inside the marked triangle as the two short legs of the anchor exactly equalize the longer one.

Superordering, on an average over the whole monolayer, there is an equal number of A-particles on the $a$, $b$, and $c$ lattice. As a result, by summing the structure factor over the whole lattice we reach 0. For the special case where the domain structures form a structure of (regular) hexagons which could be created by domain-wall domain-wall interactions such a structure could be conceived as a large unit cell, thereby giving Bragg-scattering at its finely divided super-net. But at the before discussed super-lines the structure factor will be vanishing, as for such a configuration both the A and the B particles are evenly distributed on the $a$, $b$ and $c$ sublattices. Of course, there could be shortrange scattering, that is, the Fourier transformed of the pair-correlation function. The intensity in
our high-resolution diffraction geometry enables a resolution of approximately 1200 Å in a Gaussian description; the statistics do not allow for the study of short-range order correlations less than 150-200 Å (Lorenzian), at the upper diffraction spots as illustrated in Fig. 8.9.

3D

In 3D the rare gases crystallize in the fcc structure. Mixtures of atoms not too different in size can thus possibly form fcc alloys. In this way similar questions as those for the 2D can arise. Curzon and Mascall studied mixtures of argon and krypton and argon and neon by electron diffraction. Argon and krypton do form fcc alloys but show absence of chemical ordering at 7 K. Neon and argon phase separate at low temperature. Their work also models the relatively small deviation from Vegards law which was observed. If I calculate the summarized Lennard-Jones energies similar to the 2D system, however due to the more complex structure I will here include all bonds shorter or equal to \( \sqrt{2} \) times the side of the unitcell, only KrAr\(_3\) and XeKr\(_3\) have a slight energy difference in favour of ordering. All other Ne, Ar, Kr, and Xe systems favour phase separation. The 3D systems do not likely seem to be obvious candidates for an extension of the 2D study.

With

\[
\sigma_{AB} = (\sigma_A + \sigma_B)/2, \quad \epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}, \quad d^{fcc} = (d_{AA}^{fcc} + 3d_{BB}^{fcc})/4
\]

\[
\sigma_{ij}^* = \sigma_{ij}/d_{AB}^{fcc}, \quad E_{ij}(x) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}^*}{x}\right)^{12} - \left(\frac{\sigma_{ij}^*}{x}\right)^{6}\right]
\]

the energy is given as

\[
E_{\text{order, per atom}} = \frac{1}{4} \left[ 3E_{AA}(1) + 4E_{AA}(\sqrt{2}) + 12E_{AB}(\sqrt{2}/2) + 24E_{AB}(\sqrt{6}/2) + 12E_{BB}(\sqrt{2}/2) + 3E_{BB}(1) \right]
\]
\[ E_{\text{disorder}} = \frac{1}{32} \left( 3E_{AA}(1) + 2E_{AA}(\sqrt{2}) + 12E_{AA}(\sqrt{2}/2) \right. \]

\[ + 12E_{BB}(\sqrt{2}/2) + 18E_{AB}(1) + 12E_{AB}(\sqrt{2}) \]

\[ + 72E_{AB}(\sqrt{2}/2) + 72E_{AB}(\sqrt{6}/2) + 27E_{BB}(1) \]

\[ + 18E_{BB}(\sqrt{2}) + 108E_{BB}(\sqrt{2}/2) + 108E_{BB}(\sqrt{6}/2) \]

Table 8.1. Calculation of Lennard-Jones energies per atom, when summing bounds up to those \( \sqrt{2} \) times the unit cell length in fcc AB\(_3\) structure.

<table>
<thead>
<tr>
<th>A-atoms</th>
<th>B-atoms</th>
<th>( E_{\text{Order}} )</th>
<th>( E_{\text{Disorder}} )</th>
<th>( E_{\text{Phase sep.}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>Ar</td>
<td>-522</td>
<td>-559</td>
<td>-669</td>
</tr>
<tr>
<td>Ar</td>
<td>Ne</td>
<td>-361</td>
<td>-233</td>
<td>-381</td>
</tr>
<tr>
<td>Ne</td>
<td>Kr</td>
<td>-701</td>
<td>-769</td>
<td>-933</td>
</tr>
<tr>
<td>Kr</td>
<td>Ne</td>
<td>-421</td>
<td>-107</td>
<td>-470</td>
</tr>
<tr>
<td>Ar</td>
<td>Kr</td>
<td>-1046</td>
<td>-1067</td>
<td>-1077</td>
</tr>
<tr>
<td>Kr</td>
<td>Ar</td>
<td>-916</td>
<td>-885</td>
<td>-901</td>
</tr>
<tr>
<td>Ar</td>
<td>Xe</td>
<td>-968</td>
<td>-1004</td>
<td>-1261</td>
</tr>
<tr>
<td>Xe</td>
<td>Ar</td>
<td>-902</td>
<td>-604</td>
<td>-963</td>
</tr>
<tr>
<td>Kr</td>
<td>Xe</td>
<td>-1238</td>
<td>-1262</td>
<td>-1350</td>
</tr>
<tr>
<td>Xe</td>
<td>Kr</td>
<td>-1250</td>
<td>-1143</td>
<td>-1227</td>
</tr>
</tbody>
</table>

I have used

\( d_{\text{Ne}} = 4.429 \) Å \( \quad d_{\text{Kr}} = 5.721 \) Å

\( d_{\text{Ar}} = 5.256 \) Å \( \quad d_{\text{Xe}} = 6.197 \) Å
REFERENCES


9. ARGON-XENON MIXTURES

We are familiar with the phase diagrams of pure argon, xenon, and krypton (see McTague and others), which were three examples of such diagrams obtainable from single-component monolayers. The phase diagram of a two-component system involves an additional parameter, the chemical composition. The diagram can thus be composed of, for example, the three parameters: the spreading pressure in the layer ($\phi$), chemical composition of the layer, ($x$) and temperature ($T$).

The equilibrium situation of the binary film at constant temperature involves two chemical potentials, that of an A- and a B-particle. Thus the Gibbs phase rule becomes

"degrees of freedom" = 4 - "number of phases present".

From this it follows that a single phase has three degrees of freedom and therefore is allowed to take up a three-dimensional volume of the ($\phi\times T$) phase diagram. If, however, a coexistence of two phases takes up a three-dimensional volume of the phase diagram, the degrees of freedom is reduced to two; one degree of freedom must be tied, and this happens in accordance with a lever rule. So the coexistence of the two phases in the volume comes about by actually not having three continuous parameters, but represents coexistence of the phases present at the boundary of the volume. The lever rule then applies in a way such that along a constant $\phi$ (spreading pressure) line the phases which coexist are those of the intersection of this line at the boundary of the volume. The phase rule may be applied to more complicated configurations.

The spreading pressure can be measured only indirectly or arduously (Kensington). For a single component film a monotonous measure for this is given by the 3D vapour pressure above the film, which can be measured in the high-temperature regimes. At
low temperature this quantity is not measureable; furthermore, any attempt for this are dangerous to perform as the cell may be contaminated from the gas handling system due to cryogenic pumping. For a binary film the situation is more complicated due to the partial vapour pressure of each of the film's two components. The experiment on the mixtures is performed with the sample valved off from the gas-filling system, and the directly measured quantity which replaces $\phi$ of the phase diagram is the filling $\rho$ of the sample cells, i.e. how many particles there are for each (n) graphite honeycomb hexagon of the substrate. An interval of values of $\rho$ may correspond to just one value of $\phi$. This is, for instance, the case of solid gas coexistence on the surface layer. As long as there is still space for the gas phase the chemical potentials are unchanged when more solid layers are built. This ambiguity in the choice of using $\rho$ as a coordinate of the phase diagram therefore introduces a lever rule along lines parallel with the $\rho$-axis of the phase diagram. The phases in co-existence are the phases of the ends of these lines. Altogether a ($\rho \times T$) phase diagram involves lever rule applications in the planes at constant $T$. Prenzlon and Halsey did an early isotherm study of successive layers of xenon and argon on carbon black.

A series of constant-$T$ phase diagrams derived from the argon-xenon study under discussion (Bohr et al.) are shown in the Fig. 9.1. The lines of the diagram are determined by the diffraction groups and by applying a lever rule on them. The line in the diagram of 11 K are fairly accurate. At higher temperatures some regions of the phase diagram are less explored than others. The lines of these cuts are thus only possible configurations. They are the simplest which have a high likelihood of occurring. The compositions and temperatures actually covered in this study and which produce the basis for the phase diagram are given on peak intensity graphs (see Fig. 9.2a-m).

The diagram in Fig. 9.1 at 11 K shall be understood in this way: 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 in solution in the xenon film forming an incommensurate
Fig. 9.1. A series of constant temperature phase diagrams for argon-xenon mixtures. $x$ gives the composition in (mol) per cent of argon, $\rho$ the coverage. The signature A stands for incommensurate argon like structure, X for xenon like, C for commensurate structure, V for vapour, L for liquid like vapour. The phase rule imply that the boundaries of the three-phase regions are hyperbolic segments.
Fig. 9.2. Peak intensity graphs for different compositions with the various structures. Some figures show clear coexistence.

"Xe-like" structure whose lattice parameter changes with the argon contents. Then at about \( x = 18\% \) Ar the film forms a coexistence of two structures, an incommensurate and a commensurate, of which the reciprocal lattice parameters are \( \tau_{10} = 1.64 \text{ Å}^{-1} \) and \( 1.703 \text{ Å}^{-1} \). Their lattice parameter implies that
they are of dissimilar composition. As the argon content is increased to about $\chi = 32\%$ only the commensurate structure is present, and for an argon content up to about 88% the alloy forms commensurate structures. The solid phases mentioned coexist with a dilute gas V in Fig. 9.1. In the three-phase coexistence "triangle", the phases defined by the corners coexist. It is incidental that the two upper corners lie at the same coverage. 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 solidliquid transition. There is probably no "quadruple point".

For the xenon-rich commensurate-incommensurate transition at 11 K, an understanding by use of a content of an average particle size can be justified by the lack of chemical ordering in the film. This allows us to study the commensurate-incommensurate phase transition driven by average particle size (see Fig. 9.3). 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 2D vapour, therefore, in the coexistence region. The 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 is determined by the positions of the upper corners of the triangle in the phase diagram. The numbers given by the Lennard-Jones estimate

$$
u = \left( \rho_{Ar} \pi (0.56 \sigma_{Ar})^2 + \rho_{Xe} \pi (0.56 \sigma_{Xe})^2 \right) / \rho_{tot}$$

are 14.70 Å$^2$ for the commensurate and 15.84 Å$^2$ for the incommensurate structure. These estimates are not quantitatively accurate. The graphite geometrical size of the commensurate structure is $\pi \cdot 2.13^2$ Å$^2 = 14.25$ Å$^2$. A first-order jump of above 1.14 Å$^2$ leads to a jump in the reciprocal lattice vector of 0.065 Å$^{-1}$, which is close to the observed jump of 0.068 Å$^{-1}$. From this I 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
Fig. 9.3. 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.
two-component system. It might be that the observed first-order jump in density here is larger than it would be in a hypothetical single-component film, where the particle size is varied. Note that in a one-component particle-size-driven commensurate-incommensurate phase transition one would not see coexistence of these two phases for a sub-monolayer coverage, but instead a dilute gas coexisting with either of the two.

An understanding of why the commensurate structure in the coexistence regime has an average particle size close to the one that ideally fits the lattice may be had on the basis of a hard-core repulsion which then will apply only in the "big particle" rich end of the phase diagram.

Conventionally the phase diagrams are given as ρT cuts. A series of 4 such cuts are given in Fig. 9.2. Note that in the case of a two-component system the lines along which the lever rules apply do not lie in the (ρT) planes. The curve in the second diagram of Fig. 9.2, therefore, has a slope relative to that of a one-component triple-point curve as for xenon.

Figure 9.5 shows the melting of a commensurate alloy with 60% argon and 40% xenon; coverage ρ = 0.81 particle per 3 graphite hexagons. The melting is first order going through a coexistence region. It is similar to melting of commensurate sub-monolayer Kr-films, but the correlation of the liquid is stronger. Using the liquid droplet model which was referred to in paragraph 5 for the Lorentzian correlation lengths ξ(77.21 K) = 150 Å, ξ(78.34 K) = 130 Å and ξ(85.04 K) = 80 Å. It is interesting to notice that the strong correlation of this liquid is preserved at temperatures more the 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, there is no mechanism to observe this in a (10) diffraction signal from disordered commensurate alloys.

Figure 9.6 shows the melting of a one to one argon-xenon alloy, coverate ρ = 0.73 particle per 3 graphite hexagons. This par-
Fig. 9.4. A series of constant compositions phase diagrams for the argon-xenon mixtures. T gives the temperature, \( \rho \) the coverage. The signature A stands for incommensurate argon like, X for xenon like, C for commensurate, V for vapour and L for liquid like vapour.

A particular alloy forms coexistence of a commensurate and an incommensurate structure at high temperature, and the two structures melt at the same temperature. This happens close to the particular compositions (\( x \)) and coverages (\( \rho \)) which are given by the V-points of the X+C+V coexistence region of the phase diagram (See Fig. 9.1). At the V point the two solids merge, as well as their diffraction signal merge. It has the important
Fig. 9.5. The figure shows the melting of a commensurate alloy, $x = 40\%$ Ar, $\rho = 81\%$. 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.
Argon: Xenon = 0.50 Coverage = 73%

Fig. 9.6. 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 \( x = 50\% \) Ar, coverage \( \phi = 73\% \). At \( T = 79.83 \text{ K} \) the correlation of the liquid is about 300 Å.
consequence for the phase diagram that for argon-xenon alloys the commensurate-incommensurate phase the transition stays first order all the way to the melting line that is it takes place in a phase separation manner. At 79.83 K the Lorenzian correlation length is about 300 Å.

REFERENCES


10. KRYPTON-XENON MIXTURES

Our krypton-xenon study is less detailed than the one of argon-xenon. The krypton-xenon study involves the analysis of six different compositions, most of them being commensurate or krypton-like for all temperatures, this tendency to commensuration was independently found by Regnier et al. in an isotherm study. The actual study of structural changes reduces to a few compositions in a coexistence region similar to that found for the argon-xenon system. The mechanism looks entirely the same. A krypton monolayer is commensurate by itself. Thus only the xenon rich half of the argon-xenon diagrams are taken over by the krypton-xenon system, meaning a slightly lesser degree of complexity.

Figure 10.1 shows diffraction groups from 1:2 krypton-xenon mixtures. The first-order jump or the difference in lattice parameters of the incommensurate and the commensurate structures which coexist at the point in the phase diagram where phase separation takes place is smaller than that of the argon-xenon case. This clearly indicates that at the point of phase separation there is a considerable amount of krypton in solution in the xenon-like film. At the high-Q side of the commensurate structure there is a slight indication of additional intensity at half the distance from the commensurate structure of that of the distance between the incommensurate and commensurate structures in coexistence. This is an indication of a possible super-hexagonal domain structure in the incommensurate xenon-like film. Such a super-hexagonal domain structure is clearly expressed in an almost identical system, xenon and methane. In this case the difference between the two particles is even smaller.
Fig. 10.1. The figure shows the diffraction groups from a krypton-xenon mixtures with 41% krypton and 59% xenon. The total coverage is 0.73 monolayers. At low temperature there is only commensurate structure, at an intermediate temperature there is coexistence of commensurate and incommensurate structure. At high temperatures there seems to be a strongly correlated liquid like structure.

REFERENCES

11. METHANE-XENON MIXTURES

The methane-xenon system is a favourable one for studies of a possible order-disorder phase transition, because of the large difference in the scattering factor of the two components, but as was shown in paragraph 8 the existence of a chemically order phase was not established. The amplitude of scattered intensity from methane with the formfactor of its ten electrons is approximately a fourth of that from argon. The set-up for X-ray diffraction at DORIS does not permit study of pure methane films. At a composition ratio of one-to-two and two-to-one, methane-xenon mixtures were found to form incommensurate structures at submonolayer coverages. Figure 11.1 show the diffraction pattern at T = 11 Kelvin. At the composition of one-to-two and at sub-

![Diffraction Pattern](image)

Fig. 11.1. The diffraction pattern at T = 11 K of a one-methane-to-two-xenon film on graphite with a total coverage of 0.91 monolayer. The smaller peak is due to the monolayer having taken up a structure with super-hexagonal domain structure.
monolayer coverage \( \rho = 0.9 \) at 11 K there is a clear indication of intensity of the high-Q side of the commensurate position in Q-space (see Fig. 11.1). The intensity falls at the position where it should be expected from a super-hexagonal domain structure classified by Nielsen et al. (see also Stephens et al.) as "type \( \Delta a/\lambda = 4/3 \)" and the existence of "wall particles". Thus Bragg scattering occurs at

\[ \ldots, \tau_0 - 5/2 \epsilon, \tau_0 - \epsilon, \tau_0 + 1/2 \epsilon, \tau_0 + 2 \epsilon, \ldots \]

It is seen that two satellites can be identified by the eye. This is the first system of monolayers on graphite where the identification of higher Fourier component of a mass-density modulation is this clear. In addition, very weak scattering which may be a third satellite on the very high Q-side exist. Not only are the equidistant positions of the intensities from the monolayer a strong indication for a super-hexagonal domain ordering in the monolayer. An even stronger measure of this interpretation is the movement of the satellites with the thermal expansion of the lattice (or main peak of the diffraction pattern). That is given in Fig. 11.2. It is seen that the two satellites move consistently with the hexagonal domain structure picture.

The substrate field can introduce the creation of a super-hexagonal structure in the 2D lattice two ways:

i) by perturbing the lattice by a displacement field, and

ii) on a fixed lattice, by rearranging the two kinds of particles at the lattice sites in an energetically favourable way both to the substrate field and the lattice.

It is easily seen that mechanism i) and ii) cooperate and therefore the domain walls in a binary system may be narrower than for a one-component Lennard-Jones monolayer. Both i) and ii) lead to satellites at the right wave vectors; although a chemical modulation is believed to have the minor effect on the satellites, one must not forget the huge difference in the X-ray scattering
cross-section between Xe and CH₄. Without assuming a domain wall, for a chemical modulation and its degree of disorder, the way to understand the origin of the satellites is by comparing the satellite intensity relative to the main peak at the (10) Bragg- and at higher Bragg-spots (an account is given by Guinier). Unfortunately, the higher Bragg-spots are not observable with the present X-ray beam intensity at our experimental set-up. The relative intensity of the different satellites around

Fig. 11.2. The main Bragg peak and the satellite position as function of temperature from a one-methane-to-two-xenon film with total coverage of 0.91 monolayer. For all temperatures the peaks' distance to the commensurate position of 1.703 Å⁻¹ stays in a ratio of 2:1 in agreement to what is expected from a super-hexagonal domain structure.
the (10) Bragg-spot can change particularly if both i) and ii) play a major role (Guinier).

At above one monolayer in the two layer regime a commensurate-incommensurate transition exists. It is interesting to note that the first order jump is small. (See Fig. 11.3).

\[ \Delta Q = 0.02 \, \text{Å}^{-1} \]

Applying the picture of films consisting of average sized particles then energetically the first order jump of the commensurate-incommensurate transition is determined by the differ-

![Fig. 11.3. A series of diffraction patterns from a double-layer methane-xenon film, showing a commensurate-incommensurate transition.](image-url)
ence in the bond length which just makes up for the gain in average adsorption energy by commensuration (the commensuration energy). The more misfit there is between the average particle size and the particle size for the commensurate structure, the larger is the gradient for the ad-adparticle potential at the distance of commensuration, and therefore for a given commensuration energy the first order jump of the C-I transition will be smaller. This is consistent with the observed decreasing jumps of argon-xenon (0.68 Å⁻¹), krypton-xenon (0.04 Å⁻¹) and methane-xenon (0.02 Å⁻¹). The variation in commensuration energy for the different mixture systems should also be taken into account. For lighter gases Hellemans et al. found that a Lennard-Jones description is applicable for the carbon-adatom interaction, with pseudo graphite parameters of \( \sigma = 3.39 \) Å and \( \epsilon = 28.3 \) K and with the carbon-adatom interaction described by the usual arithmetic and geometric mean taking. This allow us to calculate a naive commensuration energy as

\[
\langle E_{\text{adsorption (all positions)}} \rangle - E_{\text{adsorption (commensurate position)}}
\]

where each \( E_{\text{adsorption}} \) is minimized with respect to the adsorption height. By summing bonds shorter than 11 Å to the first layer of carbon atoms, I found the values given in Table 11.a when using the Lennard-Jones parameter given in Table 8.a.

The commensuration energies for the mixtures which can be derived from Table 11.a are several times too large to be in quantitative argument with the first order jumps observed, similarly this commensuration energy also fails to explain the first order jump of a pure krypton film. It is plausible that this is due to the incommensurate structure having showed some susceptibility to the substrate. This is just what is confirmed by the observation fo superhexagonal domain structures, then the commensuration energy basically becomes a function of domain-wall length per unit area of the film.
Table 11.a gives mean adsorption energy, commensurate adsorption energy and the naive commensuration energy.

<table>
<thead>
<tr>
<th>Units of Kelvin</th>
<th>(\langle E_{ad}\rangle)</th>
<th>(E_{ad,\text{com}})</th>
<th>(E_{\text{com}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>-484</td>
<td>-556</td>
<td>72</td>
</tr>
<tr>
<td>Methane</td>
<td>-602</td>
<td>-676</td>
<td>74</td>
</tr>
<tr>
<td>Krypton</td>
<td>-878</td>
<td>-996</td>
<td>118</td>
</tr>
<tr>
<td>Xenon</td>
<td>-1524</td>
<td>-1685</td>
<td>161</td>
</tr>
</tbody>
</table>

It is reasonable to ask whether or not a pure xenon film can undergo a commensurate-incommensurate phase transition, when we allow for several layers. Primary results indicate that if so, then the area of the phase diagram in which the structure gives only commensurate scattering is very narrow. However coexistence of commensurate and incommensurate scattering is a common signature. Such diffraction patterns have been observed at a filling of about two layers. Those may be interpreted as the bottom-layer having taken up a commensurate structure. A more detailed study is necessary on which to base a conclusion. At a filling of \(\rho = 1.25\) there is no signal of this commensuration (see Fig. 11.4). The system is as close to commensuration as the methane-xenon mixtures are in the sub-monolayer region.

Also, this pure xenon-film shows the existence of two satellites coming from the strong influence of the substrate potential creating superhexagonal ordering in the film.
Fig. 11.4. A low-temperature diffraction pattern for a pure xenon film with coverage of $\rho = 1.25$ monolayers. Note the similarity with the submonolayer methane-xenon film given in Fig.11.1.

REFERENCES

Xenon-freon mixtures have been studied in the xenon rich end of the phase diagram. Fig. 12.1 shows the peak intensity of the (10) Bragg spots for the melting transitions of films with small but increasing contents of freon. For contents from 0 to 16% there is always signature of a fully correlated structure until the intensity has disappeared. There is thus no clear qualitative change in the nature of the melting transition. I interpret the rounding of the peak intensity curves to be associated with a phase separation which occurs during the melting. In the case of xenon the melting temperature is 99 K, and in that of freon it is 76 K. Figure 12.2 shows a series of diffraction

Fig. 12.1. Shows the peak intensities of the (10) Bragg peak during the melting of a xenon and freon mixture. Sub-monolayer films with 0, 6, 10, 16 and 33% freon respectively were studied. All show sharp Bragg peak. Note: The temperatures stated are slightly too large due to a miscalibration of the thermometer.
Fig. 12.2. The figure shows a temperature series of diffraction patterns for a 0.60 monolayer xenon and freon film with 16% freon. At high temperature a well-developed diffraction peak shows sign of a homogeneously triangular lattice with correlations corresponding to about 850 Å in a Gaussian description. At 40 Kelvin or below a new phase exists, it cannot be described in terms of a single diffraction line in a Gaussian or Lorentzian model.
scans for a xenon film with 16% freon as a function of temperature. First, the melting takes place through a coexistence regime. This is similar to the argon-xenon melting where the melting takes place through a cigar-like part of the phase diagram consisting of the coexistence of a solid and a liquid in accordance to a lever rule.

As the temperature is lowered, the solid phase is entered, and the peak intensity increased. The sharpness corresponds to correlations of about 850 Å in a Gaussian description. When the temperature is lowered to 40 K the peak intensity has decreased and has a significantly broader full-width-at-half-maximum. This ex-

![Graph showing FWHM and WLS as functions of temperature.](image)

**Fig. 12.3.** Shows the full-width-at-half-maximum and the 20%-90% width-of-left-side for the diffraction groups given in Figure 12.2. There is an abrupt change in the FWHM but not in the 20%-90% width-of-left-side. This may imply that the low temperature peaks have their origin in structural features.
tends all the way to 11 Kelvin. Figure 12.3 shows the FWHM of the diffraction groups as a function of temperature. On the same figure is the 20% 90% defined width-of-left-side of the Bragg (10) profile given*. It is seen that a broadening of the front of the Bragg profile is partly unobserved. The ratio between the WLS and FWHM is so that the observed Bragg profile cannot be described in a Gaussian or low temperature Lorentzian model. There may be unresolved structure in the profile. By enlarging the distance from the slit to the PSD to 1280 mm the resolution of the set-up is increased to what corresponds 2300 Å in a Gaussian description, and the result is shown in Fig. 12.4. These diffraction profiles differ in no way from those taken with the 1200 Å resolution. No additional structure is resolved. This may not be that surprising because the resolution used in these experiments is set to match the finite-size distribution of the area coherent for adsorption, approximately. Therefore, information in the diffraction pattern may be limited equally by the substrate as by the experimental resolution.

The broadening of the line shape existed for xenon-freon films of various compositions. Figure 12.5 shows the 11 K diffraction pattern for different films. It is seen that the films with 10, 16, and 33% freon have virtually identical signature of the broad peak. Moreover a film with 6% freon had the same signature. At a composition with 3.5% freon there is a broadening of the diffraction pattern compared to that of a pure xenon film or that of a high-temperature mixture film. But it is not as broad as those with a higher content of freon. At a composition of 33% there is a clear signal of intensity at the position close to that of almost pure freon (1.475 Å⁻¹ the 2x2 structure). This signal is weak, but the scattering power of xenon and freon also

* This width-of-left-side differ slightly from the WLS defined in paragraph 5. It is approximately 70% of the WLS. The reason for using this other measure is that for these data the peak position is not well defined.
Fig. 12.4. Same as Figure 12.2 but with improved resolution enabling us to study coherens properties over 2300 Å in a Gaussian description, however, no additional structural features has been disclosed. The temperatures is 60.03 and 10.01 Kelvin, respectively.

differs considerably. They have to be scaled in accordance with the form factors. The diffraction experiments showed that an intensity from a full 2x2 commensurate freon monolayer relative to an \( p = 1 \) incommensurate xenon monolayer is a factor of 5 lower at the (10) Bragg peak.

One is therefore attempted to believe that the peculiar diffraction shape at low temperature of the xenon-freon mixture is caused by a structure of a xenon film with a residual content of freon. At this low temperature the film has been phase separated. On the basis of these diffraction measurements the amount of freon in the xenon film can be estimated to be less than 6%. It may be due to a residual solubility of freon in the xenon film. Another viewpoint is that the residual amount of freon in the xenon film is due to the final cooling time, leaving some freon molecules quenched into the xenon film. In such a
Fig. 12.5. The low temperature diffraction signal from submonolayer films of freon and xenon, with various compositions, only the film with 3.5% freon is shaper than the others. \(T = 10.5\) Kelvin.
case the amount of freon in films with a fully developed peculiar
diffraction pattern, those with 6 to 33%, may be even less than
3%. It is clear that a film with a smaller content of the foreign
molecules phase separates easier with a smaller fraction
quenched. That means that those of 6 to 33% have so many freon
molecules that they all end up with approximately the same amount
of freon. But that film of only 3.5% freon may separate easier.

One argument against these quenching interpretations is that
whether the film was cooled as fast as the displex manages, that
is one hour from 100 K to 11 K, or the film was slowly annealed
over 12 hours it made absolutely no difference in the observed
diffraction pattern. It could be useful with a cryostat having a
much faster cooling ability.

Nelson has indeed suggested that in a film with a small number
of quenched-in particles that are too large there may be a re-
entrance to a hexatic phase at low temperature. The mechanism
suggested is that at 0 Kelvin a certain fraction of the quenched-
in excessively large molecules will be associated with a dislo-
cation in the film. This will break down the quasi-long-range
order as in the case of the Kosterlitz-Throwles-Halpern-Nelson
melting transition. When the temperature is raised, this single
dislocation may take part in thermally excited dislocation pairs.
The impurities in the films have in this way been screened, and
quasilong-range-order restablished. A qualitative phase diagram
was given as in Fig. 12.6. The maximum impurity content, the
point P in the phase diagram, was given as

\[ \sigma_c = \frac{R_{2}^{2}}{64\pi^2\left(R_{2}^{2}_{\text{CP}_4} - R_{2}^{2}_{\text{Xe}}\right)} = 0.8 \]

which corresponds to approximately 1% freon in xenon. However,
not all of the freon molecules need to be associated with a dis-
location. Nelson et al. verified the zero temperature hexatic
phase in an experiment of hard spheres on a shake table.
Fig. 12.6. The phase diagram of David R. Nelson's theory on Reentrant Melting in Solid Films with Quenched Random Impurities, showing a reentrant to a hexatic phase at low temperature. The maximum concentration of impurities $c_c$ is estimated to about 1%.

A more comprehensive study of the xenon-freon mixtures is needed in order to understand the diffraction groups. They cannot directly be interpreted following the Nelson model, due to the observed diffraction profiles dissimilarity to that of a powder average Lorentzian line-shape. It cannot be ruled out that the nonisotropic structure of the freon molecules may cause additional structural complications. As in the argon study an experiment involving a possible interpretation of hexatic-like phases, not only involves the pair correlation function but also the orientational correlations. In powder samples and low-intensity diffraction measurements in particular, it is difficult to distinguish the small differences in the line shapes due to the different behaviour of the pair correlation function in the altered physical phases. Therefore a direct probe of the degree of hexaticness would prove a very useful measure. This can be done in measurements which are sensitive to angular orientation, which means that experiments on single monolayers on a surface would be very useful. It may soon be possible to do synchrotron x-ray diffraction on such a monolayer. Such monolayers have for
many years been studied by Low Energy Electron Diffraction, and LEED has confirmed angular epitaxy for many monolayers.

REFERENCES


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