Disordering of submonolayer films of electropositive elements adsorbed on metals

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The disordering of submonolayer Li, Na, Cs, Sr, and La films on the (011) faces of tungsten and molybdenum crystals was investigated by the method of slow-electron diffraction—by measuring the temperature dependences of the diffraction-reflection intensities. It is observed that the intensity of diffraction reflections from films whose structure is commensurate with the substrate structure is strongly decreased (in an interval on the order of several degrees) when the critical temperature is approached. The decrease of the intensity of reflections from incommensurate films takes place in a wide temperature interval (dozens or hundreds of degrees). The results are discussed on the basis of notions concerning the character of the order of quasi-two-dimensional systems of various types.

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1. INTRODUCTION

Submonolayer adsorbed films are objects that can be used as examples for the study of the properties of matter in the quasi-two-dimensional state.

The temperature dependence of the heat capacity C_v of submonolayer helium films on the basal face of graphite was investigated in[1]. At low and medium degrees of surface coating, the $C_v(T)$ plot has a sharp peak, whereas when the coatings come close to forming a solid monolayer they have a rather broad maximum. Although the atomic structure of the films was not investigated directly by Bretz *et al.*,[1] they have concluded from indirect data that the film structure is commensurate with that of the substrate in the former case, but not in the latter. The obtained $C_v(T)$ were interpreted on the basis of the assumptions that in commensurate films an order-disorder phase transition takes place at a certain temperature T_c, whereas in incommensurate films there is no true long-range order at all at $T \neq 0$. A similar conclusion was drawn in a recent paper[2] as a result of an investigation of neutron scattering by nitrogen films adsorbed on graphite.

The present paper is also devoted to the disordering of submonolayer films. In contrast to[1,2], however, we have studied systems of an essentially different type—films of the electropositive metals Li, Na, Cs, Sr, and La chemosorbed on tungsten and molybdenum. In this case the adsorption bond is strongly polar and a major role is played by the dipole-dipole interaction of the adsorbed atoms. We have investigated the film structure by slow-electron diffraction (SED), and the information on their disorder was obtained by measuring the intensity of the diffraction reflections as a function of the temperature. A preliminary report of the present results was published earlier.[3]

2. EXPERIMENTAL PROCEDURE

The experimental data were obtained with low-voltage electron-diffraction of two types—all-glass[4] and the metal apparatus of the RIBER firm. The films of the electropositive elements were produced with evaporators of the Knudsen-chamber type on a substrate constituting a tungsten or molybdenum crystal cut in the form of a plate with dimensions $6\times4\times0.5$ mm parallel (within $<0.5°$) to the (011) face, which has the closest packing. Prior to being placed in the apparatus, the samples were ground and polished mechanically and electrolytically, and after being placed in the apparatus they were carefully outgassed and rid of carbon by the well known procedure of carbon oxidation.[5] The adsorbate sources were also subjected to prolonged conditioning, until a vacuum of 10^{-11}–10^{-12} Torr was reached in the apparatus.

Since the ordering of the investigated films takes place at rather low temperatures,[4,6,7] the all-glass electron-diffraction cameras were provided with means of cooling the samples. To this end, the crystals were mounted on dewar supports that could be filled with liquid nitrogen or helium. The substrate temperature was measured with a W-Ta or with a VR5-VR20 thermocouple, as well as with an optical pyrometer. The surface concentration of the adsorbed atoms was determined from the time of the exposure of the crystal to an atom beam of known intensity (the coefficient of condensation of metal on metal is equal to unity). To calibrate the beam we measured the time within which the minimum of the system work function was reached, while the adsorbed-atom concentration corresponding to the minimum of the work function was determined in separate experiments. In these experiments the beams were calibrated with quartz microbalances,[8,9] by the surface-ionization current,[10] or by the time required for the formation of a definite two-dimensional lattice of adsorbed atoms, corresponding to attaining a maximum intensity of the superstructure reflections on the electron-diffraction pattern.[4,7] If certain conditions are satisfied (it is necessary to ensure uniqueness of the interpretation of the electron-diffraction pattern and to ascertain that the film is solid), the last method ensures the highest accuracy—on the order of several per cent. This was the predominantly used method.

We assessed the ordering of the film from the intensity I of the additional (superstructure) reflections. The intensities were measured with a telescopic photometer.

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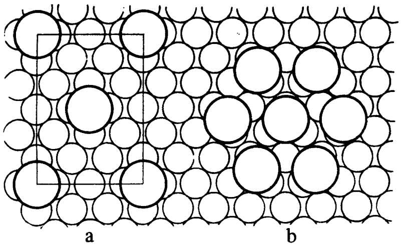

FIG. 1. Models of commensurate (a) and incommensurate (b) structures of a strontium film adsorbed on the (011) face of molybdenum: a) $c(3\times3)$; b) hexagonal.

The selected section of the electron-diffraction camera screen was projected by a system of lenses on the receiving diaphragm of a photomultiplier, and the dimension of the diaphragm was chosen such as to cover only the central part of the reflection (somewhat less than its half-width). The experiments were performed in the following manner: The crystal with the film sputtered on it was heated, by passing current through it, to a temperature not high enough to cause evaporation of the adsorbate, and was cooled, after turning the current off, to the temperature of the crystal holder (usually the temperature of liquid nitrogen or helium). In the course of the cooling we registered the intensity as a function of temperature. The cooling rates were such that thermodynamic equilibrium could be established at each temperature, as evidenced by the constancy of the shapes of the $I(T)$ curves at different cooling rates. Additional data on the character of the ordering of the films could be obtained by examining the variation of the dimensions of the reflections.

The SED method yields information on the degree of ordering within an area of diameter equal to the coherence width of the diffracted electrons. The presently used low-voltage electron-diffraction cameras are characterized by an electron-coherence width of several hundred angstroms. It is this width which determines for the most part the instrumental broadening of the reflections. In addition, the diffraction broadening due to the imperfection or to the limited dimensions of the lattice comes into play if the actual (or effective[11]) dimension of the coherently scattering region of the surface becomes less than the coherence width of the electrons.

Our experiments were performed with electrons of energy $E=10-60$ eV. This choice of energy was dictated by the following considerations: First, as shown by an estimate,[12] in this region the instrumental broadening of the reflections is minimal in the existing electron diffraction cameras. Second, the maxima of the energy dependences of the atomic factor of electron scattering into the rear hemisphere (relative to the propagation direction of the primary beam) fall precisely in this interval of E.[13] It is therefore possible to find within the limits of the present region an interval with the largest ratio of the atomic scattering factors of the adsorbate and the substrate. In addition, when a concrete energy E was chosen in this interval, attention was paid to the conditions of interference in multiple scattering of the electrons between the film and the substrate.[14]

3. RESULTS OF EXPERIMENT

The investigated adsorbates, whose bond with the substrate is strongly polar (dipole moment ~5–10 D), form on the (011) faces of tungsten and molybdenum two-dimensional lattices of two different types. a) At low concentrations of the adsorbed atoms, when there are many free spots on the surface, the produced lattices are commensurate with the substrate lattice. In particular, in the so-called simple commensurate structures, all the adsorbed atoms occupy identical positions relative to the substrate atom. An example of such a structure is shown in Fig. 1a. A pattern of the type $c(N\times M)$, where N and M are integers, means that the lattice of the film is centered, and that its periods are larger by N and M times than the periods of the substrate lattice in the corresponding directions.[15] b) At coatings approaching a solid monolayer (and in the case of a particularly strong polar bond even at relatively small coverings), incommensurate films are produced, whose atom arrangement is not determined by the substrate structure. The substrate fixes only the orientation of the film. All the incommensurate films investigated in the present study have a hexagonal structure, whereas the substrate surface has a rectangular centered lattice (Fig. 1b). With increasing surface concentration n_a of the adsorbed atoms, the period of the hexagonal structure decreases smoothly, and it is therefore convenient to characterize it by the degree of coating θ, i.e., the ratio of n_a in the given structure and in a close-packed monolayer of adsorbed atoms. The formation of an incommensurate structure indicates that the interaction between the adsorbed particle prevails over the potential relief of the substrate. The incommensurate film can therefore be regarded, to some approximation, as the model of a film on a smooth (structureless) substrate.

Figure 2 shows characteristic electron-diffraction patterns of matched and mismatched films, obtained at low T. In both cases the dimension of the reflections from the film does not differ from the dimension of the reflections on the electron-diffraction pattern of the clean substrate. This means that, at least within the limits of an area with dimensions equal to the electron-coherence width, these films are well ordered.

We consider now the temperature dependences of the intensity of reflections from adsorbed films (Fig. 3). In this study they were measured for Sr films on Mo (011), and also Li and La on W (011). To complete the picture, Fig. 3 shows also the results obtained earlier for Sr, Na, and Cs films on W (011).[4,6,7] We note that all the data given here were obtained at coatings such that the film remained single-phase (solid).

Although, as already indicated, the diffraction reflections from commensurate and incommensurate films are practically indistinguishable in size and intensity at low temperatures (and at comparable n_a), the character of the variation of their intensity with temperature is greatly different.

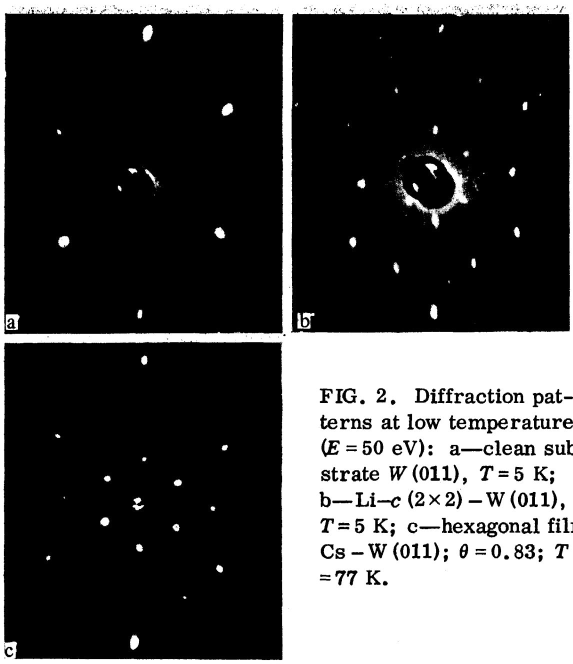

FIG. 2. Diffraction patterns at low temperatures ($E = 50$ eV): a—clean substrate $W(011)$, $T = 5$ K; b—Li–c (2×2)–W(011), $T = 5$ K; c—hexagonal film Cs–W(011); $\theta = 0.83$; $T = 77$ K.

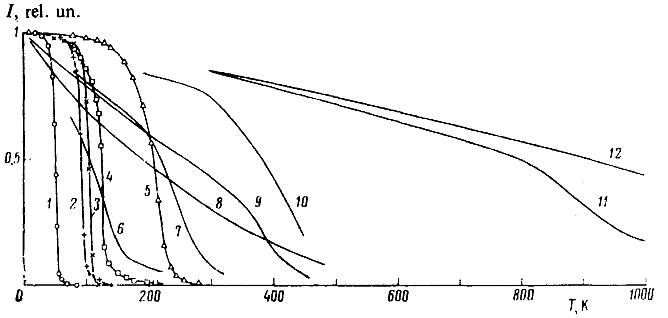

FIG. 3. Temperature dependences of the intensities of superstructure reflections 1—Sr–c (3×3)–Mo(011), $E = 11.2$ eV; 2—Li–(3×2)–W(011), nonprimitive unit cell containing 2 adsorbed atoms, $E = 40$ eV; 3—Li–c (2×2)–W(011), $E = 26$ eV; 4—Na–c (2×2)–W(011), $E = 27$ eV; 5—Li–c (1×3)–W(011), $E = 26$ eV; 6—Cs–W(011), $\theta = 0.48$, $E = 13$ eV; 7—Na–W(011), $\theta = 0.80$, $E = 27$ eV; 8—Sr–Mo(011), $\theta = 0.75$, $E = 55$ eV; 9—Sr–Mo(011), $\theta = 0.64$, $E = 55$ eV; 10—Sr–W(011), $\theta = 0.70$, $E = 31$ eV, 11—La–W(011), $\theta = 0.75$, $E = 15$ eV; 12—La–W(011); $\theta = 0.80$, $E = 18$ eV.

The $I(T)$ plots for commensurate films (curves 1–5) have a clearly pronounced low-temperature saturation region, a region where I drops sharply (its width is usually not more than several degrees), and a relatively small high-temperature tail. We note that in the region of the sharp intensity drop the reflections undergo no noticeable broadening.

In contrast, the $I(T)$ curves for incommensurate films (curves 6–12 on Fig. 3) have a much smoother character—the region where the intensity drops stretches over tens and hundred of degrees. On some curves (7, 9, 10, and 11 on Fig. 3) one can note two sections with different slopes, but even in this case there are no strong changes of I similar to those observed for the commensurate films. The steeper section of the curve usually corresponds to the appearance of a certain broadening of the diffraction reflections, which increases with increasing T (see, e.g., Fig. 4).

4. DISCUSSION OF RESULTS

The results can be explained on the basis of the notion that the commensurate and incommensurate films differ fundamentally in the character of their ordering. The same notions were used by others[1,2,16] to interpret data on the heat capacity of helium films on graphite and on the scattering of neutrons by nitrogen films on graphite. The specifics of the ordering in films of various types are governed essentially by the singularities of their frequency spectra. According to Ying[17] the frequency spectrum of a commensurate film begins with a nonzero frequency ω_i that characterizes the vibrations of a single adsorbed atom in the potential well occupied by it. Consequently long-range order is maintained in such a film at temperatures below a certain critical value T_c. On the other hand the spectrum of an incommensurate film extends all the way to $\omega = 0$, and this film is similar in this respect to a two-dimensional film on a smooth substrate. The theory predicts[18,19] that in such a system at $T > 0$ there is no long range order, and only a more or less extended short-range order is present.1) Actually, in this case the mean square of the quantity $\delta_n = x_n - x_0 - nd$ (x_n and x_0 are the instantaneous coordinates of the n-th and zeroth atoms, and d is the period of an ideal lattice at $T = 0$) diverges with increasing n: $\langle \delta_n^2 \rangle \sim T \ln n$.

Naturally, the noted difference in the character of the ordering should manifest themselves in the diffraction by the films. For commensurate films the intensity of the superstructure reflections (see, e.g.,[21,22]) can be represented in the form

$$I = I_0 e^{-2W} \eta^2,$$

where $I_0 = I$ as $T \to 0$, e^{-2W} is the Debye-Waller factor, and η is the long-range order parameter. The function $\eta(T)$ describes an order–disorder phase transition, while the factor e^{-2W} takes into account the thermal vibrations of the adsorbed atoms. The amplitude of these vibrations increases when the bond between the adsorbed atoms and the adsorption centers weakens.[23] At low

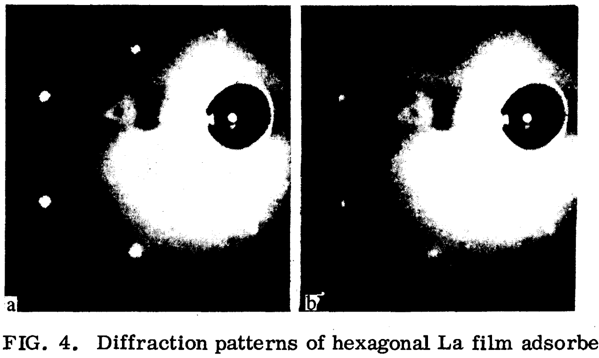

FIG. 4. Diffraction patterns of hexagonal La film adsorbed on the face (011) W ($\theta = 0.75$; $E = 33$ eV) at different temperatures: a—$T = 300$ K; b—$T = 940$ K.

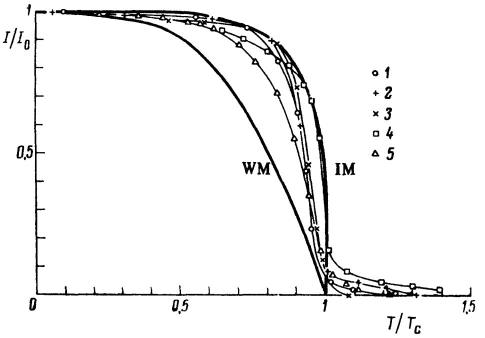

FIG. 5. Temperature dependences of the intensities of superstructure reflections of commensurate films: 1–5—for the same systems as 1–5 on Fig. 3: IM and WM—calculations for the Ising and Weiss models, respectively.[25]

temperatures, W is practically independent of T, and below the Debye temperature we have $W \sim T$. The width of the diffraction reflections should be independent in this case all the way to the phase transition.[11]

Diffraction by a two-dimensional system in which there is no long-range order but only an extended short-range order has been considered in[24]. The theory predicts that in this case, too, under conditions of real experiments (samples with finite dimensions) there should exist a certain temperature below which the reflections become sharp. This is caused by the rather weak (logarithmic) divergence of the quantity $\langle \delta_n^2 \rangle$. Formally, an order–disorder phase transition is realized in this situation at $T = 0$, and the change of the intensity at $T > 0$ should proceed relatively smoothly on account of the thermal vibrations of the atoms.

Accordingly, the abrupt decrease of the intensity of the superstructure reflections from commensurate films which takes place in a narrow interval of T (Fig. 3, curves 1–5), can be interpreted as the result of an order–disorder phase transition. The high-temperature tails on these curves seem to be connected with the fact that short-range order is preserved after the phase transition and that the electrons have a limited coherence width.[22] At the same time, the smooth character of the $I(T)$ plots for incommensurate films agrees with the theoretical predictions for two-dimensional systems in which there is no long-range order at $T \neq 0$.

The intensity of the reflections from the incommensurate films is significantly decreased starting already with the lowest temperatures. This result agrees with the theoretical conclusion that the spectrum of such a film has an abundance of low-frequency oscillation modes, the excitation of which weakens the reflections on account of the Debye-Waller effect. The sharpness of the reflection from incommensurate films in a wide interval of T can be attributed to the fact that over distances on the order of the electron coherence width the deviations from strict periodicity of the arrangement of the atoms are not large enough to make the broadening of the reflections discernible against the background of their instrumental width. If the temperature is raised enough, the value of $\langle \delta_n^2 \rangle$ increases to such an extent that the additional broadening of the reflections becomes discernible (Fig. 4). This decreases the relative fraction of the light passing through the entrance aperture of the photometer. Special observations have shown that this is precisely the cause of some change in the rate of decrease of the intensity on curves 7 and 9–11 (Fig. 3).

In conclusion, we consider in greater detail the functions $I(T)$ for commensurate films. It is difficult to separate on these curves any extended exponential sections corresponding to intensity fall-off on account of the Debye-Waller effect. We shall therefore assume that the curves are governed mainly by variation of the long-range order parameter with temperature. The corresponding curves in Fig. 5 are plotted in relative coordinates, $I(T)/I(0) = f(T/T_c)$, where T_c is the critical temperature of the order–disorder transition, which we determined by continuing the steeply dropping section of the intensity curve until it intersected the T axis. For comparison, Fig. 5 shows also the calculated plots for two models[25]: 1) for a two-dimensional Ising model that takes into account of the interaction of only the nearest neighbors (curve IM); 2) for the classical model of the average molecular field with an infinite interaction radius (the Weiss model, WM). It can be stated that in the region $T < T_c$ the experimental plots deviate noticeably from both calculated curves (the high-temperature tails are disregarded and assumed to be caused by the change of the short-range order).

It is known that in the systems studied by us the adsorbed atoms are positively charged and an important contribution is made to the interaction between them by the dipole-dipole potential $U \sim r^{-3}$, where r is the distance between the adsorbed atoms. It appears that the positions of the experimental curves on Fig. 5 is determined by the fact that the dipole-dipole potential has a long-range character intermediate between the potentials for the considered limiting cases of interaction. We indicate for comparison that disordering of commensurate helium films on graphite[1] and of hydrogen films on tungsten[26,22] could be satisfactorily described within the framework of the Ising model, since these systems are characterized by a small radius of interaction between the atoms.

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1) Throughout the article we have in mind the crystalline (positional) long-range order. The system in question can, however, have also a so-called topological (orientational) long-range order that determines the rigidity of the system.[16,20]

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Paramagnetic relaxation of conduction electrons, due to indirect spin-spin interaction via a phonon field

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The longitudinal paramagnetic conduction-electron relaxation times due to electron-electron interaction via the phonon field are calculated. In the case considered, the contribution to the relaxation process is made by that part of the indirect phonon interaction which leads to a change in the spin states of the interacting electrons. It is found that, in the temperature range $T \geq 10$ K, the rate of relaxation via the mechanism under consideration is independent of the temperature and is proportional to $T_1^{-1} \propto N^{4/3}$, where N is the electron concentration. At temperatures below 10 K, $T_1^{-1} \propto T^2 N^{2/3}$. The effect of multiple phonon exchange and of collective excitations of the electron system by indirect phonon interaction on the magnitude of T_1 is analyzed.

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Paramagnetic relaxation of conduction electrons in metals and semiconductors is due to the scattering of electrons with spin flip. The basic scattering mechanisms are: interaction with phonons[1] or with impurities[2] and scattering of electrons by one another.[3] The paramagnetic relaxation of the conduction electrons in metals and semiconductors, due to electron-electron interaction, is described by the function $f(\mathbf{p}, \sigma; \mathbf{p}', \sigma')$, which characterizes the amplitude of scattering of particles by one another with spin flip. For a system that is invariant relative to rotations, the general form of this function is[4]

$$f(\mathbf{p}_i, \boldsymbol{\sigma}_i; \mathbf{p}_j', \boldsymbol{\sigma}_j') = \sum_{\alpha,\beta} [f(\mathbf{p}_i, \mathbf{p}_j') + \boldsymbol{\sigma}_i \mathbf{g}(p_i, p_j') + \sigma_j' \mathbf{g}'(p_i, p_j') + \sigma_{i\alpha}\sigma_{j\beta}' \xi^{\alpha\beta}(\mathbf{p}_i, \mathbf{p}_j')], \qquad (1)$$

where $\alpha, \beta = x, y, z$. The terms in (1) that are linear in the spin describe the spin-orbit interaction of the spin of the i-th (or j-th) electron with the magnetic field produced by the orbital motion of the j-th (or i-th) electron. Terms that are quadratic in the spin operator describe the magnetic dipole-dipole and exchange interactions between electrons.

It is known that the indirect exchange interaction of electrons via the phonon field is the principal real mechanism, leading to the appearance of the superconducting state. In works on the theory of superconductivity, the process of exchange of phonons without change in the ground states of the interacting electrons is considered. However, in materials with strong spin-orbit interaction $\mathscr{H}_{c0}$ of the conduction electrons with the ion core of the lattice,