
Yu.S. Vedula, V.K. Medvedev, A.G. Naumovets, and A.G. Fedorus. *Experimental investigation of two-dimensional crystals*. Atoms or molecules adsorbed on the surface of a solid in no greater than monolayer numbers may form two-dimensional crystals at low enough temperatures. Investigation of the structure of these crystals and their phase transitions is just as important for understanding of the physicochemical properties of a surface as is investigation of three-dimensional structure for understanding of bulk properties.

A major series of studies in this area has been conducted by the Institute of Physics of the Academy of

Sciences of the Ukrainian SSR—for the most part using slow-electron-diffraction and contact-potential-difference techniques.

Among the adsorbates that have been investigated thus far, adsorbed atoms (adatoms) of alkali and alkaline-earth elements on the surfaces of crystals of refractory metals—tungsten, molybdenum, rhenium, etc.—present the richest range of two-dimensional crystals. They form a whole series of lattices whose unit cells are commensurable with (matched to) the unit cell of the base at low degrees of surface coverage, and lattices that are incommensurable with the base at converges approaching a continuous monolayer.¹

Lattices of the latter type form when the adatom interaction energy exceeds the potential-relief amplitude of the base. Since the adsorption bond is strongly polar in these systems, the dipole-dipole repulsion of the adatoms is an important factor. Superimposed on this is the interaction of the adatoms via the base, which oscillates with distance and is, in the general case, anisotropic (see, for example, Refs. 2 and 3). It is the superposition of these interactions that is responsible for the wide variety of symmetries of the two-dimensional crystals. Relatively "isotropic" adatom lattices form on surfaces with smooth atomic relief (closed-packed crystal faces). On the other hand, the symmetry of two-dimensional lattices on bases with furrowed relief—for example, on the (112) faces of tungsten and molybdenum—indicates sharp anisotropy of the adatom interaction. In this case, the lattices are constructed of relatively light linear chains of adatoms spaced regularly at comparatively large distances from one another (distances of 20–25 Å have been observed at low surface coverages³).

Information on the melting of two-dimensional crystals has been obtained by studying the intensity of superstructural diffraction spots as function of temperature: $I(T)$. It has been shown for many adsorbates on surfaces with smooth atomic relief that the $I(T)$ curves of commensurate and incommensurate lattices differ significantly.⁴ In the former case, the intensity is practically constant at low T , but then it drops sharply, indicating a loss of long-range order in the film at a certain critical T ; in the latter case, the intensity varies smoothly, beginning at low T (Fig. 1, curves 1 and 2). This result is consistent with the theoretical prediction of a fundamental difference between the vibrational spectra of commensurate and incommensurate two-dimensional crystals.^{5,6} The vibrational spectrum of a commensurate film has a gap whose boundary frequency is determined by the shape of the base potential well and by the adatom interaction. As a result, long-range order exists in the film at low T but is violated at the critical temperature. On loss of commensurability with the base, and acoustic vibrational branch appears in the spectrum of the film, with a resulting decrease in the intensity of the superstructural reflections due to the Debye-Waller effect beginning at the lowest T .⁶ Another consequence is that it is impossible for positional long-range order to exist

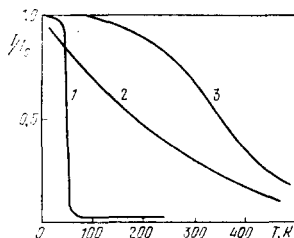


FIG. 1. Temperature dependence of superstructure-reflection intensity. 1) Commensurate $c(3 \times 3)$ Sr lattice on Mo (011); 2) incommensurate Sr lattice on Mo (011); 3) $p(1 \times 3)$ Mg chain lattice on Re (10 $\bar{1}$ 0). I_0 is the intensity of the reflections as $T \rightarrow 0$.

in the two-dimensional incommensurate film, which serves in this sense as a model of the two-dimensional film on an ideally smooth base.

The $I(T)$ curves for commensurate chain crystals on surfaces with furrowed atomic relief are smoother than those for "isotropic" commensurate lattices (Fig. 1, curve 3). This can be explained by pointing out that the interaction of the adatoms in the chains is much stronger than the interaction between chains.⁷ The elementary excitations in these lattices are chain segments that have been shifted from their equilibrium positions; their lengths can vary quite easily, thus rendering the spectrum quasicontinuous. For this reason, the $I(T)$ curves for commensurate chain lattices have shapes intermediate between those for commensurate and incommensurate "isotropic" lattices.

Major improvements to the techniques used in investigating the surface diffusion of adatoms have made it possible to study the appearance of phase transitions in submonolayer films during diffusion processes.⁸ The diffusion distributions present clear-cut steps that correspond to different two-dimensional adatom lattices (Fig. 2). Multiphase ("reactive") surface diffusion has been demonstrated in this way. The diffusion coefficient was observed to increase sharply in the region of the transition from commensurate to incommensurate structure. In this case, theory predicts that the film will have local regions of disturbed commensurability in the form of a lattice of solitons representing linear interstitial configurations in the commensurate lattice.⁹ The high diffusion coefficients are presumably due to high mobility of the solitons. The adsorbates studied diffuse out of polylayer coatings not by the "unrolling carpet" mechanism assumed earlier (Fig. 3a), but apparently by the advance of solitons in the first layer to the edge of the two-dimensional phase spreading across the surface (Fig. 3b).

The disordering of two-dimensional crystals under electron bombardment of the surface, i. e., the formation of radiation-induced defects in the crystals, is of interest in itself. The results of experiments in-

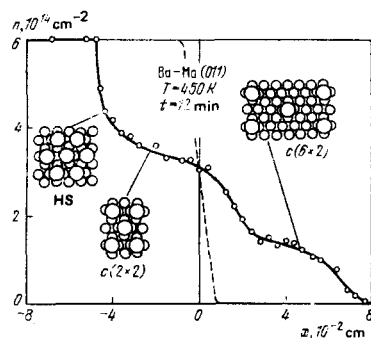


FIG. 2. Ba-atom concentration distribution on Mo (011) in diffusion from a tight monolayer. The dashed line represents the initial distribution. Models of the barium lattice are shown for various concentrations (HS is the hexagonal structure).



FIG. 3. Possible surface diffusion mechanisms. a) "unrolling carpet" (does not occur in the systems studied); b) proposed mechanism. 1) interstitial configuration (soliton).

dicates that there are various possible mechanisms of this effect. In the disordering of lithium films on tungsten, the primary event is the creation of a vacancy in the K shell of the lithium atom by an incident electron.¹⁰ It has been found in recent years that electron-stimulated desorption may also be initiated in certain cases with ionization of an inner shell.¹¹ In contrast, the disordering of hydrogen films on tungsten occurs even on recombination of thermal electrons with the surface, i.e., by release of the electron's "inverse work function" as it enters the solid.¹²

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