Disordering of linear superstructures in submonolayer films

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The disordering of the linear superstructures $p(1\times3)$ in the Mg–Re(10$\bar{1}$0) system and $p(1\times5)$ in the Ba–Mo(112) system have been investigated by the low-energy-electron-diffraction method. A marked decrease in the intensity of the reflections has been found to occur at $T\sim100$ K, but the reflections are observable up to $T\sim500$ K for Mg$p(1\times3)$ and up to $T\sim700$ K for Ba$p(1\times5)$. The results obtained are discussed on the basis of the assumption that the excitation spectrum of the linear superstructures has a quasicontinuous character.

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INTRODUCTION

Investigations of the structure of adsorbed films have shown that on substrates with a furrowed atomic surface structure many adsorbates in thin coatings form linear adatom chains stretched in the direction perpendicular to the furrows. We have in earlier experiments observed such chains on the (112) face of bcc tungsten and molybdenum crystals,[1-8] and Engelhardt and Menzel[9] have observed the formation of linear chains of oxygen adatoms on the (110) face of a fcc silver crystal. The potential relief of all these substrates can be represented in the form of deep furrows with a relatively shallow modulation along the furrows. The period of the linear superstructures is equal to the lattice constant of the substrate across the furrows and several times the lattice constant of the substrate (up to 9 times) along the furrows [structures of the $p(1\times n)$ type]. In the present experiment we studied the disordering of the linear chains formed by Mg [the $p(1\times3)$ structure] on the hitherto uninvestigated (10$\bar{1}$0) face of a hcp Re crystal and Ba [the $p(1\times5)$ structure] on the (112) face of a Mo crystal. These data together with the results obtained earlier exhibit a number of interesting characteristics common to all the investigated $p(1\times n)$ structures with a large period ($n=3-9$), although these systems differ from each other in that they have different periods and the absorbates and substrates involved differ in their chemical characters. First, the disordering temperature varies slowly with the period of the superstructure, and attain a value of the order of hundreds of degrees, although estimates of the characteristic energy of the interaction between the chains yield a value of the order of tens of degrees. Secondly, a marked decrease in the intensity of the superstructure reflections is observed at temperatures significantly lower than the transition temperature, a behavioral anomaly which is characteristic of incommensurable structures, although the $p(1\times n)$ structures are certainly commensurable. These anomalies are explained in the present paper on the basis of the assumption that the excitation spectrum of the linear superstructures has a quasicontinuous character at not very low temperatures.

EXPERIMENT

The investigations were performed by the low-energy-electron-diffraction method in a sealed glass apparatus with a planar system for the acceleration of the reflected electrons. The intensities of the diffraction reflections were measured with a telescopic photometer. The samples, which were cut from a bulk molybdenum or rhenium single crystal, were 10×4×0.35 mm plates with surfaces parallel to the corresponding crystallographic planes to within 20′. After the electric-spark cutting, grinding, and mechanical polishing, the preparation of the samples was finished off with electropolishing, in the course of which a layer of thickness not less than 0.1 mm was removed. The sample was welded through four tungsten wires of diameter 0.25 mm on to molybdenum leads sealed in a Dewar leg. Such a mounting allowed us to cool the crystals down to the temperature of liquid nitrogen, or heat them to $T\leqslant1500$ K by passing a current through the leads. The crystals were heated to higher temperatures by bombarding them with electrons from guns located behind them. The crystal temperature was measured with VR-05 and VR-20 tungsten-rhenium-alloy thermocouples. The crystals were thoroughly degassed and decarbonized by annealing them at 1700 K in an oxygen atmosphere (~10^{-6} Torr) for ~20 h.

The adsorbates used were the alkaline-earth elements magnesium and barium. The sources of the magnesium was a tantalum Knudsen cell filled with a CaO, MgO, and Al mixture. The barium source was the same cell filled with tablets of the alloy BaTi. Each source was subjected to a suitable vacuum heat treatment that allowed us to obtain in the end pure atomic beams of absorbates under conditions of slow gas evolution from it. The purity of the atomic beams was mass-spectrometrically monitored. The experimental tubes were equipped with titanium getter pumps and field-emission manometric projectors. The pressure of the active component of the residual gas during the experiment did not exceed 10^{-11} Torr.

Figure 1 shows diffraction patterns and their identification for the Mg–Re(10$\bar{1}$0) system. The diffraction patterns of this system [Fig. 1(b)] for $\vartheta=\frac{1}{3}$ (ϑ is the degree of coating) exhibit secondary reflections at points dividing the distance between the principal reflections into three equal parts. This diffraction pattern corresponds to the $p(1\times3)$ structure of the adsorbed Mg film, in which the adatoms form linear chains in the

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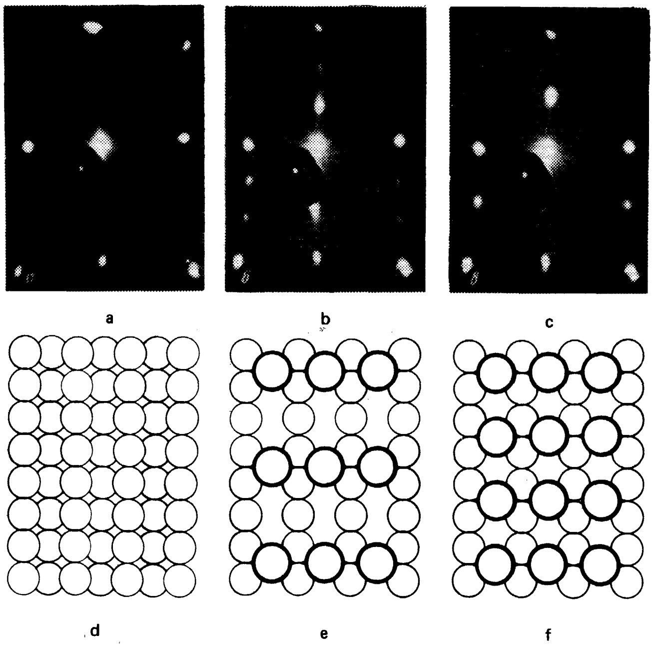

FIG. 1. Diffraction patterns for the Mg—Re(10$\bar{1}$0) system and the corresponding surface-structure schemes. The degree of coating ϑ: a), d) 0; b), e) 0.33; c), f) 0.5. Only the top atoms of the substrate are shown in the schemes e) and f).

direction perpendicular to the furrows on the surface of the Re(10$\bar{1}$0) face (one adatom to each furrow) and the interchain distance is equal to three lattice constants of the substrate in the direction parallel to the furrows. The analogous diffraction pattern for $\vartheta = \frac{1}{2}$ [Fig. 1(c)] corresponds to the $p(1\times 2)$ linear superstructure of the Mg film [Fig. 1(f)].

Figure 2 shows on a relative scale (with respect to the intensity at 77 K) the temperature dependences of the intensity of the diffraction reflections for the Mg $p(1\times 3)$ and Ba $p(1\times 5)$ structures. As can be seen from the figure, the temperatures at which the reflections disappear are not low, being of the order of several hundred degrees (500–700 K), although a substantial decrease in the intensity is already observable at temperatures of the order of 100 K.

DISCUSSION OF THE RESULTS

The available data on the disordering of the linear superstructures can be presented unified in the form of a dependence of the intensity of the diffraction reflections on the reduced temperature (the ratio of the crystal temperature T to the temperature, $T_{0.5}$, at which the intensity of the reflections decreases to half its value at $T=77$ K). This is precisely how the data in Fig. 3 are presented. Besides the data obtained in the present investigation, we show in Fig. 3 the results obtained by us earlier for the systems La-W(112),[3] Li-W(112),[1] Sr-Mo(112),[4] and Li-Mo(112).[5] For comparison, we also show in the same figure typical temperature-versus-reflection intensity curves obtained for commensurable [the $c(3\times 3)$ structure] and incommensurable (the hexagonal structure; $\vartheta = 0.75$) Sr films on the W(110) face by Naumovets and Fedorus.[10] This method of presenting the data exhibits two important distinctive features characteristic of all the investigated linear superstructures. First, it exhibits the distinctive universality of the dependence $I(T/T_{0.5})$: the curves designated by the symbols ●, △, +, and ○, ▽, × in Fig. 3 practically coincide, although the systems corresponding to them have different substrates, adatoms, and structure periods. This indicates that the details of the interaction between the adatoms do not exert a significant influence on the character of the thermal disordering of the linear superstructures. Secondly, a substantial decrease in the intensity occurs at temperatures much lower than the transition temperature. Finally, the $I(T/T_{0.5})$ curves are closer in character to curves for incommensurable, than to curves for commensurable, structures.

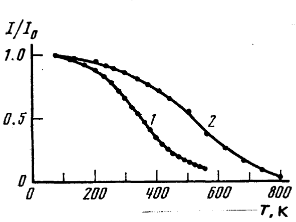

FIG. 2. Dependence of the intensity of the superstructure reflections on temperature for the systems: 1) Mg—Re(10$\bar{1}$0), $p(1\times3)$; 2) Ba—Mo(112), $p(1\times5)$.

The character of the temperature dependence of the superstructure reflection intensity is determined by the excitation spectrum of the system. In the case of commensurable structures on isotropic substrates the spectrum is discrete, and, so long as the temperature is less than the interaction energy, the imperfection of the order is exponentially small; the intensity falls sharply in the vicinity of the phase transition point when the temperature is raised further (the curve 2 in Fig. 3). In the case of incommensurable structures, the excitation spectrum is continuous at arbitrarily low energies (a gapless spectrum). Therefore, even at very low temperatures, the intensity decreases linearly with temperature because of the excitation of acoustic (gapless) modes[11] (the curve 1 in Fig. 3).

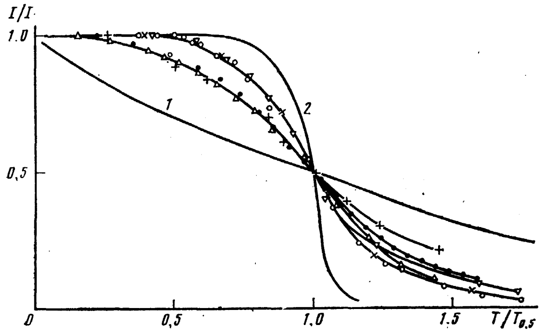

FIG. 3. Dependence of the intensity of the superstructure reflections on the reduced temperature (normalized to the temperature at which the intensity decreases to half its peak value) for the following systems: 1) Sr—Mo(110), $\vartheta = 0.75$, hexagonal structure; 2) Sr—Mo(110), $c(3\times3)$; ○) La—W(112), $p(1\times7)$; ●) Mg—Re(10$\bar{1}$0), $p(1\times3)$; △) Ba—Mo(112), $p(1\times5)$; ▽) Li—W(112), $p(1\times4)$; +) Sr—Mo(112), $p(1\times5)$; ×) Li—Mo(112), $p(1\times4)$.

What distinguishes the excitation spectrum of the linear superstructures is the strong anisotropy of the interaction: the binding energy of the adatoms in a chain is significantly higher than the interaction energy for adatoms in different chains. Let us consider the thermal excitations in such an anisotropic system. It is clear that at temperatures much lower than the magnitudes of both interactions, the thermal excitations are individual adatoms displaced from the chain [Fig. 4(a)]. If we are in a region of temperatures appreciably higher than the interchain interaction energy (but less than the binding energy in a chain), the excitations will be whole displaced adatom lines [Fig. 4(b)]. Let us denote by $2\varepsilon_0$ the energy connected with the rupture of a line, and by ε_1 the energy associated with the change in the interaction of the displaced part of the line with neighboring chains (as reckoned for one adatom of the line). Simple estimates show than the magnitude of the constant ε_1 will, for any theoretically proposed laws of decrease of the strength of the interaction between the adatoms,[12-14] be one or even several orders of magnitude smaller than the binding energy ε_0 in a chain when the superstructure has a large period. At temperatures less than ε_0, the distance L between the displaced parts is large:

$$L\sim a\exp(2\varepsilon_0/T)$$

where a is the lattice constant of the substrate in the direction perpendicular to the striations. But the length l of the displaced part is not small, and is determined from the condition $\varepsilon_1 l/a\sim T$. Thus, at temperatures $\varepsilon_1\ll T<\varepsilon_0$, the thermal excitations have the form of pairs of breaks in the adatom chain. The dimension of a pair is the distance l between the breaks. It is clear that the disordering of the film occurs in the region of temperatures at which the distance L between the pairs becomes roughly equal to the pair dimension l, i.e., at temperatures corresponding to the integration of the pairs into isolated breaks. The foregoing considerations allow us to estimate the order of magnitude of the transition temperature. Indeed, from the condition that $l\sim L$, we have

$$T_c\sim\varepsilon_1\exp(2\varepsilon_0/T_c), \qquad (1)$$

A distinctive feature of a condition of the type (1) is that the transition temperature T_c will be of the order of ε_0 even when $\varepsilon_1\ll\varepsilon_0$. Notice that the situation in which two transitions occur is also possible: the breaks become unpaired at a temperature T_c and the order in the film disappears at $T_c'>T_c$. But T_c' should be of the order of T_c, differing from it by a numerical factor determined by the details of the excitation spectrum.

For simplicity, the transition temperature was estimated in a model containing only one constant, i.e., the constant characterizing the interaction between the chains. The actual excitation spectrum may be significantly more complex, and may contain several low-lying levels with energies ε_2, ε_3, etc. (associated, for example, with the displacement of adatoms from a base chain through distances equal to two, three, etc., times the lattice constant of the substrate). But what is important for the estimates made in the present paper is just the fact that the spectrum contains low-energy excitations, and the consideration of the details of the structure of the spectrum will not change the qualitative results of the analysis.

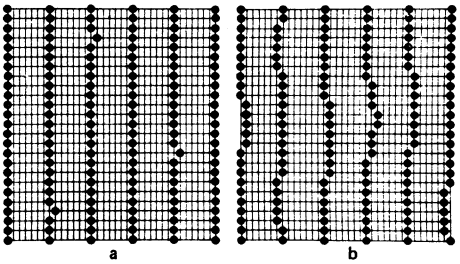

FIG. 4. Thermal excitations in linear structures: a) $T<\varepsilon_1$; b) $\varepsilon_1\ll T<\varepsilon_0$.

The most important feature of the system under consideration is the quasicontinuity of the excitation spectrum in the temperature range $\varepsilon_1\ll T<T_c$. Indeed, the change that occurs in the energy of the system when the length of any of the pairs is increased by an amount equal to one lattice constant is $\varepsilon_1\ll T$. Let us use this fact to estimate the Debye-Waller factor, which describes well the decrease of the intensity $I(T)$ of the superstructure reflections at temperatures not too close to the transition temperature according to the formula

$$I(T)=I(0)\exp(-2W(T)).$$

The quantity $W(T)$ is determined by the mean square displacements $\langle u^2\rangle$ of the adatoms and the period λ of the structure[11] according to the formula

$$2W(T)=\langle u^2\rangle(2\pi/\lambda)^2.$$

For the estimate we shall assume that the characteristic magnitude of the displacement of adatoms from a base chain is u_0. Then the mean square fluctuations for one chain will be $u_0^2 l/L$ (l/L is the fraction of adatoms in the chain that have shifted). Allowance for the collective effects (the simultaneous displacement of many chains) will lead to the appearance of the factor $\ln(R/\lambda)$, where R is the dimension of the system (by it may be meant the dimension of the investigated part of the surface in the low-energy-electron-diffraction method: $R\sim 100$ Å). This factor is due to the logarithmic divergence of fluctuations in two-dimensional systems with a continuous excitation spectrum.[11] The final expression for the Debye-Waller factor has the form

$$2W(T)\approx\left(2\pi\frac{u_0}{\lambda}\right)^2\frac{l}{L}\ln\frac{R}{\lambda}.$$

It can be seen that the Debye-Waller factor can be large even when $l\ll L$ if the quantity u_0 is not small (i.e., if the displacement of adatoms from a chain through a distance equal to several lattice constants of the substrate is possible). Thus, an appreciable decrease in the intensity can occur as a result of the quasicontinuous nature of the excitation spectrum even at temperatures significantly lower than the transition temperature. Another consequence of such an excitation spectrum is that the temperature dependence of the intensity in the temperature region $T\gg\varepsilon_1$ should be primarily determined by the ratio ε_0/T. Therefore, it can be expected that some of the intensity-versus-$T/T_{0.5}$ curves will be close. The experimental data indeed exhibit such a universality (see the curves marked by the symbols ○, ●, △, etc., in Fig. 3).

The experimental data presented show that linear superstructures with long periods can, on the basis of the nature of their thermal disordering, be assigned to a separate class of systems. The similarity of the patterns of thermal disordering of these structures, despite the differences in the lattice periods and the chemical characters of the adsorbates and substrates, is due to the quasicontinuous character of the excitation spectrum. The anomalies of the excitation spectrum should manifest themselves not only in the general pattern of thermal disordering, but also in, for example, the behavior of the system in the vicinity of the phase-transition point, diffusion, etc. Therefore, further detailed investigations (both theoretical and experimental) of linear superstructures with large periods is of indubitable interest.

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