

Diffusion and phase transitions in anisotropic submonolayer adsorbed films with coherent structures

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Introduction. The development of modern nanotechnologies requires new information about influencing the physical and chemical properties of various types of nanoparticles existed as 2D adsorbed films. These objects have such physical and chemical properties that can significantly differ from the properties of macroscopic samples of the same substance [1, 2]. 2D adsorbed films are widely used in practice, but today's level of understanding of processes in such films is still relatively low.

The aim of the work is to study phase transitions in submonolayer adsorbed films with strongly pronounced anisotropy, mutual influence of the structure and physical and chemical properties of the film and surface self-diffusion of adatoms. In the case of adsorption, the nanometer size of the objects and the substrate itself significantly limit the possibilities of adatoms making random movements. On the other hand, the substrate potential relief imposes on the adatoms the allowed variants of possible structures.

Methods. We used molecular dynamics to create a mathematical model for the computer study of 2D self-diffusion and phase transformations in submonolayer films. It was as close as possible to the real Li – Mo(112) and Li – W(112) systems in terms of its properties [1, 3, 4]. The Einstein-Smolukhovskiy equation was used to calculate the diffusion coefficients. The research of structural transformations was carried out using Fourier analysis, visualization of individual frames and other approaches proposed by us. Note that real crystal surfaces always contain a certain number of defects [3, 5]. Models can be free from such defects and provide an excellent opportunity to investigate diffusion processes at the atomic level.

Results. In both mentioned systems, strongly anisotropic long-period stoichiometric $p(4 \times 1)$ and $p(2 \times 1)$ chain structures arise. The chains are separated from each other by 4 and 2 crystal lattice constants respectively in the $[111]$ direction, that is films take place (Fig. 1).

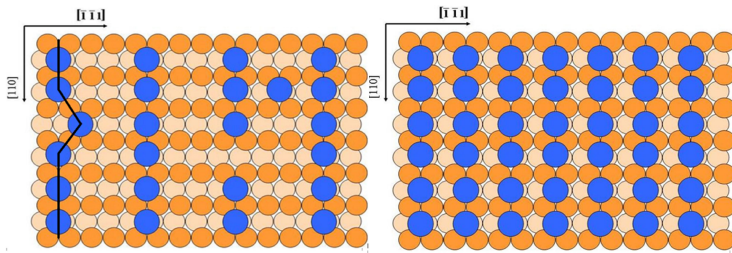


Fig. 1. Models of $p(4 \times 1)$ and $p(2 \times 1)$ structures (blue discs) on the (112) face of the v.c.c. crystal. The left figure shows all possible defects of the $p(4 \times 1)$ chain structure: kink, vacancy and interchain adatom

Chains of Li adatoms in our case cannot be considered as one-dimensional objects due to the existence of long-range repulsive interaction between neighboring chains. Such a system is definitely 2D. The reason for anisotropy is the presence of two types of long-range interaction: dipole-dipole repulsion and Friedel oscillations [4, 5].

Phase transformations in submonolayer adsorbed films are accompanied by an alteration in the character of diffusion processes. This is clearly manifested in the changes in the activation energy and the pre-exponential factor when moving from one temperature range to another. Corresponding changes in the phase state can be fixed by the presence of breaks on the Arrhenius graphs (Fig. 2).

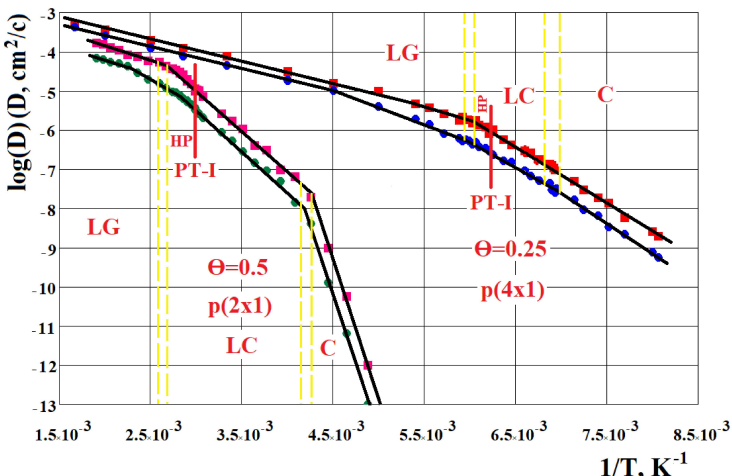


Fig. 2. Temperature dependencies of $\log(D)$ and regions of phase coexistence. LG - lattice gas, HP - hexatic phase, C - crystal phase, PT-I - first order phase transition. Yellow lines denote fuzzy boundaries of phase transitions

The pattern of growth of the defect number (kinks and vacancies) with temperature in Fig. 3 indicates their nonlinear increasing in the presence of two discontinuities at temperatures of 144 K and 159.5 K for the $p(4 \times 1)$ structure. This is accompanied by sharp jumps in the order parameter (Fig. 4). In the case of the $p(2 \times 1)$ structure, only one jump was detected at $T = 337$ K. We associate these effects with first order phase transitions.

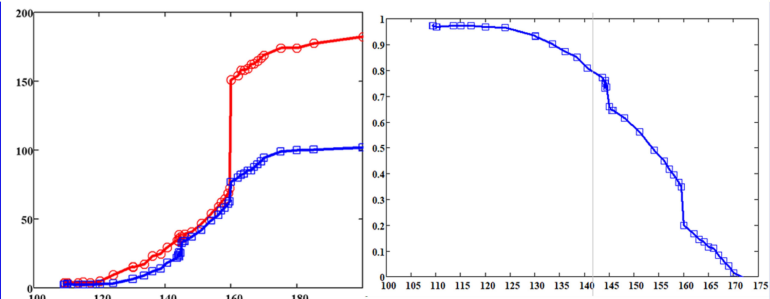


Fig. 3. Temperature dependence of the number of kinks (upper line) and vacancies (lower line)

Fig. 4. Temperature dependence of the order parameter

At higher temperatures, as the temperature increases, the destruction of the hexatic phase occurs smoothly. A break is observed in the Arrhenius graphs at $T = 170$ K, which indicates a change in diffusion mechanisms. This point is not clearly fixed on the temperature dependence of the order parameter. On the Arrhenius graphs, this is the temperature of the intersection of the graphs obtained in two temperature intervals: 160 – 170 K and 170 – 250 K.

Generalized diagrams of changes over time (vertical axis) of the average values of the adatom number in the $[110]$ direction (on each frame recorded in the computer memory) at two different temperatures are shown in Figs. 5 and 6.

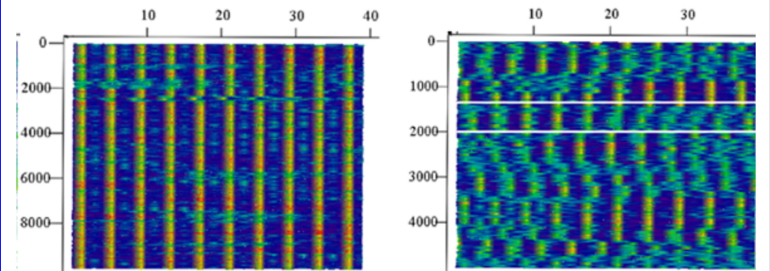


Fig. 5. The coordinates of lithium chains do not change over time at $T = 159.5$ K

Fig. 6. A different number of chains is observed in frames 1300 and 2000 at $T = 160$ K

When the temperature changes by only 0.5 K, the chains or their separate sections are destroyed and recreated again, changing their coordinates, which can be seen in Fig. 6. Two separate frames taken from this figure, marked with white lines, show different numbers of chains. This may be a sign of soliton formation. At frame 2000, the number of chains is 11, not 10, as seen at frame 1300. So, here the film becomes temporarily incoherent. A similar situation is observed in the case of the $p(2 \times 1)$ structure at $T = 337$ K (Figs. 7 and 8), but with much less number of vacancies.

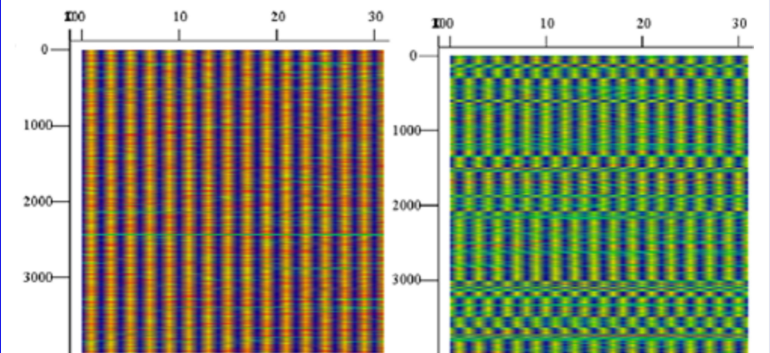


Fig. 7. The structure $p(2 \times 1)$ at $T = 335$ K. The chains remain immobile and there are no free atoms between them

Fig. 8. The process of catastrophic destruction of $p(2 \times 1)$ chains occurs similar to one shown in Fig. 6

Conclusions. It is shown that submonolayer films on surfaces with highly anisotropic potential relief in the process of melting a 2D crystal can easily change their neighbors preserving the translational order. This is not characteristic of the hexatic phase [6, 7]. In this case, we believe it is appropriate to use the term "liquid crystal" [3]. We have shown that a liquid crystal in the process of temperature degradation is transformed into the hexatic phase through a first order phase transition. This is due to the catastrophic increase in the number of defects in the films at stoichiometric coverages $\theta_{Li} = 0.25$ ($T = 144$ K and 159.5 K) and $\theta_{Li} = 0.5$ ($T = 337$ K).

References. 1. Naumovets, A.G. (2016) *Adsorption of Alkali and Other Electropositive Metals*. Wandelt, K. (ed.) *Surface and Interface Science*, (p. 157-205). Wiley-VCH Verlag GmbH & Co. KGaA. 2. Andryushechkin, B. V. (2015). *Halogen Adsorption on Metals*. Wandelt, K. (ed.) *Surface and Interface Science*, (p. 207-254). Wiley-VCH Verlag GmbH & Co. KGaA. 3. Fedorus, A. G., Lyuksyutov, I. F., Kolthoff, D., Koval, V., Naumovets, A. G., & Pfnür, H. (1999). Orientational phase transitions in a lithium overlayer on Mo(112). *Europhysics Letters*, (4), 442-448. 4. Браун, О.М. & Медведев, В.К. (1989). Взаимодействие между частицами, адсорбированными на поверхности металлов. *УФН*, (4), 631-666. 5. Люксютов, И.Ф., Наумовец, А.Г. & Покровский, В.Л. (1988). *Делурические кристаллы*. Киев: Наукова думка. 6. Nelson, D.R. & Halperin, B.I. (1979). Dislocation-mediated melting in two dimensions. *Phys Rev B.*, (19), 2457-2484. 7. Ryzhov, V.N., Tareyeva, E.E., Fomin, Yu.D. & Tsiok, E.N. (2017). Berezinskii – Kosterlitz – Thouless transition and two-dimensional melting. *Physics-Uspekhi*, (9), 921-951.