Diffusion in two-dimensional crystals

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The attachment of solitons to their lattice leads to certain features in the behavior of the diffusion coefficients in a monolayer of adsorbed atoms.

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In experiments on the diffusion of a submonolayer barium film on the Mo(110) face, Vedula *et al.*[1,2] found that the diffusion coefficient D, the activation energy ϵ_a, and the coefficient (D_0) of the exponential function are all nonmonotonic functions of the degree of surface coverage θ (the ratio of the actual concentration of adatoms to the concentration in a closely packed monolayer). Earlier studies of structures in this system[3] had demonstrated the existence of several commensurable phases at small values of θ and of an incommensurable phase at $\theta > 0.6$. Comparison of structural data with data on diffusion reveals a correlation. In particular, ϵ_a and D_0 have minima at coverages corresponding to the phases $C(2\times 6)$ ($\theta = 0.8$) and $C(2\times 2)$ ($\theta = 0.6$). The activation energy near these minima has clearly defined plateaus in an interval $\Delta\theta \sim 0.1$, while D_0 increases by a factor of $10^3 - 10^5$ in an interval[1)] $\Delta\theta \sim 0.1$.

According to the present theoretical understanding, a lattice of solitons (regions of compression or extension) compensates for a mismatch of the film and substrate lattice constants in the case of a small deviation from commensurability.[4,5] For an anisotropic substrate potential relief, the soliton lattice may be thought of as a system of equidistant bands with some period l. For a given number of particles this period is related to the deviation of the surface coverage θ from its value at the commensurability point, θ_0, by $l = a(\theta - \theta_0)^{-1}$, where a is the lattice constant of the substrate. For simplicity, we assume here that θ_0 corresponds to the case in which the film and substrate lattice constants are equal. The energy of an isolated soliton varies periodically with the position of its center, with a period equal to the substrate lattice constant. This effect is analogous to the Peierls barriers for dislocations in a three-dimensional crystal. At large values of l the height of the periodic barriers is greater than the soliton interaction energy, and the solitons are pinned to the substrate. Since the solitons in a two-dimensional crystal are line defects, their pinning energy is proportional to the dimensions of the crystal. At a certain critical l_c the interaction between solitons overcomes the pinning energy, and the solitons are torn out of the lattice.[6] As a result, the incommensurable crystal acquires a continuous translation group, with which additional acoustic modes are associated.[5,7] Acoustic modes in incommensurable crystals have been observed[8] in the Sr–Mo[110] system in experiments by low-energy electron diffraction. In the present letter we wish to offer an explanation for these aspects of the diffusion, working from a mechanism for mass transfer by solitons.

In the region $l > l_c$, in which the soliton as a whole is pinned, its motion may correspond to dislocation climb in a glide plane in a three-dimensional crystal. A soliton has a certain number of kinks whose motion leads to the climb of the soliton over one lattice constant. The energy of one of these kinks, ϵ_k, is of order $(\lambda V)^{1/2} a^2$, where λ is the elastic constant of the two-dimensional crystal, and V is the amplitude of the substrate potential relief. The number of such kinks is $n_k \sim \exp(-\epsilon_k/T)$. A real system has substrate defects that pin solitons. The energy of a point defect, ϵ_d, in an incommensurable lattice is of order λa^2. The time over which a soliton is torn away from a point defect is $\tau_d \sim \omega_0^{-1} \exp(\epsilon_d/T)$, where ω_0 is a characteristic frequency. Let us compare this time with the time required for a kink to move between two defects, τ_k. This time can be estimated in order of magnitude from $\tau_k \sim (c\omega_0 N^2/k)^{-1}$, where c is the defect concentration (the number of defects per lattice site). The motion of the kinks determines the diffusion coefficient if $\tau_k > \tau_d$, i.e., if $c < \exp[(2\epsilon_k - \epsilon_d)/T]$. Consequently, at sufficiently small values of c the temperature dependence of D is determined by the factor $\exp(-\epsilon_k/T)$.

If $l < l_c$, the motion of solitons in the absence of defects should be a purely mechanical motion (with friction), so that the diffusion would be determined by the time τ_d. Consequently, when we go from $l > l_c$ to $l < l_c$ we find a change in the activation energy, from ϵ_k to ϵ_d. The condition for the existence of incommensurable structures is $V < \lambda$, and under this condition we have $\epsilon_d > \epsilon_k$. Upon further compression the activation energy increases because of the increase in λ.

Let us examine the behavior of the coefficient of the exponential function. In the region $l > l_c$ there is a diffusion of kinks, each containing an additional adatom, so the $D_0 \sim \omega_0 a^3 l^{-1}$. When a soliton is torn away from a defect in the case $l < l_c$ there is a displacement l of a region with an area of order a^2/c, which contains $(\theta - \theta_0)/c$ additional adatoms. Such a region may be thought of as a "particle" which is moving under the influence of the pressure gradient caused in the elastic lattice of solitons by a concentration gradient. The force F acting on such a "particle" is proportional to the product of the pressure difference Δp and the transverse dimension of the "particle", $ac^{-1/2}$: $F \approx \Delta p / ac^{-1/2}$, where $\Delta p \approx (\partial\theta/\partial p)(\partial p/\partial x)\, ac^{-1/2}$. Using the standard expression for the diffusion flux caused by a constant force, we find

$$D_0 = \frac{\theta - \theta_0}{c^2} \frac{l}{T} \omega_0 a^3 \frac{\partial p}{\partial \theta}. \tag{1}$$

The pressure in the soliton system, p, is of order $\lambda a^2 l_0^{-2} \times \exp(-l/l_0)$, where $l_0 \sim a(\lambda/V)^{1/2}$ is the width of the soliton. Substituting this value in (1) we find

$$D_0 = \omega_0 a^2 \frac{\lambda a^3}{c^2 T l_0} \left(\frac{l}{l_0}\right)^2 \exp(-l/l_0). \tag{2}$$

Equation (2) shows that D_0 is a very strong function of l or, equivalently, of $\theta - \theta_0$. The characteristic value of this coefficient differs by the large factor $\lambda a^3/c^2 T l_0$ from the value $D_0 \sim \omega_0 a^2$ which corresponds to point carriers.

Pinning by defects leads to a small gap Δ in the energy spectrum. In order of magnitude this gap is $\Delta \sim sac^{-1/2}$, where s is the velocity of sound, given by

$s^2 = (\partial p/\partial l)/Ma$. Hence,

$$\Delta \sim \left(\frac{a}{l_0}\right)^{3/2} c^{1/2} T_D \exp\left(-l/2l_0\right), \tag{3}$$

where T_D is the Debye temperature for the adatom lattice, and M is the adatom mass. The gap is obviously small (no greater then 1 K) for realistic values of the parameters. This result explains why defects are not reflected in measurements of the Debye-Waller factor.[8]

A similar behavior of ϵ_a and D_0 has been observed near concentrations corresponding to the commensurable phases $C(2\times 3)$, $C(2\times 2)$, and $C(1\times 1)$ in the Li-W[110] system.[9]

[1)]These results were graciously furnished by Vedula *et al.*[1,2]

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