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Scattering of He Atoms from Crystal Surfaces: A Tentative Analysis on the Surface Crystallography of LiF(001)

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This Letter describes a theoretical treatment of the excellent experimental results of Boato, Cantini, and Mattera for the He-LiF(001) system, in terms of a hard corrugated model for the surface. From the agreement achieved between theory and experiments, I conclude that one can represent the corrugated surface by $z_1(x,y) = \frac{1}{2}\zeta_1[\cos(2\pi x/a) + \cos(2\pi y/a)] + \frac{1}{2}\zeta_2\{\cos[2\pi(x+y)/a] + \cos[2\pi(x-y)/a]\}$, with $\zeta_1 = 0.307 \pm 0.003$ Å and $\zeta_2 = 0.017 \pm 0.003$ Å. This implies that the Li^+ appear to be displaced upwards from the crystal surface by 0.036 ± 0.006 Å.

In very recent experiments carried out by Boato, Cantini, and Mattera[1] on scattering of He atoms from a LiF(001) surface, it appears that the inelastic component of the scattering process has been practically eliminated except for a Debye-Waller factor of around 0.28. The surface is at liquid-nitrogen temperature, which accounts for the very small amplitudes of the crystal vibrations. The crystal is cleaved in air; and the experimental vacuum is about 3×10^{-8} Torr. The elastic diffraction peaks are very well resolved, and their intensities follow an oscillating pattern called a "rainbow pattern" over and above a small inelastic background. Independently of these data, Stel *et al.*[2] have shown, also recently, that there is no adsorbed monolayer of H_2O under the physical conditions of the experiments of Boato, Cantini, and Mattera.[1] Furthermore, these data are in good agreement with those obtained previously by Williams[3] and Bledsoe and Fisher[4] with a vacuum of 10^{-7}–10^{-8} Torr and surface temperatures of 150 and 300°K, respectively. In this Letter I show that in explaining these results by the theory of elastic surface scattering, one might use this technique to deduce information on the surface crystallography as an alternative to low-energy electron diffraction.

It appears that the scattering of He thermal beams from crystal surfaces is accounted for theoretically by a corrugated-wall model of the surface as was proposed by Garibaldi *et al.*[5] following the theory of Rayleigh[6] on sound waves diffracted from a corrugated surface. This implies that the interaction between He and LiF is assumed to be purely repulsive. Recently, García and co-workers[7,8] have developed a new method (called the GR method) for solving the scattering amplitudes of the beams diffracted from a hard corrugated surface. This method simplifies and gives complete control over all the computations. It also has the great practical advantage of allowing the corrugation shape to be changed very easily. These details are very useful when one tries to obtain the best surface topography from comparison between the experimental diffracted intensities and the theoretical ones.

The aim of this Letter is to show, for the first time, calculated curves which are in good agreement with experimental data[1] for the He-LiF(001) system using He thermal beams (incident wave vector $k = 11$ Å^{-1}) and covering the range of incident angles $\theta_i = 0$ to $\theta_i = 60°$. With such an agreement I study the surface crystallography of the LiF(001) surface, obtaining the "best" corrugated surface and concluding tentatively a relative displacement of the Li^+ of 0.036 ± 0.006 Å outwards from the surface.

The set of scattering equations that are obtained for the diffracted He atoms from a hard corrugated surface is the following[5,7,8]:

$$\sum_{\vec{G}} \exp[i(k_{\vec{G}z} + k_z) Z_1(\vec{R})] \exp(i\vec{G}\cdot\vec{R}) A_{\vec{G}} = -1, \qquad (1)$$

where $\vec{G}$ are the infinite set of two-dimensional reciprocal vectors, with propagation wave vectors $\vec{k}_{\vec{G}} = (\vec{K}+\vec{G}, k_{\vec{G}z})$, $\vec{K}$ being the tangential component of the incident vector $\vec{k}$, $k_{\vec{G}z}$ its normal component, and k_z the value of $k_{\vec{G}z}$ for $\vec{G} = 0$ (specular beam). $A_{\vec{G}}$ are the scattering amplitudes and $Z_1(\vec{R})$ is the shape corrugation function which has the two-dimensional periodicity and symmetry defined by the vectors $\vec{G}$. The position vector of the atom is $\vec{r} = (\vec{R}, z)$.

The intensities $P_{\vec{F}}$ of the outgoing beams satisfy the sum rule

$$\sum_{\vec{F}} P_{\vec{F}} = 1; \quad P_{\vec{F}} = (k_{\vec{F}z}/k_z)|A_{\vec{F}}|^2, \qquad (2)$$

where $\vec{F}$ represent the $\vec{G}$ vectors corresponding to the diffracted beams.

The GR method consists in establishing a set of linear equations relating the continuous set of points $\vec{R}$ within the elementary unit cell of the two-dimensional periodical space to the discrete infinite set of $\vec{G}$ vectors. In other words, for each $\vec{R}$ value we can write a linear equation for the infinite number of $A_{\vec{G}}$'s. Now, if we consider a finite number of points $\vec{R}$, that satisfy the symmetry of the surface unit cell and are nonequivalents, and an equal finite number of $\vec{G}$ vectors, Eqs. (1) reduce to a finite set of linear equations. It has been shown[7,8] that this method of treating and solving the scattering equations presents great advantages over others which involve Fourier transformation of Eqs. (1) into a set of equations in $\vec{G}$ and $\vec{G}'$.[5,7,8]

As I mentioned above, we are interested in determining the function $Z_1(\vec{R})$ which gives agreement between the observed[1] and calculated diffracted beams for the system He-LiF(001). The unit cell is a square with lattice constant $a = 2.84$ Å. I take the x axis along the ⟨110⟩ direction. Then the beam direction of the atoms impinging on the surface is specified by θ_i and φ_i, where θ_i is measured from the normal to the surface and φ_i is taken from the x axis ($\varphi_i = 0$) to the ⟨100⟩ direction ($\varphi_i = 45°$). Under these conditions, I write down the following expression for the shape corrugation function $Z_1(\vec{R})$:

$$Z_1(x,y) = \tfrac{1}{2}\zeta_1[\cos(2\pi x/a) + \cos(2\pi y/a)] + \tfrac{1}{2}\zeta_2\{\cos[2\pi(x+y)/a] + \cos[2\pi(x-y)/a]\} + \tfrac{1}{2}\zeta_3[\cos(4\pi x/a) + \cos(4\pi y/a)] + \dots . \qquad (3)$$

I determine the "best" coefficients ζ_1, ζ_2, and ζ_3 which account for the experimental diffracted intensities. I found for as many as twelve in-plane beams in the ⟨100⟩ and ⟨110⟩ directions that the "best" coefficients are $\zeta_1 = 0.307 \pm 0.003$ Å, $\zeta_2 = 0.017 \pm 0.003$ Å, and $\zeta_3 \approx 0$. The results for the ⟨100⟩ and ⟨110⟩ azimuths are presented in Figs. 1 and 2 in comparison with the experimental data. The values of the coefficients have been chosen with the following two criteria: (i) Looking for the coefficient ζ_1 which made the set of beams $\{2, 2\}$, at normal incidence, be a maximum rainbow peak as seen in the experimental data[1]; this gives a value of $\zeta_1 \simeq 0.3$ Å. (ii) Choosing those which best reproduce the experimental features among as many as ten different sets of curves with their respective coefficients. In particular, the most relevant feature is that corresponding to the two minima on the specular beam for the ⟨110⟩ azimuth.[10] These figures show the diffracted intensities as functions of the incident angle θ_i. The

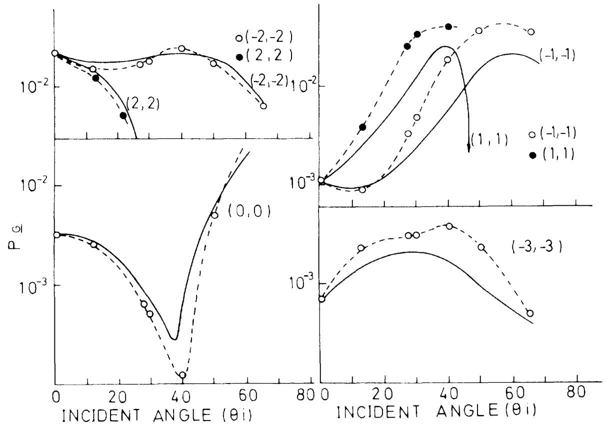

FIG. 1. The ordinates represent the logarithm of the diffracted probabilities in the ⟨100⟩ plane and the abcissae, the incident angle θ_1. Dashed lines are the observed intensities (Ref. 1). ●, beams of indices (n, m); O, beams of indices $(-n, m)$. Continuous lines are the calculated probabilities. These curves are normalized to the experimental ones at $\theta_1 = 0$. This normalization implies a Debye-Waller factor which ranges between 0.18 and 0.37. The averaged experimental Debye-Waller factor is 0.18. Observe that the beams (1, 1) and (2, 2) disappear with a vertical tangent as they should (Ref. 9). This is very difficult to measure because the outgoing beam grazes the surface (Ref. 10).

incident energy corresponds always to $k_1 = 11$ Å^{-1} (thermal beams).

On these diffraction patterns I observe the following: (a) The agreement is quite good for all beams with a total computer time of only 30 min in an IBM 360/65 machine. (b) To obtain the two minima observed in the specular beam in the ⟨110⟩ azimuth at $\theta_i \simeq 28°$ and $\theta_i \simeq 50°$, a second small coefficient ζ_2 is needed. More specifically, although with a single coefficient ζ_1 it is possible to have good agreement in the ⟨100⟩ direction, in order to fit the experimental data in the ⟨110⟩ azimuth we must introduce another small coefficient ζ_2. It must be stressed that by changing the large coefficient ζ_1 by 0.003 Å I obtain variations of 10% in some intensities. (c) I have noticed that the theory reflects very well the behavior of the beams (−2, −2), (−1, −1), and (−2, 0) as well as the different trends of the beams of positive indices (2, 2), (1, 1), and (2, 0). The agreement for the peak (1, 1) is good for $\theta_i < 40°$. After that the experimental intensity disappears because the beam becomes submerged in the background (see Fig. 1). This is a proof that the theory works quite well for He atoms, disagreeing with the conclusions given by Jewsbury[11] for Ne atoms. I do not know what happens with Ne atoms, as it is impossible to handle it with our computer (IBM 360/65) because of the large number of open channels (~250) for thermal beams. Ne also presents an inelastic scattering 10 times larger than He whereas I am analyzing the elastic component of the scattering processes.

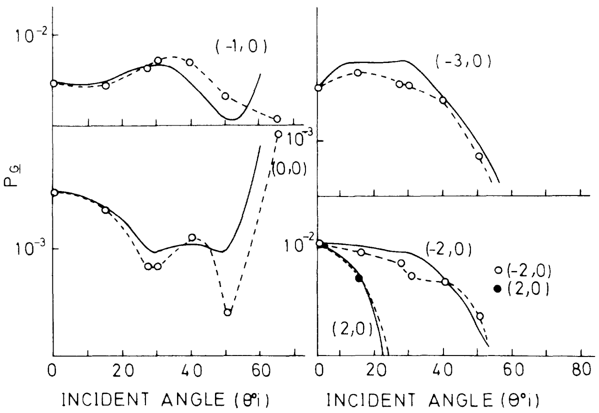

FIG. 2. The same notation as in Fig. 1 for ⟨110⟩ in-plane scattered beams.

An atomic interpretation of the "best" corrugated surface is still an open question. However, one can tentatively account for it with a hard-sphere model, which presumes the following: (a) The surface LiF(001) is indeed pure and does not contain an adsorbed layer of, say, H_2O.[2] (b) The He-LiF interaction is indeed infinitely repulsive. (c) It permits one to make some predictions about the possible surface configuration.

The F^- and Li^+ surface ions are assumed to be spheres with radii $r(Li^+) = 0.68$ Å and $r(F^-) = 1.33$ Å located at the points of the unit square cell for the F^- ions and at their centers for the Li^+ with a possible upward displacement normal to the crystal surface. Similarly, I assume that the He atoms are hard spheres with radius r(He) to be determined. The corrugated surface is then "arbitrarily" defined by the contact between the He surface and the LiF surface, as is illustrated in Fig. 3(a) for the two azimuths ⟨110⟩ and ⟨100⟩. These profiles are four times magnified in Fig. 3(b). In Fig. 3(c) I present the topography of the corrugation through all the unit cell. The values of the two parameters, r(He) = 1.78 Å and the upward displacement 0.036 Å of the Li^+ ions, are finally fixed by the values of the coefficients previously determined, $\zeta_1 = 0.307$ Å and $\zeta_2 = 0.017$ Å. The radius of 1.78 Å is that corresponding to the sphere of solid He,[12] while the radius of He-F^- interaction should be ~1.3 Å.

The present results appear to indicate that pre-

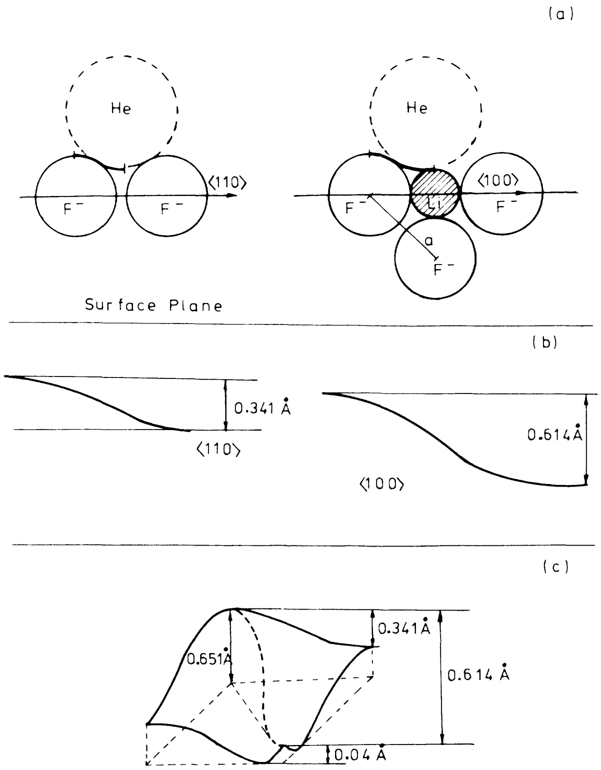

FIG. 3. (a) The geometrical construction with the hard-sphere model along the ⟨100⟩ and ⟨110⟩ azimuths. (b) The same profiles as in (a) four times magnified. (c) The total corrugated surface which corresponds to the profiles of (b). The value 0.614 Å indicates the difference in ordinates between the topmost of Li^+ and F^-, while the value 0.651 Å is that between the minima and the maxima on the corrugated surface.

cise measurements of He scattering should be an effective alternative method for the study of surface crystallography. Whether or not this will be so depends on more accurate measurements for different energies and incident angles as well as out-of-plane diffracted beams. The influence of the attractive interaction between He and the crystal is being considered, adding a well to the hard corrugated surface. For the energy used by Boato, Cantini, and Mattera,[1] this does not appear to play an important role[9]; this, however, will not be so at lower incident energies.[13]

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