phys. stat. sol. (b) **140**, 459 (1987) Subject classification: 68.30; S5.2

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Vibrational States of Surface Crystal Atoms

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The momenta-time correlation functions and their spectral densities are studied for rare gas crystal atoms at the (100) and (110) surfaces. Their characteristics essentially differ from the bulk behaviour for particles lying in the surface plane, but already in the third subsurface atomic plane the differences from the bulk crystal spectrum are only slight. Distinct quasi-resonance peaks observed in the spectral densities may be an information source for experimental analysis of the surfaces.

Изучен характер временных корреляционных функций импульса и их спектральных плотностей для частиц кристаллов благородных газов вблизи поверхностей (100) и (110). Эти характеристики существенно отличаются от объемного поведения для частиц, лежащих в плоскости поверхности, но уже в третьей от поверхности плоскости наблюдаются лишь небольшие количественные отличия от объемного спектра кристалла. Наличие в спектральных плотностях четко выраженных квазирезонансных пиков может служить источником информации при экспериментальной диагностике поверхности.

1. Introduction

The presence of surfaces brings about some changes in the spectral properties of crystals and in the vibrational characteristics of their particles. These changes are localized in the near-surface region [1, 2] and may be viewed as specific surface states. Advances made by vibrational spectroscopy in the research of crystal surfaces, particularly due to the experiments on low-energy atomic beam scattering [3, 4], encourage more detailed theoretical investigations of the spectral and correlation properties of crystal atoms in the near-surface region.

The time correlation functions (TCF) of particle momenta contain important information about the dynamical properties of crystals [2]. The vibrational spectral densities of crystal particles can be obtained as the Fourier transform of the TCF.

According to definition the TCF of dynamical functions A and B is

$$C(t) \equiv \langle A(0) | B(t) \rangle = \int_{\Gamma_N} A(0) | B(t) | D_N^{(0)}(\Gamma_N) \, \mathrm{d}\Gamma_N$$
,

where $D_N^{(0)}$ is the equilibrium Gibbs distribution function and I'_N the phase space of a system of N particles. $D_N^{(0)}$ being the integral of a Liouville operator L_N , one can obtain [8]

$$B(t) D_N^{(0)}(\Gamma_N) = \mathrm{e}^{iL_N t} [B(0) D_N^{(0)}(\Gamma_N)] = B_N(t) ,$$

where $B_N(t)$ obeys the Liouville equation

$$\frac{\partial B_N(t)}{\partial t} = i L_N B_N(t)$$

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with the initial value

$$B_N(0) = BD_N^{(0)}$$
.

C(t) becomes the momentum TCF if one puts $A = p^i$, $B = p^k$, where p^i and p^k are momenta of *i*-th and *k*-th particles.

The reduced dynamical functions

$$b_N(t) = \int_{\Gamma_{N-n}} B_N(t) \,\mathrm{d}\Gamma_{N-n}$$

and the integrodifferential chain of equations for them can be then generated. As usual the chain is truncated after a few lowest equations and the younger functions $b_1, b_2, ...$ are represented [5] in terms of Hermitian polynomials H_s in the momentum subspace and special orthogonal polynomials Q_s (s = 0, 1, 2, ...) in the configurational subspace. For example, the representation of the one-particle function is as follows:

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$$\begin{split} b_1(q^k, p^k, l) &= \left[\beta_1^{(0)}(q^k, l) + H_1\beta_1^{(1)}(q^k, l) + H_2\beta_1^{(2)}(q^k, l) + \dots\right] F_{11}(p^k) ,\\ \beta_1^{(0)}(q^k, l) &= \left[q_k^{(0,0)}(l) + Q_1q_k^{(0,1)}(l) + \dots\right] F_{11}(q^k) ,\\ \beta_1^{(1)}(q^k, l) &= \left[q_k^{(1,0)}(l) + Q_1q_k^{(1,1)}(l) + \dots\right] F_{11}(q^k) \quad \text{etc.} \end{split}$$

Here $F_{11}(p^k)$ and $F_{11}(q^k)$ are the equilibrium Maxwell distribution function and the one-particle equilibrium distribution function of a crystal particle near a lattice point, respectively. The latter is used as the generating function for the orthogonal polynomials Q_s .

The functions $\varphi_k^{(l,n)}(t)$ obey a system of ordinary differential equations and after some transformations and restriction of the coefficients of the polynomials to the first order this system of equations can be written [5] with respect to functions $\varphi_k^{(1,0)}(t) \equiv = \hat{\varphi}_k(t) \ (k = 1, 2, ..., N)$. It is easy to see that due to the orthogonality of the polynomials these very functions describe the momentum TCF.

Earlier, the time correlation functions of particle momenta for perfect and imperfect crystals were considered within the method of conditional distributions [5, 6]. In what follows, characteristic features of the particle behaviour in the near-surface region will be discussed.

2. Constitutive Equations and Method of Their Solution

The system of equations describing the TCF evolution in the first order with respect to the orthogonal polynomial series [5] is of the form

$$\ddot{\hat{\varphi}}_k = \sum_{j+k}^N \hat{C}_{kj} (\hat{\varphi}_j - \hat{\varphi}_k) , \qquad (1)$$

$$\hat{C}_{kj} = \left\langle \frac{\partial^2 \Phi_{kj}}{\partial q^k \ \partial q^k} \right\rangle,\tag{2}$$

where Φ_{kj} is the potential of the central pair interaction between the *j*-th and *k*-th particles, N the total number of crystal particles, q^k are the coordinates of the *k*-th particle.

Angular brackets in (2) imply Gibbs averaging. In accordance with the adopted method of conditional distributions, averaging is performed over the Wigner-Seitz cells containing the j-th and k-th particles with the use of the equilibrium distribution

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functions. The latter are determined from the solution of the special system of nonlinear integral equations [7].

In order to calculate the momentum TCFs of the crystal particles, (1) should be solved with the following initial conditions [8]:

$$\hat{\varphi}_{1}(0) = \tilde{E}, \quad \hat{\varphi}_{k}(0) = 0; \quad \hat{\varphi}_{1}(0) = 0, \quad \hat{\varphi}_{k}(0) = 0;$$

 $k = 2, 3, ..., N.$
(3)

The disturbance is prescribed at a certain cell (e.g., with index 1), and its subsequent propagation over the crystal provides information on the evolution of momentum TCFs according to the relations

$$egin{array}{ll} \widehat{arphi}_1(t) &= \langle p^1(0) \; p^1(t)
angle / \langle p^2
angle \; , \ \widehat{arphi}_k(t) &= \langle p^1(0) \; p^k(t)
angle / \langle p^2
angle \; , \ \langle p^2
angle &= 3mk_{
m B}T \; , \end{array}$$

$$(4)$$

where m is the particle mass, $k_{\rm B}$ the Boltzmann constant.

In a perfect infinite centrosymmetrical crystal, TCF tensors such as $\langle p_i(0) \ p_k(t) \rangle$ are symmetrical, which may be proved by using the time reversibility of microscopic equations of motion and the lattice invariance for translation and inversion. With impurities or surfaces present, the crystal symmetry if lowered, and in a general case, the TCF tensors become asymmetrical [6, 9]. The tensors remain symmetrical only for the particle pairs lying in the symmetry planes of the crystal considered. Therefore, when the crystal is restricted by a surface, the tensors $\hat{\varphi}_k$ are expressed for the general case by the nine components $\varphi_k^{\gamma \sigma}$,

$$\widehat{\varphi}_k = \varphi_k^{\gamma o} i_{\gamma} i_{\sigma}; \qquad \gamma, \sigma = 1, 2, 3.$$
 (5)

The unit vectors i_{γ} make up an orthogonal basis. As follows from the definition (2), the tensor \hat{C}_{kj} is symmetrical and may be expressed by

$$C_{kj} = C_{kj}^{\kappa} E + C_{kj}^{n} \boldsymbol{n}_{kj} \boldsymbol{n}_{kj} \,. \tag{6}$$

It is assumed here that the principal values of the tensor for the axes perpendicular to the line connecting the centres of the k-th and j-th cells $(n_{kj}$ is the unit vector along this direction) are equal. The coefficients C_{kj}^{B} and C_{kj}^{n} are estimated from (2).

The substitution of (5) and (6) into (1) and scalar multiplication of the resultant relation by i and then by i, give a system of equations defining the components of q_k (summation over repeated indices is implied),

$$\bar{q}_{k} = \sum_{j=k}^{N} \left[C_{kj}^{h}(q_{j} - q_{k}) + C_{kj}^{h}(n_{kj} - i_{j}) \left(n_{kj} \cdot i_{j} \right) \left(q_{j}^{y\xi} - q_{k}^{y\xi} \right) \right].$$
(7)

For concrete estimations a system was chosen in which the interparticle interaction is described by the Lennard Jones potential (6–12). Rare gas crystals forming a facecentred cubic lattice afford an example of such systems. The linear length σ and energetic potential ε are dimensional parameters. The coefficients C^n and C^k were found with $\vartheta = k_{\rm B}T/\varepsilon = 1$ and $1 = 0.98\sigma^3$ (V is the Wigner-Seitz cell volume). The time is expressed in units of $\tau = \sigma \frac{r}{m/c}$ equal to 2.16×10^{-12} s for argon and 2.88 $\times 10^{-12}$ s for krypton.

The system (7) was solved on a EC-1033 computer with a numerical method using Verlet's difference scheme [6, 10]. The motion of particles near the (100) and (110) surfaces was studied. The axes x_1 and x_2 were brought in coincidence with the atomic surface plane, and x_3 was directed normally to the surface into the bulk crystal. At

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the initial moment, a particle which was either at the surface or in the neighbouring atomic planes, was excited. The boundary conditions (presence of the surface) were observed by the suitable rearrangement of summation on the right-hand side of (7) involving just those particles which belong to the system.

Naturally, numerical methods cannot be used for a semi-infinite system. The computations were carried out for the case when the lattice point coordinates satisfy the inequalities

$$-4.5a \le x_{k1}, \qquad x_{k2} \le 4.5a, \qquad 0 \le x_{k3} \le 4.5a, \tag{8}$$

where $a = (4V)^{1/3}$ is the lattice parameter, $x_3 = 0$ being the crystal surface. The other confining planes isolated a system of particles from the infinite half-space for the subsequent computer operation. It is noteworthy that when numerical methods are used in the dynamic lattice theory for computation of the spectral properties, the size of the system considered is implicitly restricted by choosing the interval in the inverse *k*-space.

Since only one particle was excited at the initial moment, the disturbance propagated over the system with time and was reflected from the confining planes. When the reflected signal was returned to the considered particle, the restriction of the system dimensions began to affect its motion [11]. Therefore, the system dimensions prescribed by (9) were chosen so that the boundary effects (naturally, except for the crystal surface $x_3 = 0$) might be neglected during the time interval of interest.

3. Results and Discussion

3.1 (100) surface

The computed momentum autocorrelation functions (ACF) $\hat{\varphi}_1(t)$ of particles lying in the near-surface region (see Fig. 1 a, b) show that only the time interval $(0, 2\tau)$ may be taken for the study. It should be noted that a negligibly small influence of the model system dimensions constrained by (8) on the computation results is ensured during this interval.

The momentum ACF $\hat{\varphi}(t)$ of a particle lying in the crystal surface atomic plane (plane 1) and the vibrational spectral density $\hat{\varphi}(\omega)$ (Fig. 1 a, c) essentially differ from the bulk ones. When the vibrations are polarized normal to the surface, a distinct quasi-resonance peak is present in the low-frequency spectral range. The momentum ACF is markedly different from the bulk case, quickly and regularly decaying with time. When vibrations are polarized parallel with the surface, the spectrum retains its main features characteristic of the bulk vibrations but with a lower high-frequency peak and an additional narrow peak in the low-frequency range.

For a particle in the second atomic plane, these essential differences from the bulk behaviour are not observed (Fig. 1b, d), but for the perpendicular polarization, $\varphi(t)$ is rapidly, though irregularly, damped with time, and in $\varphi(\omega)$ a typical trough of antiresonance type is observed at the frequencies corresponding to the peak in the surface particle spectrum.

An adatom is characterized by irregular and slowly decaying momentum ACF and a complicated spectrum composed of several distinct peaks. For both polarizations, a peak at $\omega \tau = 9$ is observed, and there are three non-coinciding peaks at $15 < \omega \tau <$ < 30. All the peaks are located within the allowed vibrational frequency range of the perfect infinite crystal. It seems of interest that four adatoms located at nearest square vertices, ensure for the atom of the surface plane under the square centre that

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Fig. 1. Correlation and spectral properties of the particles in the a), c) first and b), d) second near-surface (100) planes. The solid and dashed curves indicate vibrations perpendicular to the surface plane and parallel to it, respectively

all the characteristic features of the particle vibrations in the second plane in the absence of adatoms would be preserved, the former being more pronounced than the latter (Fig. 2 and Fig. 1 d).

For a heavy substitutional impurity (⁸⁶Kr for ⁴⁰Ar) in the first surface plane, quasiresonance peaks in the low-frequency spectral range (at $\omega \tau = 9$) are observed for both polarizations, and in the case of light impurities (⁴⁰Ar for ⁸⁶Kr), the peaks are found in different spectral ranges (Fig. 3). It seems important that local vibrations are not split off from the major frequency range as is observed for light impurities in the bulk [6, 9].

3.2 (110) surface

There are three inequivalent vibrational polarizations: [110], [001] in the surface plane, and [110] prependicular to the plane. In the surface plane, the points make up a rectangular lattice with the sides $a/\sqrt{2}$ ([110] direction) and a ([001] direction).

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Fig. 2. Spectral densities of the particle vibrations in the (100) surface plane under four adatoms. Notations as in Fig. 1

Fig. 3. Spectral densities of ⁴⁰Ar substitutional impurity in the surface plane of the ⁸⁶Kr matrix. Notations as in Fig. 1

For a particle belonging to the surface plane, the spectral vibrational density in the direction perpendicular to the surface, just as for the (100) surface, has a peak at $\omega \tau \approx 13$ but with a larger half-width (Fig. 4a). The lowest-frequency vibrations con-



Fig. 4. Spectral densities of particle vibrations in the a) first and b) second near-surface (110) planes. The solid, dashed, and dash-dotted curves show [110], [001], and [110] vibrations, respectively



Fig. 5. Spectral vibrational densities of the particles in the second near-surface (110) plane with an adatom. Notations as in Fig. 4

centrated within a narrow frequency range are observed in the [001] direction, whereas the [110] frequencies are actually uniformly distributed over a wide range, and a peak in the highfrequency range is observed. These peculiarities are closely related to the (110) surface structure.

For a particle in the second subsurface plane, the differences from the bulk spectrum are still essential (Fig. 4b). Only for the [110] direction, there appear particular features of the particle behaviour in the bulk, and the spectral distribution for the two other polarizations resemble those for a particle in the surface plane, being, however, shifted to the higher-frequency range. It seems interesting that for second-plane particles, low-frequency vibrations are virtually suppressed up to $\omega \tau \approx 10$.

The presence of an adatom on the same line (with the particle) prependicular to the surface markedly alters only the structure of [001] vibrations (Fig. 5). The vibrational structure of the adatom itself consists of three bands with widths of about $2/\tau$ at $\omega \tau = 10.6$; 13.2; 17.7 for the [110], [100], [110] polarizations, respectively, and is much simpler than that for the (100) surface.

The vibrational spectral characteristics and momentum ACF of particles belonging to the third plane are mainly consistent with the bulk vibrational pattern.

The fact that in the vibrational spectral characteristics of the particle within the near-surface region there are distinct quasi-resonance peaks corresponding to energies $(\hbar\omega)$ of several meV may be a source of information useful for the analysis of surfaces with low-energy atom beams.

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(Received June 13, 1986; in revised form December 3, 1986)