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## Energy band-structure effects in low-energy electron scattering by a crystalline film

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**Abstract.** The fine structure of the intensity of very slow electron reflection from the surface of a size-quantized film is considered. It is shown that in the case of grazing incidence the resonance contribution to the fine structure is due to the non-parabolic dispersion of the Rydberg-type bands caused by their hybridization with the states of the size-quantized film. The existence of such bands is supported by calculation of the energy bands lying near the continuous spectrum boundary for a Cu(001) film. It is demonstrated that the scattering intensity of the primary beam may strongly depend on its azimuthal orientation.

### 1. Introduction

Investigation of the fine structure of low-energy electron reflection (LEER) promoting the understanding of the processes of low-energy electron–solid interaction is important in many fields of solid state physics. At very low energies (0–20 eV) the LEER spectra contain a wealth of information about the processes of elastic and inelastic scattering, the structure of the potential barrier, and the electron states of empty bands. The mechanism of the LEER fine-structure formation has been studied in [1–6]. As a rule, the appearance of LEER oscillations is attributed to either the resonance scattering [1–5] or a special interference process [6]. Le Bosse *et al* [6] contend that, due to the rather strong absorption of the electron beam, the contribution of the resonance mechanism to the effect observed is small and, in most cases, can be neglected. However, more recent experiments on crystals of noble gases [7], investigation of the quantum size effect (QSE) in the low-energy electron scattering by thin films [8], the sensitivity of low-energy electron transmission (LEET) spectra to the electronic structure of a scattering crystal [9, 10] suggest that the empty energy bands near the continuous spectrum boundary substantially affect the character of electron scattering, which is not taken into account in the interference model. This prompted us to reconsider the effect of the energy band structure of a size-quantized crystalline film on the formation of the fine structure of LEER spectra. It should be stressed that in the present paper we are dealing with the LEER fine structure of size-quantized films in the very-low-energy range well below the non-specular beam emergence threshold. The critical and detailed analysis of threshold effects given in [6] showed that the fine-structure features in the LEER intensity from bulk (i.e. non-size-quantized) crystal surfaces are mainly due to a special interference process, and the resonance contribution is negligible. However, in that paper it was demonstrated that, even in the case of scattering on the surface of a bulk

W(001) specimen, the first peak near 3 eV does not result from the interference mechanism. It arises partially because the incidence energy is going across the lower band edge.

It is worth emphasizing that the conclusions of [6] are valid only for bulk specimens, when the assumptions of projected surface band structure and asymptotic behaviour of the wavefunctions of a semi-infinite crystal hold true. In the case of a size-quantized film these assumptions are no longer valid, and the problem must be reinvestigated. In principle, the LEER fine structure can be obtained within an accurate dynamic calculation which involves numerical solution of the Lippmann–Schwinger equation (equation (1) in section 2). This procedure, however, makes it difficult to separate out the contributions to the intensity from different physical mechanisms. We use a different approach based on the investigation of analytical properties of the scattering amplitude. A similar approach was used in [1, 2] where, however, the one-dimensional treatment of the problem (a two-dimensional (2D) free-electron model) was adapted to describe the Rydberg states with a quadratic dispersion law. As shown below, it is important to take into account the three-dimensional (3D) character of the crystalline potential and anisotropic non-parabolic dispersion of upper bands. A generalization of the theory to the 3D case performed in [11, 12] and briefly discussed in section 2 cannot be obtained by analogy with the single-centre scattering as stated in [13]. The use of such an approach together with an energy band calculation for a Cu film presented in section 3 provides a better insight into the origin of the LEER fine structure of size-quantized films. Conclusions are given in section 4. Some mathematical results are carried over to the appendix.

## 2. Low-energy electron scattering by the 3D potential of a crystalline film

In the film unit cell ( $\Omega$ ) symmetrical with respect to the plane  $z = 0$ , the states of a scattered electron are described by the equation

$$\Psi_{\mathbf{k}}(\mathbf{r}, E) \exp(i\mathbf{p} \cdot \mathbf{r}) + \int_{\Omega} G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}'; E) V(\mathbf{r}') \Psi_{\mathbf{k}}(\mathbf{r}', E) d\mathbf{r}' \quad (1)$$

where  $\mathbf{k}$  is the 2D quasi-momentum of the electron,  $E = p^2$  is its energy,  $\mathbf{p} = (\mathbf{k}, \sqrt{E - k^2})$ ,  $V(\mathbf{r})$  is the optical potential [14] and  $G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}'; E)$  is the structure Green function [15, 16] given by

$$G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}'; E) = \frac{1}{2S} \sum_{\mu} \exp[i(\mathbf{k} + \mathbf{K}_{\mu}) \cdot (\mathbf{u} - \mathbf{u}')] \frac{\exp[i\sqrt{E - (\mathbf{k} + \mathbf{K}_{\mu})^2}|z - z'|]}{i\sqrt{E - (\mathbf{k} + \mathbf{K}_{\mu})^2}}. \quad (2)$$

Here  $S$  is the area of the unit mesh,  $\mathbf{K}_{\mu}$  is the reciprocal-net vector and  $\mathbf{u}$  ( $\mathbf{u}'$ ) is the surface-parallel component of the vector  $\mathbf{r}$  ( $\mathbf{r}'$ ).

A crystalline analogue of the reflection amplitude at energies below the emergence of a non-specular beam ( $k^2 < E < (\mathbf{k} + \mathbf{K}_{\mu})^2$ ) has the form [11]

$$a^{-}(\mathbf{p}) = \int_{\Omega} \exp(-i\mathbf{k} \cdot \mathbf{u}) \exp(ip_z z) V(\mathbf{r}) \Psi_{\mathbf{k}}(\mathbf{r}, E) d\mathbf{r}. \quad (3)$$

According to [12], at the point  $\mathbf{p}_0 = (\mathbf{k}, 0)$

$$a^{-}(\mathbf{p}_0) = 0 \quad (4)$$

and therefore the scattering amplitude has no pole at  $p_z = 0$  contrary to what might be expected from the fact that the Green functions of the operators  $-\Delta$  and  $-\Delta + V(\mathbf{r})$  have poles at this point. In virtue of the above and since at  $E = (\mathbf{k} + \mathbf{K}_{\mu})^2$  the Green function

$G_k$  has singularities resulting in diffraction, the conventional approach of the single-centre scattering theory is not applicable in this case in contrast with the statement in [13].

The probability of specular reflection is [11]

$$P^- = 2\pi^3 \int \frac{|C(\mathbf{p})a^-(\mathbf{p})|^2}{p_z^2} d\mathbf{p} \quad (5)$$

where  $C(\mathbf{p})$  describes the incident particle momentum distribution. According to (4),

$$a^-(\mathbf{p}) = p_z a(\mathbf{p}) \quad (6)$$

where  $a(\mathbf{p})$  is an analytical function in the vicinity of the point  $\mathbf{p}_0$ . Then, if  $C(\mathbf{p})$  is 'sufficiently localized' near  $\mathbf{p}_1$  and if  $p_{1z}$  is small, we have

$$P^- \approx |a(\mathbf{p}_1)|^2. \quad (7)$$

In the 'resonance' case of the existence of a band of bound or quasi-stationary states near the continuous spectrum boundary, the scattering amplitude as well as the wavefunction  $\Psi_k(\mathbf{r}, E) \equiv \Psi(\mathbf{r}, \mathbf{p})$  have a pole at  $p_z = \sqrt{E_n(\mathbf{k}) - k^2}$  [11, 12], where  $E_n(\mathbf{k})$  is the dispersion law of the band. Then

$$a(\mathbf{p}) = \frac{b(\mathbf{p})}{p_z - \sqrt{E_n(\mathbf{k}) - k^2}} \quad (8)$$

where  $b(\mathbf{p})$  is analytical in the vicinity of  $\mathbf{p}_0$ . Substituting (8) into (7) and separating the real part  $\mathcal{E}_n(\mathbf{k})$  and the imaginary part  $\gamma_n(\mathbf{k})$  of the energy, we get for the intensity of a grazing specular-reflected beam

$$I(\mathbf{p}) = \frac{|B(\mathbf{p})|^2}{(\sqrt{E - k^2} - \sqrt{\mathcal{E}_n(\mathbf{k}) - k^2})^2 + 2 \operatorname{Re} \sqrt{(E - k^2)(k^2 - \mathcal{E}_n(\mathbf{k}))} + \delta^2(p, \gamma_n)}$$

$$= \begin{cases} \frac{|B(\mathbf{p})|^2}{E - \mathcal{E}_n(\mathbf{k}) + \delta^2} & \text{if } \mathcal{E}_n(\mathbf{k}) < k^2 \\ \frac{|B(\mathbf{p})|^2}{(\sqrt{E - k^2} - \sqrt{\mathcal{E}_n(\mathbf{k}) - k^2})^2 + \delta^2} & \text{if } \mathcal{E}_n(\mathbf{k}) > k^2 \end{cases} \quad (9)$$

where  $|B(\mathbf{p})|$  has small variations near  $\mathbf{p}_0$ . The expression for the scattering intensity (9), obtained by rigorous mathematical treatment, is convenient for theoretical analysis as it determines the energy region in which the LEER structure arises due to the resonance contribution. However, because the 'smooth' function  $B(p)$  is indeterminate, this expression is unsuitable for a direct non-parametric calculation of the intensity which can be obtained by consistent dynamic calculations incorporating the band structure of the film.

The formulae presented in this section have been obtained in [11, 12] on the assumption of exponential asymptotics of the potential  $V(\mathbf{r})$ . The case of the image potential asymptotic behaviour is considered in the appendix where the expressions for the observable quantities including (9) are shown to remain valid.

### 3. The energy band structure of unoccupied states of a FCC Cu(001) monolayer

The energy bands of a Cu monolayer have been calculated in a film version of the Green function method [15, 16]. The film potential was constructed on the basis of the electron density parametrized according to the data of a self-consistent calculation of the Cu monolayer conduction band [18]. The Coulomb contribution to the potential was calculated by the method in [17], while the Wigner interpolation formula [18] valid in the limits of large

and small densities was used for the exchange–correlation contribution. Two versions of the calculation are presented. The first (figure 1) corresponds to the exponential asymptotics of the crystalline potential following from a local-density approximation (LDA) for exchange and correlation. In the second variant (figure 2) a potential that correctly includes the image form for large distances was employed. In constructing this potential we followed the idea of [19], where the local exchange–correlation potential in a metal  $V_{xc}$  was joined on the image plane  $z = z_0$  to a potential of the form

$$V_{xc}^{NL}(z) = -\frac{1 - [1 + \frac{1}{4}b(z - z_0)] \exp(-b(z - z_0))}{2(z - z_0)}. \quad (10)$$

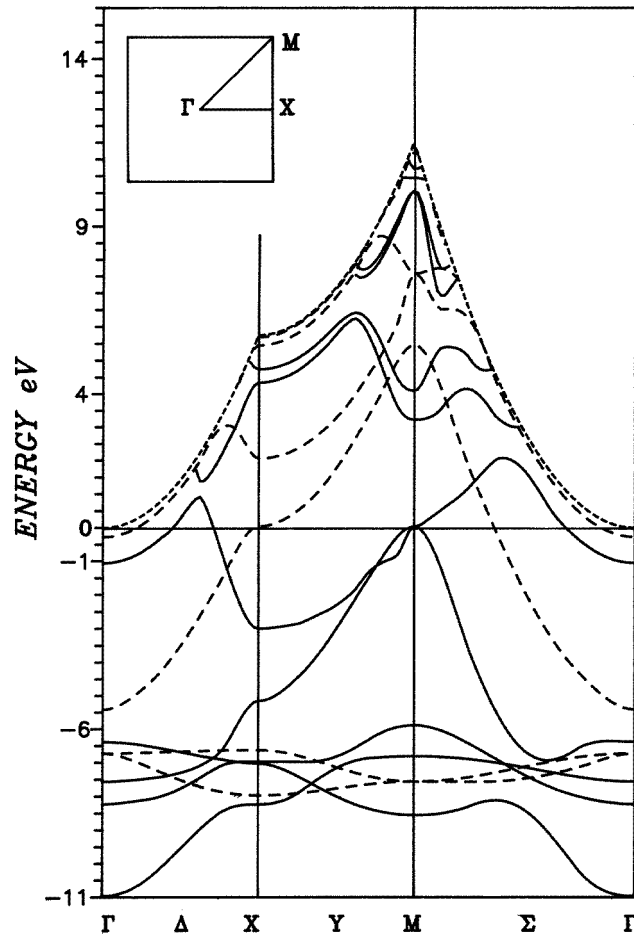
This expression results from the integration of the spherical potential produced by the local exchange–correlation hole. We have the somewhat modified expression (10), introducing a parameter  $a$  (replacing in square brackets  $\frac{1}{4}b$  by  $b/a$ ) which allows smooth joining of  $V_{xc}^{NL}$  and  $V_{xc}$  at any  $z_0$ . As predicted by jellium model theories for Cu,  $z_0 = 3$  au [20, 21]. The increase in  $z_0$  to the value of 8.6 au, which is in some sense optimal for describing the LEED structure in the modified image barrier model [22], leads to a slight band shift (table 1); this, as shown later, does not affect definitive conclusions.

**Table 1.** The dependence of the binding energy of upper bands on the image plane position  $z_0$ : +, even parity states; –, odd parity states. The energy is in electronvolts with respect to the vacuum zero.

$n$	Parity	Binding energy (eV)		
		$z_0 = 8.6$ au	$z_0 = 3$ au	[24]
3	–	–0.076	–0.065	–0.09
2	+	–0.289	–0.183	–0.19
1	–	–0.607	–0.625	–0.62
	+	–1.134	–1.183	—

The band structure below  $-3$  eV (figure 1) fits the calculations available [18, 23]. The unoccupied states are far less investigated. To our knowledge, there does not exist as yet any complete realistic calculation of dispersion curves  $\mathcal{E}_n(\mathbf{k})$  above the vacuum zero. The occurrence of energy bands near the continuous spectrum boundary which is defined by the paraboloid  $E = \mathbf{k}^2$  is a noteworthy feature of figures 1 and 2.

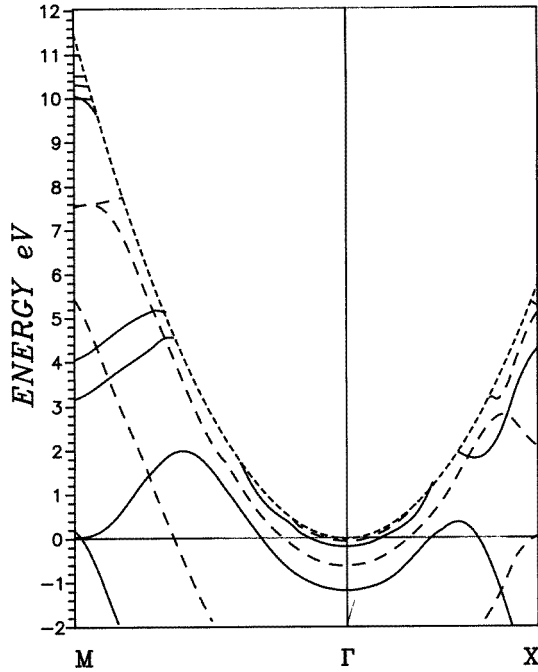
In the case of asymptotic behaviour (10) (figure 2) the states below 2 eV are almost identical with those shown in figure 1; so they are not present in figure 2. Of interest is the appearance of new bands of Rydberg states at point  $\Gamma$  at energies  $-0.065$  and  $-0.183$  eV. At  $\Gamma$  the energies of the states of upper bands are in good agreement with the  $n = 1, 2, 3$  members of the Rydberg series obtained in [24] (table 1). However, as immediately follows from comparison of figures 1 and 2, the  $n = 1$  state ( $-0.62$  eV) is a ‘crystal-derived’ state in terms of [24]. The electron density distribution for this state is similar to that obtained in [24], i.e. 94.5% of the charge of this state is localized outside the film and its wavefunction has a single maximum beyond the crystal edge at about 8 au with respect to the centre of the last row of atoms. In essence, this is an image state arising even in the LDA for exchange and correlation. The possibility of finding the low-energy image states within the framework of the LDA has been demonstrated in [25] (Ag(001)) and in [26] (Al(001) and Al(111)). The absence of these states in the LDA potential of [24] may be attributed to the influence of the particular form of LDA on the states of upper bands which has yet to be analysed (it is known that for the conduction band states this influence is substantial



**Figure 1.** The energy bands of a Cu(001) monolayer in the case of exponential asymptotics of the crystal potential: —, even parity states; ---, odd parity states; - · - ·, continuous spectrum boundary ( $E = k^2$ ).

and may produce an energy-term shift of several electronvolts), or to the use of the LAPW methods with parameters verified with respect to the occupied part of the conduction band. Near the vacuum zero, at the edge of the linearization region the accuracy of calculations considerably diminishes [27] and becomes comparable to the binding energies of upper bands. Further hypotheses could be proposed, but this is irrelevant for the discussion that follows. If there exist several bands near the continuous spectrum boundary, the possibility of the fine-structure resolution is determined by the energy broadening of these bands ( $\delta$  in equation (9)). As shown in [2, 5, 14], the quantity  $\delta$  depends to a large extent on the spatial localization of states which is closely related to the physical origin of the bands under consideration.

At the centre of the Brillouin zone (BZ) the effective masses of the bands shown in figure 2 are close to the free-electron mass  $m$ . For the above-discussed term whose binding energy at  $k = 0$  is  $e = 0.62$  eV,  $m^* = 0.97m$ , which agrees with the value of  $m^* = 0.98m$  obtained in [24]. We should note that, in the case of size-quantized films at very low



**Figure 2.** The energy bands of a Cu(001) monolayer in the case of asymptotic behaviour corresponding to the image potential form for large distances: —, even parity states; - - -, odd parity states; - · - ·, continuous spectrum boundary ( $E = k^2$ ).

energies of the primary electron beam  $(\mathbf{k} + \mathbf{K}_\mu)^2 > E > k^2$ , the conclusion [6] that the resonance contribution to the reflection intensity is small for energies lying in the gap of bulk bands does not hold true (the sum over  $\mathbf{K}_\mu$  is absent in equation (12) [6] and  $|M_{pp}^{+-}| \approx 1$ ). Moreover, the concept of asymptotic behaviour of the electron states in a semi-infinite crystal is unlikely to work in the case of size-quantized films.

Let us consider the resonance contribution to the scattering intensity from the bands near the continuous spectrum boundary which satisfy the condition  $\mathcal{E}_n(\mathbf{k}) < k^2$ . For the quadratic dispersion law, as in the 2D free-electron model,

$$\mathcal{E}_n(\mathbf{k}) = \frac{1}{2m^*} k^2 - e_n. \quad (11)$$

In the energy range under consideration  $E < e_n/[\sin^2 \vartheta(1/2m^* - 1)]$  ( $\vartheta$  is the polar angle for incident particles) the scattering intensity (9)

$$I(E, \vartheta) = B^2/[E(1 - \sin^2 \vartheta/2m^*) + e_n + \delta^2] \quad (12)$$

is a monotonic function of energy, and the resonance contribution of such a band to the LEER fine structure is absent. The situation changes, however, if the dispersion of the band is non-parabolic, as near  $\mathbf{k}_g$  corresponding to the band hybridization range (figure 2). In this case the condition

$$\partial I/\partial E = -B^2[2E - \nabla_{\mathbf{k}} \mathcal{E}(\mathbf{k}) \cdot \mathbf{k}]/[2E(E - \mathcal{E}_n(\mathbf{k}) + \delta^2)^2] = 0 \quad (13)$$

can be satisfied, and the fine structure appears. Indeed, assuming for simplicity that the azimuthal angle of incidence  $\varphi = 0$ , in the vicinity of the band extrema we have

$$\mathcal{E}_n(\mathbf{k}) = k^2/2m^* + \mathcal{E}_n(\mathbf{0}) \quad \mathcal{E}_n(\mathbf{k}) = -(\mathbf{k} - \mathbf{k}_g)^2/2M^* + \mathcal{E}_n(\mathbf{k}_g). \quad (14)$$

The intensity extremum is reached at  $E = E_{extr} = \mathbf{k}_{extr}^2 / \sin^2 \vartheta$ , where  $k_{extr}$  is the root of the equation

$$2\mathbf{k} - [\partial\mathcal{E}(\mathbf{k})/\partial\mathbf{k}] \sin^2 \vartheta = 0 \quad (15)$$

i.e. in the case of grazing incidence the surface projection of the electron beam velocity must be close to the electron velocity in the ‘resonance’ band. In the band under consideration ( $\mathcal{E}_n(\mathbf{0}) = -0.62$  eV) the electron velocity  $\partial\mathcal{E}_n/\partial\mathbf{k} = \mathbf{0}$  at  $\mathbf{k} = \mathbf{0}$  and  $\mathbf{k} = \mathbf{k}_g$  and, if  $\partial^2\mathcal{E}_n/\partial^2\mathbf{k}$  monotonically decreases on  $[0, \mathbf{k}_g]$  ( $V(\mathbf{k}) = \partial\mathcal{E}_n/\partial\mathbf{k}$  is a convex-up function), a non-zero solution of (15) exists when in the vicinity of  $\mathbf{k} = \mathbf{0}$ :

$$[\partial\mathcal{E}(\mathbf{k})/\partial\mathbf{k}] \sin^2 \vartheta > 2\mathbf{k} \quad \text{or} \quad \sin^2 \vartheta > m^*/m. \quad (16)$$

For grazing incidence ( $\vartheta = \pi/2 + \alpha$ ,  $\alpha$  being small) this yields

$$\alpha < \sqrt{2[1 - (m^*/m)^{1/2}]}. \quad (17)$$

For  $m^*/m \approx 1$  the angle  $\alpha$  is very small. In particular,  $\alpha < 10^\circ$  for the band with  $m^* = 0.97m$ .  $E_{extr}$  depends on the effective mass  $M^*$ . It is easy to show that, if the condition (16) is fulfilled, then

$$E_{extr} \leq k^2 / [\sin \vartheta (M^*/m + 1)]^2. \quad (18)$$

With increasing film thickness the number of size-quantized bands which hybridize with the band of Rydberg states increases. A typical situation is schematically shown in figure 3. The extrema of the  $i$ th hybridized band are at points  $\mathbf{k}_{g1}^{(i)}$  and  $\mathbf{k}_{g2}^{(i)}$ , the distance between which decreases with increasing number of layers. Since  $\partial\mathcal{E}_i/\partial\mathbf{k} < \mathbf{0}$  beyond the interval  $\mathbf{k}_{g2}^{(i)} \geq \mathbf{k} \geq \mathbf{k}_{g1}^{(i)}$ , the condition (15) can be satisfied only for energies  $(\mathbf{k}_{g2}^{(i)}/\sin \vartheta)^2 > E > (\mathbf{k}_{g1}^{(i)}/\sin \vartheta)^2$ . In the vicinity of  $\mathbf{k}_{g1}^{(i)}$  and  $\mathbf{k}_{g2}^{(i)}$ ,  $(\partial\mathcal{E}_i/\partial\mathbf{k}) \sin \vartheta < 2\mathbf{k}$ ; therefore equation (15) may have two roots corresponding to the maximum and the minimum of the reflection intensity. The above reasoning accounts for the observed increase in frequency of the QSE peaks with increasing thickness [7, 8].

For the lowest band, according to first-order perturbation theory for almost degenerate levels, we have

$$m/M^* = -1 + 4|P_{nm,x}|^2/\Delta_{nm} \quad (19)$$

where  $P_{nm,x}$  is the momentum matrix element between the states of the  $m$ th and  $n$ th bands belonging to the same irreducible representation of the wavevector group;  $\Delta_{mn}$  is the magnitude of the hybridization gap at point  $\mathbf{k}_g$  (figure 3). Hence, the effective mass  $M^*$  diminishes with increasing number of film layers, which in accordance with (18) leads to a shift of  $E_{extr}$  towards larger energies up to the energy corresponding to intersection of the Rydberg-type band with the projection of bulk bands, and the interference processes playing a leading part in formation of the LEER threshold effect increase in importance [6].

It should be noted that the dispersions of the resonance bands are different for the  $\Gamma$ -X and  $\Gamma$ -M directions of the BZ (figure 2). The absence in the considered energy range of ‘crystal-derived’ bands of odd parity in the  $\Gamma$ -M direction results in quadratic dispersion of the above-discussed band of Rydberg states and hence in a zero-resonance contribution to the LEER for a given azimuthal orientation of the primary beam.

#### 4. Conclusions

On the basis of the analytical properties of the scattering amplitude of a crystalline film, we have investigated and explained the fine structure observed in very-low-energy electron



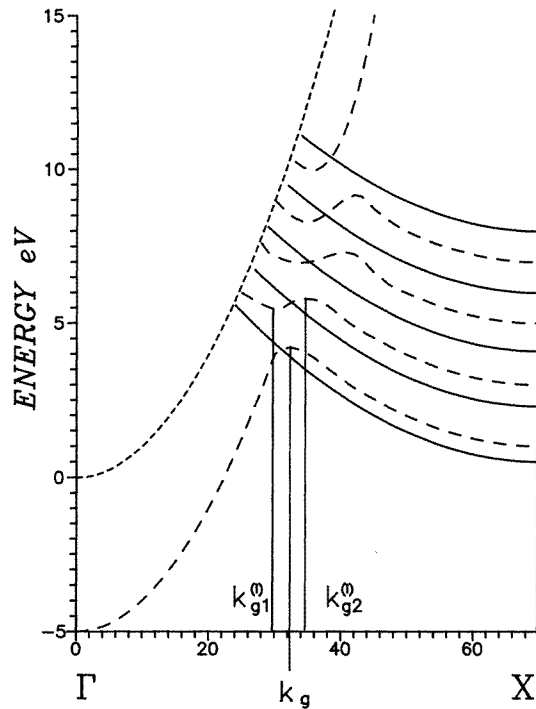


Figure 3. Schematic representation of the band crossing for a multilayer film.

reflection (VLEER) spectra of a size-quantized film. It is found that, in the case of grazing incidence of very slow electrons with energies well below the non-specular beam emergence threshold, the VLEER spectra structure of thin films depends on the dispersion of the bands near the continuous spectrum boundary. The appearance of the low-energy fine structure is shown to be due to the non-parabolic dispersion of these bands caused by hybridization of the bands of Rydberg and 'crystal-derived' types. This is a phenomenon of resonance rather than interference nature, as is the case in the threshold effect [6]. A strong dependence of VLEER spectra on the azimuthal orientation of the primary beam can appear as a result of the resonance band anisotropy due to the 3D character of the crystalline potential.

Unfortunately, no experimental data on VLEER for Cu thin films in the incident energy range well below the non-specular beam emergence threshold have come to our notice. On the other hand, as seen from the results in sections 2 and 3, the generality of the considered mechanism of formation of the VLEER spectra structure is sufficiently large that it can take place not only in metals but also in size-quantized dielectric films, if there exist resonance bands of one or other nature. From this standpoint, the results obtained agree with the LEER experiment on Ar thin films, which shows that the structures in VLEER spectra reflect essentially the band-structure characteristic of the Ar surface [7]. The band-structure effects are clearly seen in the LEER spectra obtained by Bader *et al* [30] for Ar, Kr, Xe, N<sub>2</sub>, CO and O<sub>2</sub> films, which also provides support for our results.

The importance of the energy band structure for the formation of the QSE of d-band metals is known. Nevertheless, on the basis of calculation of the unoccupied bands of *infinite crystals*, the free-electron model is frequently supposed to be suitable for the analysis [8]. In the present paper, we attempted to show the importance of taking into account the deviation

of the resonance band dispersion from the free-electron dispersion law, while interpreting the LEER data for thin films in the energy range of interest.

### Appendix

Consider for simplicity the potential  $V(z)$  averaged over  $x, y$ . Let  $V(z) = -a/|z|$  for  $|z| > d$ , where  $a, d > 0$ . Define the 'cut' potentials  $V_N(z)$ ,  $N = 1, 2, \dots$  as coinciding with  $V(z)$  for  $|z| \leq d_N$ , equal to zero for  $|z| \geq d_N + \mathcal{E}$  (where  $\mathcal{E} > 0$  and  $\lim_{N \rightarrow \infty} d_N = \infty$ ) and being smooth functions. In the case of  $E > k^2$  the Bloch solutions of the equation

$$-\Delta\psi + V\psi = E\psi \tag{A1}$$

for small  $\lambda = E - k^2$  have the form

$$\psi(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{u})\varphi(z)$$

where  $\varphi(z)$  satisfies the one-dimensional Schrödinger equation

$$-\varphi'' + V\varphi = \lambda\varphi. \tag{A2}$$

According to [28] there exist solutions of equation (A2) which for  $z \geq d$  have the form

$$\varphi_{1,2}(z) = (\lambda - V(z))^{-1/4} \exp\left(\pm i \int_a^z \sqrt{\lambda - V(\xi)} d\xi\right) + O(z^{-2}). \tag{A3}$$

Analogous expressions exist for the potentials  $V_N(z)$ , and  $N = 1, 2, \dots$ . In this case the quantity  $O(z^{-2})$  decreases uniformly in  $N$ , and all formulae permit differentiation.

Consider the solution of equation (A1) with  $V = V_N$  corresponding to a scattered state. We have

$$\psi^{(N)}(\mathbf{r}) = \begin{cases} \exp(i\mathbf{k} \cdot \mathbf{u})[\exp(i\sqrt{\lambda}z) + A(\lambda)\exp(-i\sqrt{\lambda}z)] & z \leq -d_N - \mathcal{E} \\ B(\lambda)\exp(i\mathbf{k} \cdot \mathbf{u})\exp(i\sqrt{\lambda}z) & z \geq d_N + \mathcal{E}. \end{cases} \tag{A4}$$

$A(\lambda)$  and  $B(\lambda)$  are the coefficients of reflection and transmission, respectively.

In view of the above, for sufficiently large  $N$  there exists a solution  $\psi(\mathbf{r})$  of equation (A1) which, together with the derivative with respect to  $z$ , in the neighbourhood of the point  $z = -d_N$  can be arbitrarily close to  $\psi^{(N)}(\mathbf{r})$ . Then according to (A3) at  $z \rightarrow -\infty$

$$\psi(\mathbf{r}) \approx \lambda^{-1/4} \exp(i\mathbf{k} \cdot \mathbf{u}) \{ \exp[i(\sqrt{\lambda}z + (a/2\sqrt{\lambda}) \ln(-z/d_N))] + A(\lambda) \exp[-i(\sqrt{\lambda}z + (a/2\sqrt{\lambda}) \ln(-z/d_N))] \}. \tag{A5}$$

When  $z \rightarrow \infty$ , by virtue of the continuous dependence of the ordinary differential equations for the initial conditions we have

$$\psi(\mathbf{r}) \approx \lambda^{-1/4} \exp(i\mathbf{k} \cdot \mathbf{u}) B(\lambda) \exp(i(\sqrt{\lambda}z + (a/2\sqrt{\lambda}) \ln(z/d_N))). \tag{A6}$$

Thus, in the case of the potential  $V(z)$ , the quantity  $A(\lambda) \exp(-i(a/2\sqrt{\lambda}) \ln(-z/d_N))$  fulfils the role of the reflection amplitude, and in the limit  $N \rightarrow \infty$  the observable quantities remain the same (unchanged) (cf [29]).

### References

- [1] McRae E G 1971 *Surf. Sci.* **25** 491
- [2] McRae E G 1979 *Rev. Mod. Phys.* **51** 541
- [3] Deitz R E, McRae E G and Campbell R L 1980 *Phys. Rev. Lett.* **45** 1139
- [4] Rundgren J and Malmstroem G 1977 *Phys. Rev. Lett.* **38** 836
- [5] Echenique P H and Pendry J B 1978 *J. Phys. C: Solid State Phys.* **11** 2065

- [6] Le Bosse J C, Lopez J, Gaubert C, Gauthier Y and Baudoing R 1982 *J. Phys. C: Solid State Phys.* **15** 6087
- [7] Michaud M, Sanche L, Gaubert C and Baudoing R 1988 *Surf. Sci.* **205** 447
- [8] Park R L, Jonker B T, Iwasaki H and Zhu Q-G 1985 *Appl. Surf. Sci.* **22-3** 1
- [9] Plenkiewicz B, Plenkiewicz P, Perluzzo G and Jay-Gerin J-P 1985 *Phys. Rev. B* **32** 1253
- [10] Jay-Gerin J-P, Plenkiewicz B, Plenkiewicz P, Perluzzo G and Sanche L 1985 *Solid State Commun.* **55** 1115
- [11] Chuburin Yu P 1987 *Teor. Matem. Fiz.* **72** 120
- [12] Wolf G V, Chuburin Yu P and Rubzova L A 1991 *Poverhmost* N10 81
- [13] Gersten J I and McRae E G 1972 *Surf. Sci.* **29** 483
- [14] Pendry J B 1974 *Low Energy Electron Diffraction* (New York: Academic)
- [15] Kar N and Soven P 1975 *Phys. Rev. B* **11** 3761
- [16] Kohn W 1975 *Phys. Rev. B* **11** 3756
- [17] Wolf G V and Rubzova L A 1985 *Poverhmost* N4 27
- [18] Smith J R, Gay J G and Arlinghaus F J 1980 *Phys. Rev. B* **21** 2201
- [19] Serena P A, Soler J M and Garcia N 1984 *Phys. Rev. B* **34** 6767
- [20] Appelbaum J A and Hamann D R 1972 *Phys. Rev. B* **6** 1122
- [21] Lang N D and Kohn W 1973 *Phys. Rev. B* **7** 3541
- [22] Read M N 1985 *Appl. Surf. Sci.* **22-3** 48
- [23] Dubrovskii O I, Kurganskii S I, Rubtsova L A and Wolf G V 1990 *Phys. Status Solidi b* **161** 697
- [24] Hulbert S L, Johnson P D, Weinert M and Garrett R F 1986 *Phys. Rev. B* **33** 760
- [25] Konig U, Weinberger P, Rediger J, Erschbauer H and Freeman A J 1989 *Phys. Rev. B* **39** 7492
- [26] Silkov V M, Jurczyszyn L, Chulkov E V and Steslicka M 1994 *Poverhmost* N7 36
- [27] Koelling D D and Arbman G O 1975 *J. Phys. F: Met. Phys.* **5** 2041
- [28] Fedoruk M V 1985 *Ordinary Differential Equations* (Moscow: Nauka) (in Russian)
- [29] Taylor J R 1972 *Scattering Theory. The Quantum Theory of Nonrelativistic Collisions* (New York: Wiley)
- [30] Bader G, Perluzzo G, Caron L G and Sanche L 1984 *Phys. Rev. B* **30** 78