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Fast-Electron Spectroscopy of Surface Excitations

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New theoretical results are presented for the probability of exciting surface oscillations (optical phonons or plasmons) by fast electrons reflected from the surface of a thin crystal film. Both specular and Bragg reflections are considered and the effect of the finite slab thickness is included. The theory explains successfully the energy-loss spectra measured by Powell on metallic surfaces and recent measurements by Ibach on ZnO surfaces.

Recently the authors have proposed a new semiclassical theory of the characteristic energy-loss spectra of fast electrons in solids.[1] In this approach, the electron is treated as a classical particle on the well-defined trajectory $\vec{r}(t)$ and acts as a time-dependent perturbation, linearly coupled to the quantized field of elementary excitations (e.g., optical phonons or plasmons). The response of the system can be calculated exactly to give the field excitation probability and hence the energy-loss spectrum. The trajectory could be chosen arbitrarily so that one could consider reflection cases (both specular and Bragg reflections) as well as the transmission case treated in the dielectric theory[2,3] of energy-loss spectra.

In this Letter we present general formulas for the loss probability function appropriate to the specularly or Bragg reflected electron at the surface of a slab of arbitrary thickness. Application of the theory to the inelastic scattering by surface optical phonons in ZnO and surface plasmons in metals leads to scattering probabilities in excellent agreement with recent experimental data obtained by Ibach[4] and Powell.[5]

Let $\omega_\pm(\vec{k})$ be the frequencies of the odd (even) modes of long-wavelength surface excitations (either phonons or plasmons) in a slab of thickness $2a$. The dispersion relation for these modes can be implicitly written as[6]

$$\sinh 2ka = \pm 2\epsilon(\omega)/[\epsilon^2(\omega)-1] \tag{1}$$

[which is equivalent to the relation (3.23a) of Ref.6], where $\vec{k}$ is a two-dimensional wave vector parallel to the surface and $\epsilon(\omega)$ is the frequency-dependent dielectric function of the material. The probability that the electron loses an energy $\hbar\omega$ is found to be[1]

$$P(\omega) = \frac{P_0}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{i\omega t} \exp\left[\int d^2k (Q_+ e^{-i\omega_+ t} + Q_- e^{-i\omega_- t})\right], \tag{2}$$

where P_0 is the no-loss probability (strength of the no-loss line) and where

$$Q_\pm(\vec{k}) = \frac{e^2\omega_p^2}{4\pi\hbar}\frac{\sinh 2ka}{\omega_\pm(k)}e^{-2ka}\left|\frac{1}{kv_\perp + i(\omega_\pm - \vec{k}\cdot\vec{v}_\parallel)} + \frac{1}{kv_\perp' - i(\omega_\pm - \vec{k}\cdot\vec{v}_\parallel')}\right|^2; \tag{3}$$

ω_p is the bulk plasma frequency and is given by $\omega_p^2 = 4\pi ne^2/m$ in the plasmon case and by $\omega_p^2 = 4\omega_T^2(\epsilon_0 - \epsilon_\infty)/(\epsilon_\infty+1)^2$ in the phonon case (ion plasma), where ω_T is the reststrahlen frequency and ϵ_0, ϵ_∞ are static and high-frequency dielectric constants. $\vec{v} = (\vec{v}_\parallel, v_\perp)$ and $\vec{v}' = (\vec{v}_\parallel, v_\perp')$ are the constant velocity components parallel and perpendicular to the surface for the incident and reflected electrons, respectively. In the above formulas, excitation damping and radiative losses are not considered and we have assumed that the electron does not penetrate sufficiently far into the material to interact with bulk excitations.

From (2), the ratio of the one-phonon (plasmon) loss to the no-loss probabilities is given by

$$P_1^\pm(\omega)/P_0 = \int d^2k\, Q_\pm(\vec{k})\delta(\omega - \omega_\pm(\vec{k})). \tag{4}$$

We can describe the loss spectrum using $P_1^\pm(\omega)$ if it is small so that multiple losses are negligible or, as is often the case with phonons, when the threshold for double losses is above the band of surface phonon energies. After integrating (4), one finds

$$\frac{P_1^\pm(\omega)}{P_0} = \mp\frac{e^2}{\hbar a}\frac{2\epsilon}{\epsilon^2-1}\frac{\theta(k_c - k_\pm)}{k_\pm^2}\operatorname{Im}\left\{\frac{1}{v_\perp^2}[(\alpha_\pm + i)^2 - \gamma^2]^{-1/2} + \frac{1}{v_\perp'^2}[(\alpha_\pm' + i)^2 - \gamma'^2]^{-1/2}\right.$$
$$\left. + \frac{2}{v_\perp v_\perp'}\frac{1}{\gamma - \gamma' + i(\alpha_\pm'\gamma - \alpha_\pm\gamma')}\{\gamma[(\alpha_\pm + i)^2 - \gamma^2]^{-1/2} - \gamma'[(\alpha_\pm' + i)^2 - \gamma'^2]^{-1/2}\}\right\}, \tag{5}$$

where θ is the step function, $\theta(x) = 1$ for $x > 0$ and 0 for $x < 0$; k_c is the maximum momentum transfer determined by the aperture of the spectrometer[1]; and $\alpha_\pm$, γ, and $k_\pm$ are given by

$$\alpha_\pm = \frac{\omega}{k_\pm v_\perp}, \quad \gamma = \frac{v_\parallel}{v_\perp}, \quad k_\pm = \frac{1}{2a}\ln\left(\pm\frac{1-\epsilon}{1+\epsilon}\right). \tag{6}$$

From Eqs. (3) or (5), we see that the loss probability consists of the incidence and reflection loss probabilities (first two terms) plus the interference of these two losses (third term).[7] For the specularly reflected beam ($\alpha = \alpha'$, $\gamma = \gamma'$), formula (5) reduces to

$$\frac{P_1^\pm(\omega)}{P_0} = \mp\frac{2e^2}{\hbar a}\frac{2\epsilon}{\epsilon^2-1}\frac{\theta(k_c - k_\pm)}{k_\pm^2 v_\perp^2}\operatorname{Im}\left\{[(\alpha_\pm + i)^2 - \gamma^2]^{-1/2}\left[1 + \frac{i(\alpha_\pm + i)}{(\alpha_\pm + i)^2 - \gamma^2}\right]\right\}. \tag{7}$$

Single-excitation spectra of ZnO and LiF crystal films as predicted by Eq. (7) are illustrated in Fig. 1 for several values of the parameters. For comparison, we have also plotted the Lorentzian

$$\frac{P_1(a=\infty)}{P_0} = \frac{1}{\omega_T}\frac{e^2}{\hbar v_\perp}\frac{\epsilon_\infty + 1}{\epsilon_0 + 1}\operatorname{Im}\left[\frac{-1}{1+\epsilon(\omega)}\right] \tag{8}$$

describing the one-phonon excitation probability for an electron beam reflected from a semi-infinite crystal [see below, Eq. (13)]. The broad structures arising from the spatial dispersion of the surface phonons should be easily observable: They dominate the broadening due to phonon damping for thicknesses up to several hundred angstroms. For very thin films one observes a characteristic splitting of the line at the limiting surface phonon frequency ω_s. The main contributions to the spectrum shift away from ω_s, where only a weak peak survives. One should notice that for high-energy electrons [LiF case, Fig. 1(b)], mostly long-wavelength surface phonons (with frequencies close to ω_T and ω_L) are excited, so the slab appears very "thin" even for a few thousand angstroms thickness. Experimentally these peaks should not be confused with volume excitations. For all thicknesses, the spectrum diverges at ω_s like $1/(|1+\epsilon|\ln^2|1+\epsilon|)$, $\epsilon \to -1$, as a result of the singularity in the phonon density of states. Detailed measurements on thin films which could be compared with the above predictions do not seem to have been performed.

In the case of a very thick slab ($k_c a \gg 1$) or a semi-infinite medium, one can go one step further and

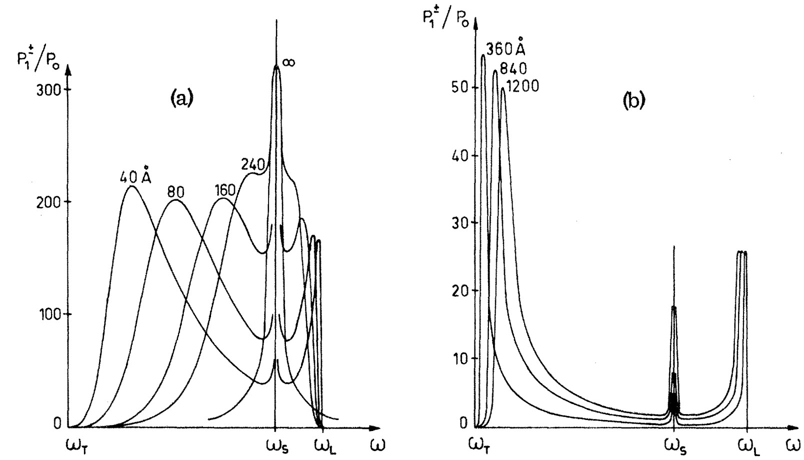

FIG. 1. (a) Theoretical single-excitation loss spectra for a 25-eV electron specularly reflected by a ZnO film at 45° incidence and for various thicknesses. For comparison, the Lorentzian at $\omega=\omega_s$ (half-width $\Delta\omega/\omega_T=0.02$, see optical constants of ZnO in Ref. 8) gives the loss spectrum for a semi-infinite crystal. The absolute values of the loss probabilities are obtained by multiplying the ordinates by $2\alpha_{FS}/\omega_T$, where $\alpha_{FS}=1/137$ is the fine structure constant. (b) Single-excitation spectra for LiF crystal slab, 25-keV beam at 10° grazing incidence and various thicknesses.

from (2) obtain the full spectrum of multiple excitations, using the limit

$$\lim_{a\to\infty}\int d^2k(Q_+e^{-i\omega_+t}+Q_-e^{-i\omega_-t})=Qe^{-i\omega_s t}, \tag{9}$$

where

$$\omega_s=\omega_p/\sqrt{2}\ \text{(plasmon)} \tag{10}$$

$$=[(\epsilon_0+1)/(\epsilon_\infty+1)]^{1/2}\omega_T\ \text{(phonon)} \tag{11}$$

is the degenerate surface-mode frequency and

$$Q=\frac{e^2\omega_p^2}{2\hbar\omega_s^2}\left\{\frac{1}{2v_\perp}F(\alpha,\gamma)+\frac{1}{2v_\perp'}F(\alpha',\gamma')+I(\alpha,\alpha';\gamma,\gamma')\right\},\quad F(\alpha,\gamma)=\operatorname{Im}\ln\{\alpha+i+[(\alpha+i)^2-\gamma^2]^{1/2}\}, \tag{12}$$

$\alpha=\omega_s/k_c v_\perp$, I being a rather complicated, generally negligible interference function. For the specular beam, (12) reduces to

$$Q_{sp}=\frac{e^2\omega_p^2}{2\hbar\omega_s^2 v_\perp}\{F(\alpha,\gamma)-\operatorname{Re}[(\alpha+i)^2-\gamma^2]^{-1/2}\}. \tag{13}$$

Equations (2) and (9) describe the spectrum composed of δ-shape lines equally separated by ω_s, i.e., the Poisson distribution. Q gives the ratio of the strengths of the one-phonon (plasmon) and no-loss lines. We shall check the validity of (12) and (13) by comparing them with the recent experimental spectra.

First we refer to Ibach's measurements[4] on ZnO surfaces. Figure 5 in Ref. 4, which corresponds to the specular beam at 45° incidence, gives $Q_{sp}=(1.3\ \text{eV}^{1/2})/\sqrt{E}$, where E is the electron beam energy. From our Eqs. (12) and (13) and using the dielectric data[8] appropriate to the $(1\bar{1}00)$ face of ZnO ($\epsilon_0=7.8$, $\epsilon_\infty=3.7$), we find $Q_{sp}=1.58/\sqrt{E}$, in reasonable agreement with the experimental result. If we use the data for the (0001) face[8] ($\epsilon_0=8.6$, $\epsilon_\infty=3.75$), we find $Q_{sp}=1.66/\sqrt{E}$, in agreement with the observed trend towards a higher loss for this face.[9] Ibach also measured[9] the loss spectrum of the (01) Bragg reflection for a 39-eV electron beam. In his experimental setup, the total scattering angle is kept constant (90°) and the Bragg beam is detected by the spectrometer when the properly oriented crystal has been rotated through an angle of 25°. This geometry therefore corresponds to 20° incidence and 70° reflection angles. From our expressions (12) and (13) we compute the following ratio of the one-phonon line strengths in the (01) Bragg beam and in the specular beam:

$$\frac{Q_{01}}{Q_{sp}}=\frac{v_\perp(45°)}{2}\left[\frac{1}{v_\perp(20°)}+\frac{1}{v_\perp(70°)}\right]\simeq 1.4. \tag{14}$$

Ibach's measured ratio[9] is precisely 1.4!

Now we consider energy-loss measurements by Powell[5] on vairous metal surfaces. We notice from (13) and (10) an interesting result, i.e., that the loss probability does not depend on ω_s ($\gamma \gg \alpha$ in these experiments), Q_{sp} reducing to

$$Q_{sp}=(e^2/\hbar v_\perp)\pi/2, \tag{15}$$

an expression independent of the material under study. For example, taking Powell's 8-keV beam at 89° (grazing) incidence ($\theta = 2°$ total scattering angle), we find from (15) $Q_{sp}=3.7$. Therefore the spectrum which is given by the Poisson distribution should culminate around the 3-plasmon loss line. This is indeed observed (see Fig. 3 in Ref. 5). Relation (15) can be written as

$$Q_{sp}=\frac{\pi e^2}{2\hbar v}\frac{1}{\cos\varphi}=\frac{0.065}{\cos\varphi}, \tag{16}$$

where φ is the incidence angle. The predicted coefficient 0.065 is in remarkable agreement with the empirical one which was used to fit the experimental points for liquid Al (see Fig. 6 in Ref. 5).

To conclude, we have presented new results for the energy-loss spectra of fast electrons reflected from the surface of a thin film and inelastically scattered by surface excitations. Using the appropriate dielectric data, we studied the loss spectra due to optical phonons in polar dielectrics and plasmons in metals. For a very thick crystal, the predicted loss spectra, including multiple losses, agree very well with recent experimental data. In this theory, one could also treat plasmon excitations in doped semiconductors or a combination of phonons and plasmons in polar semiconductors.

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