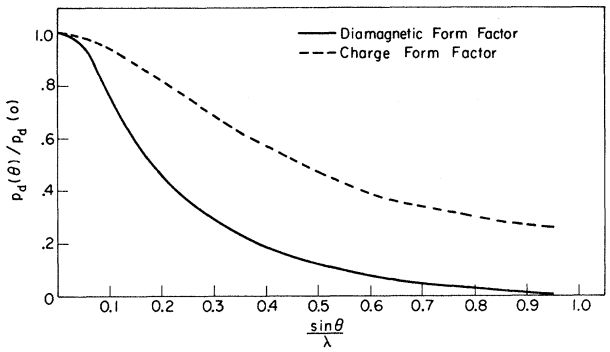

FIG. 1. Angular dependence of the calculated diamagnetic scattering amplitude of Cu compared with that of its atomic charge form factor.

litudes of this size would be very difficult to separate from the nuclear scattering amplitude (10^{-12}-10^{-13} cm/atom) in an unpolarized neutron experiment. However, with the high sensitivity of present day polarized-neutron beam techniques[5,7] and with the availability of superconducting-magnet field strengths, it becomes entirely feasible to study quantitatively the diamagnetic scattering. Such studies are presently in progress in this laboratory on metallic bismuth, a classic diamagnetic material.

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OPTICAL SURFACE PHONONS IN ZINC OXIDE DETECTED BY SLOW-ELECTRON SPECTROSCOPY

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Scattering of electrons from surfaces of ZnO single crystals has been studied in ultrahigh vacuum with a high-resolution electron-impact spectrometer ($\Delta E < 20$ meV, impact energy $E_0 = 1$-100 eV). The energy-loss spectrum in specular reflection shows a series of equally spaced loss peaks. The characteristic loss energies [68.8 meV for the $(1\bar{1}00)$ surface and 67.3 meV for the (0001) and the $(000\bar{1})$ surfaces] agree with the energies of optical surface phonons determined by the condition $\mathrm{Re}\epsilon_n(\omega) = -1$.

In the direction perpendicular to the surface of a crystal the translational symmetry is broken. The corresponding wave vector component of a vibration state may become complex and a localized state, a surface phonon, may occur.[1] Dispersion relations of surface phonons have been calculated in some simple models.[2-4] However, no experimental technique has been so far available to study surface phonons on surfaces in the required clean and well-defined state.

Recent progress in monochromatizing low-energy electrons now offers a possibility to investigate clean surfaces with an electron-impact spectrometer. The essential parts of the spectrometer in this work are taken from Ehrhardt et al.[5] The impact energy E_0 is variable between 1 and 100 eV. The optimum resolution was 12 meV. In order to obtain a higher intensity a standard resolution of 20 meV (see Fig. 1) was used in the present experiments.

Figure 1 represents a typical energy-loss spectrum obtained from a ZnO crystal (wurtzite) in specular reflection. The surfaces are prepared by cleaving the crystal in air and heating for 10 min to 300°C in an ultrahigh vacuum of 2×10^{-10} Torr.

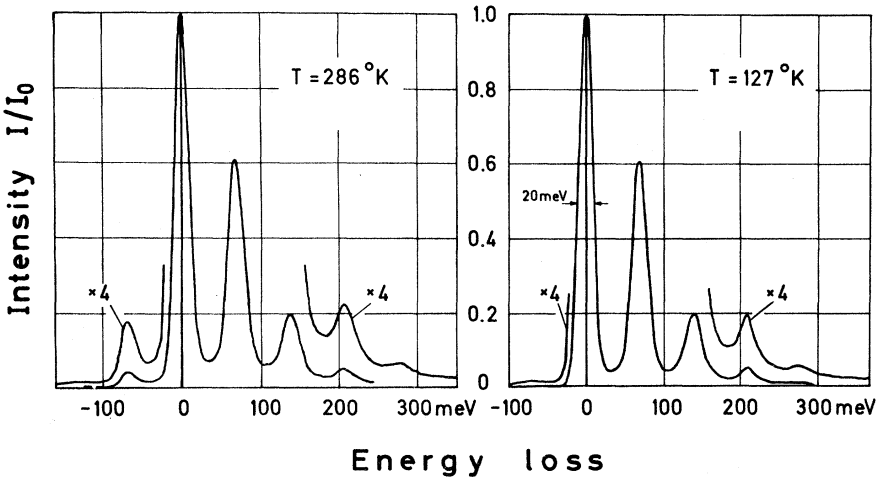

FIG. 1. Energy-loss spectrum of 7.5-eV electrons after specular reflection from the $(1\bar{1}00)$ surface of a ZnO crystal (recorder trace). The angle of incidence is approximately 45°.

The equally spaced energy losses are somewhat different for the $(1\bar{1}00)$ and the $\{0001\}$ surfaces and independent of the impact energy (E_0 = 1-100 V). The relative intensities of the energy loss peaks are equal for the different surfaces and become smaller with increasing impact energy. The half-widths of the 207-meV loss and the 69-meV loss agree within ±0.5 meV. If the crystal is turned out of the reflecting position the intensity of both the elastically and inelastically scattered electrons disappears with an angular half-width of approximately ±1°, which is supposed to be the angular resolution of the spectrometer. The energy-gain peak on the left side of Fig. 1 is related to the corresponding energy-loss peak on the right side by the Boltzmann factor $\exp(-\hbar\omega/kT)$.

The results can be interpreted as multiple excitations of phonons. From the angular distribution the wavelength of the phonons can be estimated to be greater than $20a$, where a is the lattice constant.

The experimental frequencies are close to those of the longitudinal optical bulk modes. However the two values are well separated by experimental accuracy (Table I).

It is well known that the long-range part of the electric field and displacement connected with infrared active optical bulk phonons can be treated in a continuum approximation which leads to a condition for the real part of the dielectric constant, namely $\mathrm{Re}\epsilon(\omega) = 0$. It has been noted by Ritchie[6] and Stern and Ferrell[7] that the corresponding condition for a surface phonon is $\mathrm{Re}\epsilon_n(\omega) = -1$ in the case of a semi-infinite crystal. $\epsilon_n(\omega)$ is the component of the dielectric tensor normal to the surface. Since $\epsilon(\omega)$ is known from infrared measurements,[8] the energies of the surface phonons are easily calculated and agree very well with the present results (Table I). Therefore it is concluded that the observed inelastic processes are due to scattering from surface phonons.

The intensity distribution of the multiphonon losses for low temperatures can be explained in a simple way: The intensity of the n-phonon

Table I. Experimental energy losses $\hbar\omega$ in meV for three different crystal faces. The displacements of the ions in the infrared-active optical bulk modes $\hbar\omega^{TO}$ and $\hbar\omega^{LO}$ are perpendicular to the surfaces. The surface phonons (energy $\hbar\omega^{S}$) are travelling parallel to the surfaces. The difference in the energies for the prism surfaces $(1\bar{1}00)$ and the polar surfaces (0001) and $(000\bar{1})$ arises from the anisotropy of the dielectric tensor.

Surface	$\hbar\omega$ This work	$\hbar\omega^{TO}$ Infrared reflection	$\hbar\omega^{LO}$ Infrared reflection	$\hbar\omega^{S}$ Calc. from $\mathrm{Re}\epsilon(\omega) = -1$
$(1\bar{1}00)$	68.8 ±0.5	50.3	73.1	69.0
(0001), $(000\bar{1})$	67.5 ±0.5	46.8	71.5	67.3

loss is proportional to the transition probability of the lattice oscillator from the ground state to the nth excited state. In the long-wavelength optical surface phonon, neighboring positive (Zn) and negative (O) ions vibrate in opposite phase. The passing electron acts as a time-dependent perturbation. In a first order approximation the perturbation force $K(t)$ is independent of the oscillator amplitude. In this case the transition probabilities set up a Poisson distribution[9]:

$$W_{0\to n}=\frac{1}{n!}|G(\infty)|^{2n}e^{-|G(\infty)|^2}, \tag{1}$$

$$G(\infty)=\frac{i}{(2m\hbar\omega)^{1/2}}\int_0^\infty e^{i\omega t}K(t)dt. \tag{2}$$

As shown in Fig. 2 the result is in agreement with the experiment. The interaction of the incident electron with optical phonons of the frequency ω can be treated by continuum approximation if

$$v \gg \omega a, \tag{3}$$

with v the electron velocity and a the lattice constant.[10] Then the total scattering probability for excitation of surface phonons for normal incidence is

$$W(\hbar\omega)d(\hbar\omega)=\frac{4}{a_0k_0}\,\mathrm{Im}\left(\frac{-1}{\epsilon+1}\right)\frac{d(\hbar\omega)}{\hbar\omega}, \tag{4}$$

with a_0 the Bohr radius, k_0 the wave vector of the incident electron.[11] Since phonons of long wavelength are excited, the intensity is concentrated on small scattering angles (80% within $\delta\theta_E$; $\theta_E=\hbar\omega/2E_0$). Condition (3) is fulfilled even for 1-eV electrons. Since the spectrometer integrates over a scattering angle of $\approx 6\theta_E$, the scattering probability according to Eq. (4) may be compared with the experimental results. The k_0^{-1} dependence is in excellent agreement with the experimental one-phonon excitation probability (to be published). The calculated value of $\int W(\hbar\omega)d(\hbar\omega)$ agrees within a factor of 2.

However, the situation in the reported experiments is more complex than the conditions to which Eq. (4) refers. First, the probability of phonon excitation is not small. Second, Fig. 1 represents an energetic fine structure of a reflected and not a penetrating beam as is assumed in Eq. (4). The same loss spectrum with a somewhat different intensity distribution has been obtained with the I_{10} and I_{20} reflection at the $(1\bar{1}00)$ surface. An extension of the dielectric scattering theory to this case still has to be developed.

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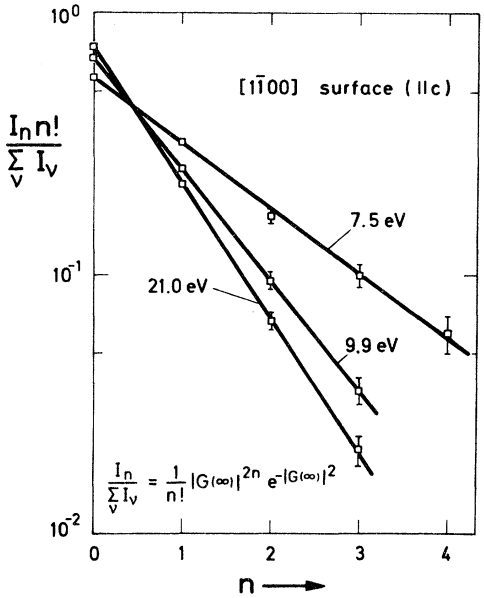

FIG. 2. Probability of n-phonon excitation multiplied with $n!$ vs n for three different impact energies. The intensities I_n are taken from the energy-loss spectra (Fig. 1). A continuous background has been subtracted. The error bars mainly result from the uncertainty in the determination of the background.

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