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Infrared optical constants of insulators determined by high-resolution electron-energy-loss spectroscopy

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High-resolution electron-energy-loss spectroscopy can be applied to insulators by use of an auxiliary electron gun. Fuchs-Kliewer phonons of the MgO(001) surface were recorded with excellent resolution (27 cm^{-1}). Specular intensities were analyzed for angles of incidence from 40° to 85°. Data processing by use of the dielectric-function theory yields optical constants as accurate as by IR spectroscopy: resonance frequency $\omega_{\mathrm{TO}} = 393 \pm 2\ \mathrm{cm}^{-1}$; damping $\gamma = 35 \pm 2\ \mathrm{cm}^{-1}$, and Szigeti charge $e^* = (0.83 \pm 0.07)e$.

In this Rapid Communication we report the first high-resolution (< 3.5 meV) electron-energy-loss spectroscopy (HREELS) measurements at room temperature on a thick insulating material, with a special experimental setup to eliminate the charging effects.

It has been demonstrated[1] that even small concentrations of free carriers facilitate the use of HREELS. On the other hand, this induces broadening effects due to the creation of low-energy surface plasmons and thus lowers the resolution. Consequently, one could expect to obtain the best resolution on highly insulating materials, such as MgO which has a wide optical gap of 8 eV.[2] An excellent resolution should also make possible an accurate quantitative analysis.

HREELS spectra of ionic materials exhibit strong features related to the excitation of surface optical phonons, usually called Fuchs-Kliewer phonons. The oscillations of the two ionic sublattices produce around the surface a long-range electric field that extends into the vacuum and into the bulk and couples to the electric field of the incoming probing electron. The properties of Fuchs-Kliewer phonons are mainly determined by bulk parameters, e.g., the transverse optical phonon frequency (ω_{TO}).

Fuchs-Kliewer phonons were evidenced with HREELS on ZnO by the pioneering work of Ibach.[3] Simultaneously to this measurement, a comprehensive theory of surface excitations in solids by "fast" electrons was developed by Lucas and Šunjić[4] and has been successfully applied to ZnO. Other measurements have been reported since on compound semiconductors GaAs,[1] InSb, and GaP[5] and also on $\mathrm{TiO_2}$,[6] $\mathrm{SrTiO_3}$,[7] and LiF.[8] All these measurements were performed with rather low resolutions (around 80 cm^{-1} or more) due to the presence of free electrons. Therefore no attempts could be made up to now to determine accurately optical constants by means of the existing theory.

The samples were MgO single crystals (99.999% purity) from Spicer Ltd. They were cleaved in air along the (001) surface before introduction in the analysis chamber. Cleavage produced a flat surface of good quality with a relatively low number of macroscopic steps. *In situ* cleaning involved only annealing up to 900 K. The measurements were performed with a spectrometer (RIBER) consisting of two 180°-hemispherical electrostatic condensors used, respectively, as monochromator and analyzer. In order to eliminate the charging effect, an auxiliary electron gun was installed which delivered on the sample an unfocused electron beam within the plane of incidence. This beam makes a fixed angle of 45° with the primary low-energy beam and is always closer to the surface normal. Typical parameters of this second beam were 2.8-keV incident energy and 1-μA emission current.[9] Within the range of energy losses scanned (0–8000 cm^{-1}) the only negative influence of the second gun was the creation of a linear, nearly constant background which could be easily subtracted for data analysis.

Figure 1 shows a result obtained at room temperature with an angle of incidence and analysis of 45°. The beam energy indicated (6.1 eV) was measured by scanning the energy range up to the cutoff of the loss spectrum. Up to seven loss peaks and two gain peaks were detected at an angle of incidence of 80°. This allowed the accurate determination of the phonon resonance frequency from the distance between the successive multiple losses. The resulting value is $651 \pm 2\ \mathrm{cm}^{-1}$. This coincides, within less than 0.2%, with the surface-phonon frequency calculated from the relation:

$$\omega_s^2 = \omega_{\mathrm{TO}}^2[\epsilon(0)+1]/[\epsilon(\infty)+1] \ ,$$

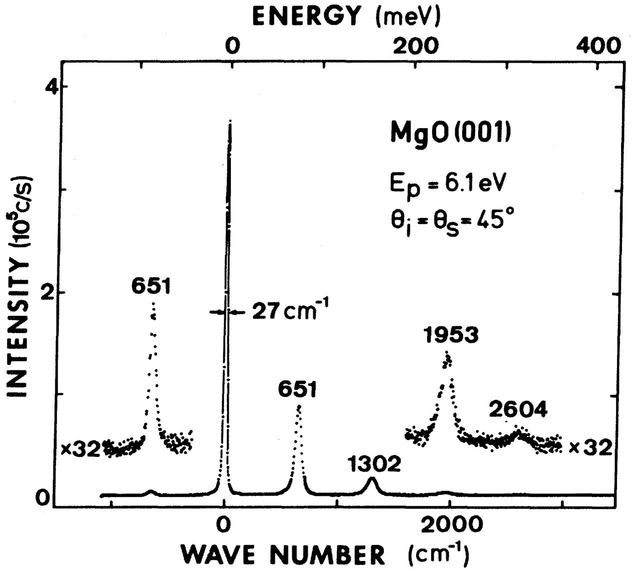

FIG. 1. Energy-loss spectrum of 6.1-eV electrons after reflection on a MgO(001) surface.

where ω_{TO} is the frequency of the bulk transverse optical mode, 393 cm^{-1}; $\epsilon(0)=9.8$ and $\epsilon(\infty)=2.95$ are, respectively, the static and high-frequency dielectric constants.[10,11]

The width of the elastic peak reproduces nearly the minimal instrumental broadening achievable with our spectrometer. This is interpreted as indicating the absence of any coupling possibility for the incoming electrons other than the surface phonon excitation.

HREELS data were fitted by generating the surface loss function $1/\omega \,\mathrm{Im}\{-1/[\epsilon(\omega)+1]\}$, with

$$\epsilon(\omega)=\epsilon(\infty)+\frac{[\epsilon(0)-\epsilon(\infty)]\omega_{\mathrm{TO}}^2}{\omega_{\mathrm{TO}}^2-\omega^2-i\omega\gamma} ,$$

including damping γ. The whole spectrum of multiple losses and gains was then obtained by autocorrelating the loss function by use of the Fourier transform. Let $\tilde{f}$ be the Fourier transform of the loss function, then $\exp(Q\tilde{f})-1$ is the Fourier transform of the whole spectrum, where Q is the ratio of the single loss intensity to the elastic intensity I_1/I_0. The appropriate normalization conditions result from the conservation of the number of particles. Finally, the convolution with the instrument transfer function yields an excellent fit depending only on three parameters: the resonance frequency ω_s and the damping γ of the phonon as well as the ratio $Q=I_1/I_0$. The energy gains were obtained by multiplying the loss function with the Bose factor. Since on the scale of Fig. 1 no difference between fit and experiment can be seen the quality of the fit is visualized in Fig. 2 on an extended scale. Even smallest deviations in intensity, frequency, or damping can be detected. The values found for ω_s and γ are remarkably constant throughout the whole range of experimental conditions including variation of primary energy, angle of incidence or analysis, and the settings of the auxiliary gun. The resulting value of the damping γ is 35 ± 2 cm^{-1}. From the infrared data on MgO thin films[12] a value of 25 ± 5 cm^{-1} was extrapolated. The difference between these two values could be due to a supplementary deexcitation process in our samples perhaps connected to surface imperfections.

Specular measurements were performed at various angles of incidence from 40° to 85°. Lucas and Sunjic[4] have calculated the relative intensity $Q_{\mathrm{sp}}=I_1/I_0$ for surface phonons analyzed in the specular direction. They found

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

where

$$F(\alpha,\gamma)=\mathrm{Im}\ln\{\alpha+i+[(\alpha+i)^2-\gamma^2]^{1/2}\} ,$$

$$\omega_p^2=4\omega_{\mathrm{TO}}^2\frac{\epsilon(0)-\epsilon(\infty)}{[1+\epsilon(\infty)]^2} , \quad \alpha=\frac{\omega_s}{\theta_c k_0 v_\perp} ,$$

$$\gamma=\frac{v_\perp}{v_\parallel}=\tan\theta .$$

θ_c is the half aperture of the spectrometer (1.2°), k_0, $v_\perp(v_\parallel)$ are, respectively, the wave vector and the normal (parallel) component of the velocity of the impinging electron.

We have reproduced this calculation for the case of MgO and the results are given in Fig. 3 (solid curve A), together with the experimental values of Q obtained from the fit described above. General agreement is found between the theoretical and experimental values, but there are systematic deviations at low and high angles of incidence. Corrections that may be applied are due to two distinct effects. First the influence of the image force between the electron and the surface ultimately limits the divergence of the cross section at grazing incidence. This effect has been treated theoretically for metal surfaces only.[13] Nevertheless, the same correction was applied to the present case. Since $\epsilon(\infty)$ of MgO has the rather large value of 2.95, it is supposed that this correction is not strongly overestimated. This correction changes the theoretical curve especially at high angles of incidence where it exhibits now the same general shape as the experimental data. Anyway, there remains a small

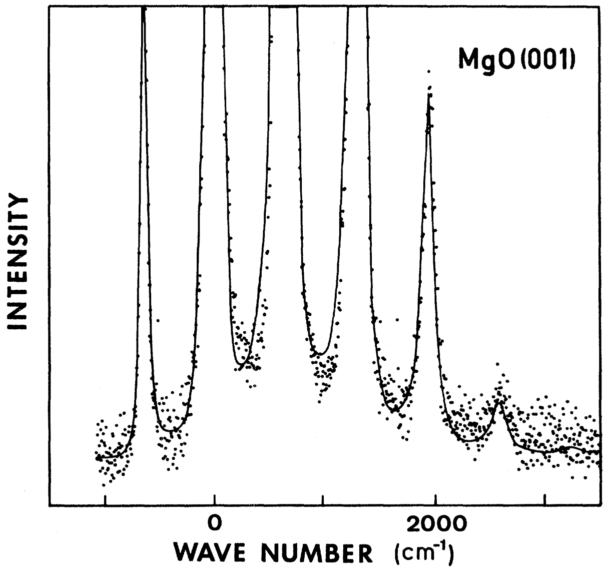

FIG. 2. Energy-loss spectrum of Fig. 1 on an extended scale. The fit explained in the text is superposed.

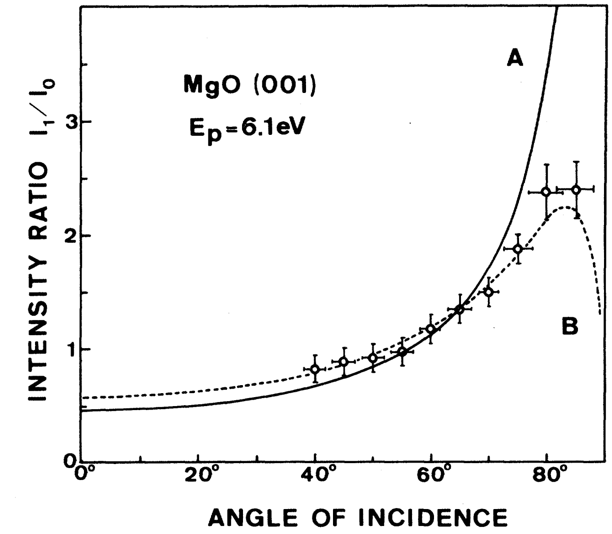

FIG. 3. Specular intensity ratio I_1/I_0 obtained for different angles of incidence. Solid curve A: calculation after Ref. 4. Dashed curve B: same as A with corrections for image force and spectrometer aperture changes.

discrepancy, which appears as an upward shift for the measured values compared with the theoretical ones. This shift can be achieved by applying a second correction. It may be explained as an instrumental effect related to work function differences between sample and spectrometer optics. This results in a dependence of the analyzer aperture on primary energy.[14] A change from a geometrical aperture of 1.2° to an effective one of 1.8° is enough to obtain a good agreement with the data for MgO. Exactly the same value (1.8°) was found to be necessary for Al_2O_3 (Ref. 15) in the same conditions. This confirms our interpretation in terms of an electron optical effect. Both corrections have been included in the dashed curve B displayed in Fig. 3. The influence of the aperture correction can be easily seen at 0° where it is the only one that applies; the image force effect being most pronounced at 80°.

When going towards normal incidence, the ratio I_1/I_0 can be described in the first Born approximation with a formula deduced from the calculations of Evans and Mills:[16]

$$\frac{I_1}{I_0}=\frac{S}{|R|^2}=\frac{4Ne^{*2}}{9\pi\epsilon_0 a_0\mu\omega_s^2 k_0\cos\theta}\left|\frac{\epsilon(\infty)+2}{\epsilon(\infty)+1}\right|^2 \times[n_s(\hbar\omega_s)+1]B(\hat{\psi}_c,\theta) \ .$$

N is the atomic density and μ is the reduced mass of the material, a_0 is the Bohr radius, k_0 is the wave vector of the incident electron, n_s is the Bose-Einstein distribution, and $B(\hat{\psi}_c,\theta)$ is a function of the incidence energy of the angle of incidence (θ) and the angle of acceptance of the spectrometer. e^* is the Szigeti charge that takes account of the ionic as well as the electronic polarizations. By using the values for the lowest angle of incidence (40°) we find $e^*=(0.83\pm0.07)e$ for a spectrometer aperture of 1.8°, which is in agreement with infrared data giving $e^*=0.84e$.

In this Rapid Communication, we have demonstrated the possibility to carry out HREELS on thick insulators. Furthermore, we were able to show that surface optical phonons of an isotropic crystal are described quantitatively by the established dielectric function theory. For MgO the only free variables for the data processing were found to be phonon frequency, damping, and oscillator strength. These parameters could be determined with a high accuracy, well comparable to that of infrared spectroscopy. Therefore we suggest that this provides room for two theoretical improvements. First, image forces must be taken into account on insulating and semiconducting samples. Second the demonstrated high resolution is able to resolve even slight anisotropic effects in dielectric crystals. Actually, the available theories are restricted to the case where the dielectric function is a scalar and describes accurately only isotropic material. With this improvement HREELS will be able to determine optical constants accurately and independently of infrared spectroscopy for any dielectric material.

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