Energy losses of fast electrons at crystal surfaces

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The energy-loss spectra observed when an electron beam of energy 100 keV and diameter 1–2 nm traverses the face of a small crystal show features which are different from those observed for transmission through thin films. For magnesium oxide smoke crystals having dimensions of 100–700 nm the most prominent features are strong peaks at energy losses of about 17 eV and oscillations in the energy-loss curves with periodicities of 2–5 eV, depending on the crystal dimensions. These features are attributed to energy losses associated with the emission of radiation as the electrons are channeled along the surface with an oscillatory motion and enter and leave the crystal surface region.

It has been predicted that surface excitations should be detected readily using electron energy-loss spectroscopy (EELS) with an incident beam of energy 20–100 keV making a small angle with a crystal surface but the number of useful results obtained in this way has been limited.[1]

Recently we have used a dedicated scanning transmission electron microscopy (STEM) instrument with a two-dimensional detector system to produce electron beams of relatively high intensity, which have diameters as small as 0.5 nm at the specimen position,[2] and have studied the interaction of such fine electron beams with crystal surfaces in some detail.[3] Diffraction patterns and EELS spectra have been observed as an electron beam of diameter about 1.5 nm directed parallel to the flat face of a small crystal of MgO smoke is moved closer to the crystal in steps of 0.1 nm or less. These data features have not been previously reported.

From analysis of the microdiffraction patterns,[4] we deduce the following behavior of the beam (see Fig. 1). If the beam runs parallel to the crystal face and less than 2–3 nm from it, it will be deflected by the potential field of the crystal which extends into the vacuum. In the diffraction plane, a strong streak or flare forms on the central (undeflected) spot. When the incident beam is closer to the crystal it is bent so that it intersects the crystal face at, or near, the Bragg angle for the crystal lattice planes parallel to the surface. Then if the Bragg angle is less than the critical angle for total internal reflection, the beam will be channeled along the surface, being alternately Bragg reflected out of the crystal and reflected back by the external potential field (see Fig. 1). At the far end of the crystal it forms two beams in directions of plus or minus the Bragg angle relative to the incident beam direction. The diffraction patterns also show a considerable amount of fine structure representing the diffraction effects introduced with a coherent convergent incident beam.[5]

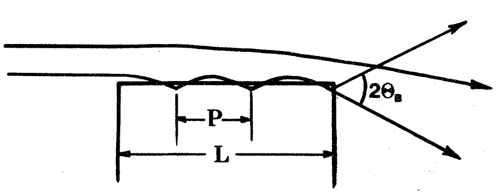

FIG. 1. Diagram illustrating the effect of the external potential field of a small crystal on the path of an electron beam incident parallel to one face. If the beam is sufficiently close to the crystal it will be deflected to enter the crystal at the Bragg angle θ_B for the crystal lattice planes and will be channeled along the surface, giving rise to incident and diffracted beams separated by $2\theta_B$.

The sets of EELS curves of Fig. 2 were given as the beam was moved successively closer to a crystal face. The sequence in which the curves appear is indicated in Fig. 2(b). With the beam 3–5 nm from the crystal, a tail on the zero-loss beam appears (curves 1 and 2). Over a range of 2–3 nm, the curves show strong maxima in the 10–20-eV loss range (curve 3). Some of these curves show near-sinusoidal oscillations having periodicities of 2–5 eV, depending on the length of the beam path along the crystal face. Finally, as most of the incident beam is transmitted through the crystal, the energy-loss spectrum is similar to that for transmission through a thin film[6,7] (curve 4) with maxima at about 20.5 eV (the bulk-plasmon loss) and around 12 eV (attributed to a surface plasmon or interband transition).

The well-defined cubic shapes of MgO smoke crystals allow the geometry of the experiment and the length of the beam paths along the crystal face, L, to be deduced with reasonable (10%) accuracy from STEM images. The period of the oscillations visible in some of the curves is, to a good approximation, inversely proportional to L (see Table I).

The most prominent peak occurring in the spectra is at about 17 eV, independent of the beam path

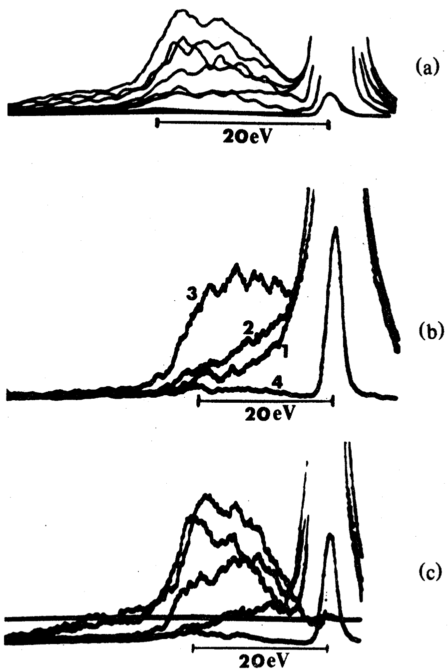

FIG. 2. Sets of energy-loss spectra obtained as an electron beam is moved successively closer to the face of an MgO smoke crystal. The numerals on (b) show the sequence in which the curves appear as the beam approaches the crystal (total translation about 3 nm). The crystal thickness in the beam direction is 350 nm for (a), 490 nm for (b), and 680 nm for (c), and the the characteristic oscillations on the curves have periodicities 4.3, 3.0, and 2.1 eV, respectively.

length. Another weaker peak at 12–13 eV may be due to an enhancement of the 12-eV peak observed in transmission experiments and attributed to a surface excitation. The bulk-plasmon peak at 20.5 eV is usually not visible in the curves showing the strong 17- and 12-eV losses.

From sets of curves obtained with known increments of amplifier gain, it is estimated that the intensity of the energy losses around 17 eV may be about 10^{-3} of that of the incident electron beam. The amplitude of the oscillatory parts of the curves is therefore about 10^{-4} of the incident beam intensity. It is difficult to make more accurate estimates of these relative intensities which vary strongly with movements of only 0.1 to 0.2 nm of the incident beam position.

An interpretation of these observations has been made in terms of energy losses due to the emission of radiation generated by the interaction of the electron beam with the crystal surface. This interaction may be separated into two parts which have their principal components at right angles. Firstly, the electron enters and leaves the crystal field at points separated by the path length of the beam across the crystal face, giving rise to the path-length-dependent oscillatory components of the EELS curves. Secondly, the near-sinusoidal motion of the electron as it is channeled along the surface (Fig. 1) gives a strong, single peak of energy loss independent of the beam path length.

The interaction of an electron with the surface may take several forms. The accelaration of the electron in the potential field will give rise to the equivalent of synchrotron radiation as in transmission electron microscopy experiments[8] or the channeling of fast charged particles in crystals.[9] Surface plasmons may be generated by electrons passing at distances of up to 5 nm from metal surfaces,[10] but for dielectrics it is probably more appropriate to consider the transition radiation generated when a fast charged particle enters or leaves a surface.[11,12] This transition radiation may be thought of as being due to the fluctuations in the electromagnetic field of the electron as it is modified by polarization of the dielectric. Its magnitude relative to the synchrotron radiation may be estimated on the basis of the simple picture of the annihilation of the image charge formed within the solid when the electron enters the solid surface,[11] i.e., the energy change depends on E_0, the incident energy, rather than V_1, the inner potential, which is a factor of 10^4 smaller.

Calculations of the transition radiation intensities have been made for transmission of a charged particle through a thin foil[13,14] but these are not directly relevant for our case. Because the calculations for the geometry of our experiments would be very

TABLE I. Values of the characteristic periodicity observed in energy-loss curves for MgO crystals.

Length L of path across crystal (nm)	ΔE calculated Eq. (4)	ΔE observed
250	5.0	7.0
280	4.5	5.0
350	3.6	4.3
490	2.6	3.0
680	1.8	2.1

cumbersome, we take advantage of the fact that, because the form and direction of the accelaration would be the same in both cases and strictly quantitative results are not required at this stage, we can make use of the relatively simple theory for the analogous case of the accelaration of the incident electron giving rise to synchrotron radiation. For this case we can apply the relation given in Jackson's book[15] for the radiation from a moving electron.

$$\frac{d^2I}{d\omega d\Omega}=\frac{e^2\omega^2}{4\Pi^2c}\left|\int_{-\infty}^{\infty}\vec{n}\times(\vec{n}\times\vec{\beta})\times\exp\left[i\omega\left(t-\frac{\vec{n}\cdot\vec{r}(t)}{c}\right)\right]dt\right|^2 \quad . (1)$$

For an electron of initial energy eE_0 which is accelerated as it enters the fringing field of a crystal (average potential $V_1 << E_0$) and decelerated as it leaves this field, we may write the velocity vector as

$$\vec{\beta}(t)=\beta_0\cdot\hat{x}+\gamma(t)\cdot\hat{x} \quad , \qquad (2)$$

where

$$\gamma(t)=\begin{cases}0 & \text{for } t<t_0 \text{ or } t>t_0+T\\ A_1 & \text{for } t_0<t<t_0+T \quad ,\end{cases}$$

with $T=L/\beta_0c$ and $A_1=(V_1/2E_0)\beta_0$. Assuming $A_1 << \beta_0$, the expression simplifies considerably to give the energy radiated at an angle α to the beam direction as

$$I(\alpha)=\frac{e^2\omega^2}{4\pi c}\beta_0^2\left[\sin^2\alpha\,\delta(\omega')+\frac{A_1^2\sin^2 2\alpha}{(1-\beta_0\cos\alpha)^2}\sin^2\frac{\omega' T}{2}\right] \quad , (3)$$

where $\omega'=\omega(1-\beta_0\cos\alpha)$.

The contribution to the energy loss therefore depends on α. For 100-keV electrons ($\beta_0=0.548$), the dominant contribution comes from a sharp maximum at $\alpha=35°$. Assuming all radiation to be at this angle, the $\sin^2$ term in the energy-loss spectrum should have a periodicity of 12.5 $\lambda\beta_0/cL$. The values for the periodicity calculated in this way are compared with the observed values in Table I. It is seen that the observed values are consistently 10–20% high, but the agreement must be considered as reasonably good in view of the uncertainties in the experimental measurements and the approximations of the theoretical treatment.

It may be assumed that for an electron entering or leaving the region of the edge of a crystal face, the intensity of radiation will be approximately half that for the transmission case if the electron path is very close to the crystal edge and will decrease with increasing distance. Since the general expression for the radiated intensity has the same form as (1), except that the Fourier transform is applied to the variation of the total electric field rather than to the variation of the electron velocity,[16] the form of the contribution to the energy-loss spectra due to transition radiation will be much the same as in (3), but the magnitude will be very much greater. Rough theoretical estimates suggest that the strength of the energy-loss peak should be 10^{-4} to 10^{-3} of the incident beam intensity.[17] This is consistent with the observation of a factor of 10^{-4} in our case.

The second component of the interaction of the electron beam with the surface comes from the oscillatory motion of the electron as it is channeled along the surface by Bragg reflection in the crystal, alternating with reflection from the external potential field. Again we may derive the form of the contribution to the energy-loss curve by considering the radiation due to the electron acceleration, but realize that the main contribution to the radiated energy will come from the very much stronger transition radiation generated as the polarization of the medium oscillates with the electron motion.

In Eq. (1) we insert the electron path vector

$$\vec{r}(t)=c\beta_0t\hat{x}+(A\cos\omega_1t)\hat{y} \quad . \qquad (4)$$

The intensity of the emitted radiation in time L/β_0c as a function of the angle α between the beam direction and the direction of observation is given for $A\omega/c << 1$, as

$$I(\alpha)=\frac{LA^2e^2\omega^2}{16\Pi\beta_0c^4}[\omega_1^2+(\beta_0\omega\sin^2\alpha-\omega_1\cos\alpha)^2]\times\delta(\omega(1-\beta_0\cos\alpha)-\omega_1) \quad . \qquad (5)$$

There is also a peak around $\omega=2\omega_1$, but for our case this is smaller by a factor of 10^{-2}.

Equation (5) gives a sharp peak in the energy-loss spectrum at about $\omega_1/(1-\beta_0)$. In terms of the spatial periodicity, P, of the oscillations of the electron beam this corresponds to an energy loss of 2.21 h $\omega_1=1.52\times10^3/P$ eV, for P in nm.

The periodicity P may be estimated very roughly by considering the average distance required for an electron to be diffracted out of a crystal plus the length of the trajectory of an electron in the external potential field (Fig. 1). The distance traveled in the crystal is put equal to half the extinction distance for an electron beam incident in the appropriate direction in the transmission case. This is equal to about 20 nm for the MgO (200) reflection in the systematics-only case, 8.7 nm for the [100] axial incidence[17] and 18 nm for the [110] axial incidence.[18] The length of the trajectory in the external potential field is strongly dependent on the form assumed for this field.

For metal surfaces a field of the form $\Phi(y)=A(y+a)^{-1}+B(y+b)^{-2}$ for $y>0$ has been used.[19] For convenience in integration, we previously[4] assumed this form with $\Phi=14$ eV for $y<0$ and $A=0$

which is incorrect for y large but reasonable if only small y values are involved as in the present case. For the (200) Bragg angle of 8.5×10^{-3} rad, and $b=0.3$ nm, which is consistent with the diffraction data, the length of the trajectory outside the crystal is 71 nm. Hence we may take $P=90$ nm, giving an energy-loss peak at 17 eV, which is in agreement with the observations.

The assumptions made in deriving this estimate of the energy-loss value are admittedly somewhat arbitrary so that the conclusion to be drawn is that the agreement with the observation is good to within 20–30%. One possible deduction is that the energy-loss value should depend to some extent on the azimuthal direction of the incident beam. Measurements on a number of crystals gave 16.8 eV for the [100] direction and 16.3 eV for the [110] direction. The difference is marginally significant since the probable error is estimated to be 0.5 eV in each case.

From Eq. (5) it may be estimated that the intensity of the energy-loss peak should be 10^{-6} to 10^{-5} of the incident beam intensity. The enhancement of the radiated intensity by a factor of 10^3 to 10^4 when the transition radiation mechanism is taken into account appears to be consistent with the available data.

We anticipate that further measurements on the microdiffraction patterns given by beams traversing the crystal surface will provide the more accurate data on the potential field needed to refine the calculations. On the experimental side it is desirable that better correlation should be achieved between the position of the beam relative to the surface plane and the form of the EELS curves.

Some observations on the surfaces of small NiO crystals show microdiffraction and EELS results similar in form but different in detail to those from MgO.[20]

ACKNOWLEDGMENTS

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