FAST COMMUNICATIONS

TEM image diffraction contrast arising from electrons exciting inner atomic shells

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It has been shown by direct experiments that, for fast electrons inelastically scattered in a crystal by the inner shells of native and non-ordered impurity atoms, the dynamic diffraction effects typical of elastic scattering are retained. A theoretical approach for finding the wave function of an electron having inner-shell losses of energy has been proposed. For small losses (when the characteristic scattering angle is much smaller than the Bragg angle), a formula for the intensity at the specimen exit surface explaining the experimental results has been derived.

Investigation of inelastic interactions between a high-energy electron beam and a substance is of interest since scattering accompanied by characteristic losses of energy is widely used in analytical electron microscopy for determining the composition of specimens. In the study of crystals, an important role belongs to the dynamic diffraction of electrons by the periodic lattice potential, which occurs both before and after the interaction. The phenomenon, as a rule, is neglected in the conventional method of electron energy loss spectroscopy, EELS (Egerton, 1986). To improve the precision of quantitative microanalysis, Rossouw & Whelan (1980) recommend the specimen is orientated far from the Bragg condition, which reduces the effect of dynamic diffraction on the intensity to be measured. The diffraction contrast, however, is weakened too, which makes it more difficult to observe the structure irregularities. At the same time, it is the connection between the local variations of chemical composition and the structure irregularities that is the aim of many investigations using methods of analytical electron microscopy.

In the papers where experiments with electrons exciting inner atomic shells are described (*e.g.* Craven, Gibson, Howie & Spalding, 1978; Rossouw & Whelan, 1980), the conclusion was reached that the diffraction contrast is retained for such electrons when the losses are small. Nevertheless, many problems remain open, *e.g.* the

effect of the crystal thickness on the relation between the intensities of elastically and inelastically scattered electrons is not yet determined. Another important question for microanalysis is the behaviour of electrons that have excited impurity atoms randomly located in the crystal matrix lattice. In the present work, direct experiments offering answers to the above questions are made.

Experimental investigations were carried out using a Philips CM30 electron microscope, with accelerating voltage 300 kV, and a Gatan 607 EELS spectrometer. The image obtained with electrons that passed through the specimen was scanned by the deflection system over the entrance aperture of the spectrometer. The signal being registered was accumulated and then displayed on the screen of the computer of the analytical system LINK AN 10000/85 as an intensity profile.

Our investigations used specimens of two types: single-crystal silicon and the alloy $Fe_{0.72}Cr_{0.24}Ni_{0.04}$, which is a disordered replacement solution of Cr and Ni atoms in the b.c.c. lattice of Fe. The specimen was oriented under strong two-beam conditions in such a way that non-systematic reflections should be weakly excited. In the bright- and dark-field images of the wedge-shaped specimen, one could observe thickness extinction fringes. The incident beam was practically parallel.

Fig. 1 shows the energy-filtered intensity profiles for the Si specimen. Filtering was made in the region of zero loss and in the vicinity of the L edge of the spectrum, which for silicon is 100 eV. It can be seen that, for inelastically scattered electrons, the intensity oscillations on the thickness fringes persist (Figs. 1*b*, *c*) and after transition through the L edge their amplitudes substantially increase. Secondly, the positions of maxima and minima at L losses (Fig. 1*c*) coincide with those in the case of elastic scattering (Fig. 1*a*). Thirdly, when the specimen thickness is increased, the behaviour of inelastically scattered electrons depends on the scattering mechanism. In the case of the multiple plasmon scattering

(Fig. 1b), the intensity oscillations of the monolations, (Fig. amplitudes on the background of inner-shell losses (Fig. creasing constant component. For inner-shell losses (Fig. 1c) when the thickness is increasing, the oscillation an-plitudes first increase reaching a maximum, then decrease, approximately repeating the curve behaviour for elastic scattering.

In Fig. 2, the results of similar investigations for the alloy $Fe_{0.72}Co_{0.24}Ni_{0.04}$ are given. Filtering was made in the region of zero loss and in the vicinity of the L edge of Cr, which is 574 eV. One can see that the behaviour of the intensity profiles is the same as in the Si specimens, although the atoms of Cr are substitutional atoms that are randomly located in the lattice of Fe. Filtering in the vicinity of the L edge of Fe (706 eV) gave similar results.

That the diffraction contrast is retained for electrons exciting plasmons is a well known fact (e.g. Howie, 1963; Rossouw & Whelan, 1981) and it can be accounted for by the long-range interaction potential, which results mainly in the intrabranch transitions for Bloch waves. Increase in the oscillation amplitudes on transition through the L edge indicates unambiguously that intrabranch tran-sitions dominate even when the inner shells of both native and impurity atoms are excited. The experimental result obtained confirms the conclusions made in earlier studies that the diffraction contrast when electrons are inelastically scattered by the native atoms is retained and that the same is true when non-ordered impurity atoms are excited.

For a theoretical description of inelastic scattering of fast electrons, different approaches have been used. Some authors (e.g. Humphreys & Whelan, 1969; Okamoto, 1984; Maslen & Rossouw, 1987; Maslen & Whelan, 1969; Ishinokawa & Ohtsuki, 1988) applied a tight-binding model to describe the wave functions of the inner-shell electrons. On the other hand, Chukhovskii, Alexanjan & Dudarev & Ryazanov, 1987), Maslen (1987) and Pinsker (1973), Saldin & Rez (1987), used wave functions of an Weickenmeier & Kohl (1989) and derived an expression isolated atom for this purpose and derived an expression for the differential scattering cross section for the crystal.

From our point of view, the second approach describes inelastic scattering with inner-shell losses of energy more adequately. The expediency of choosing wave functions of an isolated atom for the initial state of an electron of the inner shell is conditioned by its strong localization near the nucleus. In the final state, the ejected electron can be thought of as moving in the averaged potential field of the crystal, while its wave function can be treated as a superposition of the atom wave functions. Hence, scattering with inner-shell energy losses by other individual atom is not connected with scattering by each atoms and the interaction Hamiltonian depends only individual atom is not connected with scattering by other atoms and the coordinates of a fast electron and the electron Similarly, this approach is...of both native
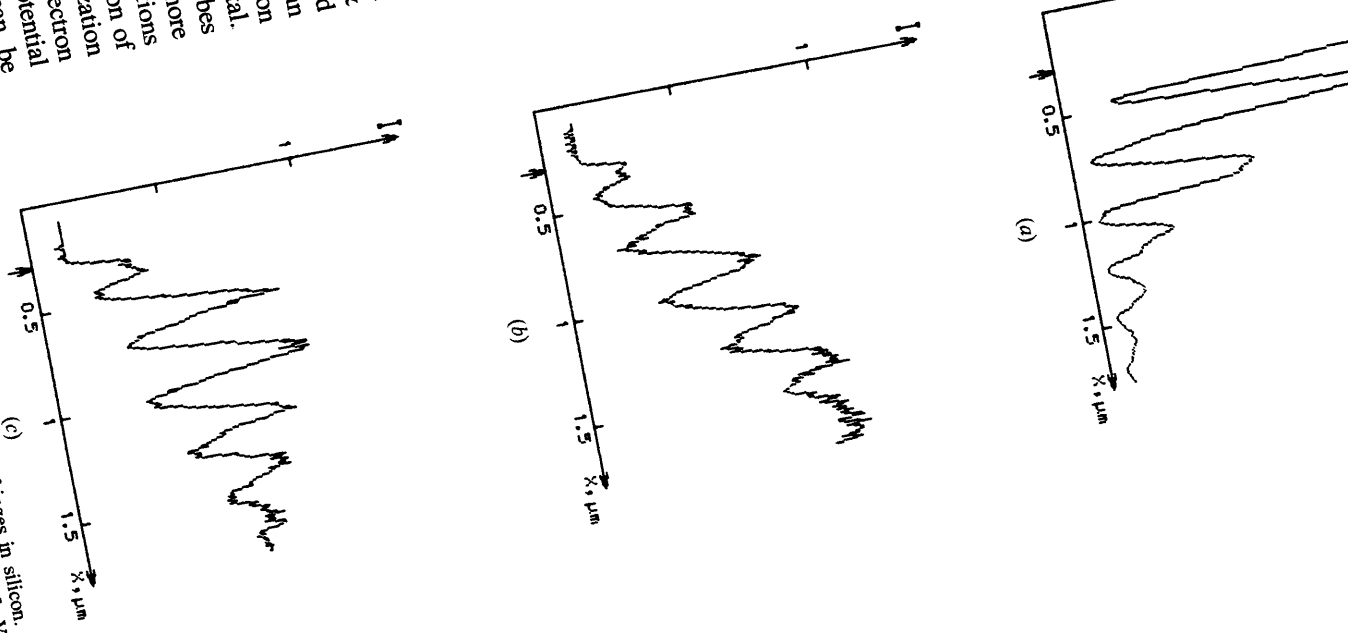

Fig. 1. Intensity profiles of the thickness fringes in silicon. Reflection 220, bright field, the width of the 'energy window' is 5 eV, its centre being localized at the following points of the spectrum: (a) 0 eV, (b) 90 eV, (c) 125 eV. The intensity was measured in arbitrary units, x is the distance measured perpendicular to the edge (shown by the arrow) of the wedge-shaped specimen. The curve in (a) is contracted along the vertical by a factor of 1000.
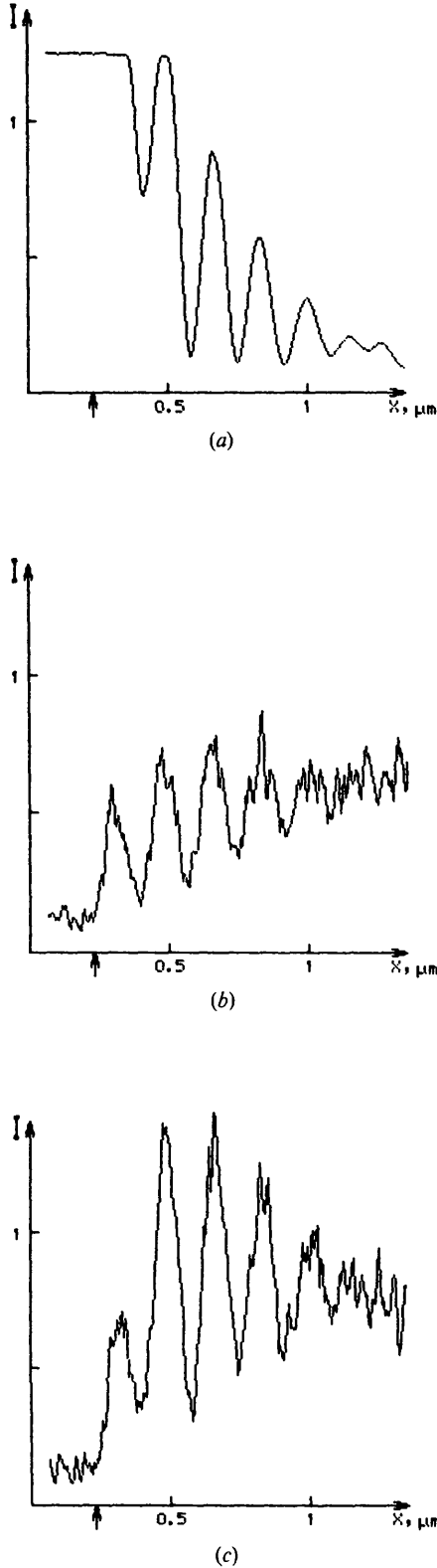
(a)

(b)

(c)

Fig. 2. Intensity profiles for the alloy $Fe_{0.72}Cr_{0.24}Ni_{0.04}$. Reflection 110, the centre of the 'energy window', 10 eV wide, was positioned at points (a) 0 eV, (b) 564 eV, (c) 582 eV. Other details are the same as in Fig. 1.

fast-electron wave function and the intensity distribution at the exit surface of the crystal.

Generalizing the treatment of Yoshioka (1957), we write the Hamiltonian of a system consisting of a fast electron and a crystal that may contain impurity atoms in the following way:

$$\hat{\mathcal{H}} = \left(-\hbar^2/8\pi^2 m\right)\nabla^2 + \hat{S}(-\mathbf{r}_{c1}, \ldots, \mathbf{r}_{cN})$$
$$+ \hat{S}'(\mathbf{r}, \mathbf{r}_{c1}, \ldots, \mathbf{r}_{cN})$$
$$+ \sum_i \hat{H}_i(\mathbf{r}_i) + \sum_i \hat{H}'_i(\mathbf{r}, \mathbf{r}_i), \tag{1}$$

where $\left(-\hbar^2/8\pi^2 m\right)\nabla^2$ is the operator of the incident electron kinetic energy, $\hat{S}(\mathbf{r}_{c1}, \ldots, \mathbf{r}_{cN})$ is the crystal Hamiltonian that describes the behaviour of the lattice atoms and of the valence electrons with coordinates $\mathbf{r}_{c1}, \ldots, \mathbf{r}_{cN}$, $\hat{S}'(\mathbf{r}, \mathbf{r}_{c1}, \ldots, \mathbf{r}_{cN})$ is the operator of the fast-electron–crystal interaction resulting in collective excitations such as plasmons and phonons, $\mathbf{r}$ is the coordinate of the fast electron, $\hat{H}_i(\mathbf{r}_i)$ is the Hamiltonian of the inner-shell electron to be excited, which belongs to the ith atom and has a coordinate $\mathbf{r}_i$, $\hat{H}'_i(\mathbf{r}, \mathbf{r}_i)$ describes the interaction with an atom electron. The index i numbers the crystal atoms, while at $i{=}s_A$, $i{=}s_B, \ldots$ the corresponding values are related to the atom types $A, B, \ldots$.

Now, expand the system wave function Φ in terms of the eigenfunctions a_m and u_{n_i} of operators $\hat{S}$ and $\hat{H}_i$

$$\Phi(\mathbf{r}, \mathbf{r}_{c1}, \ldots, \mathbf{r}_{cN}, \mathbf{r}_1, \ldots, \mathbf{r}_M)$$
$$= \sum_{mn_1\ldots n_M} \Psi_{mn_1\ldots n_M}(\mathbf{r}) a_m(\mathbf{r}_{c1}, \ldots, \mathbf{r}_{cN})$$
$$\times u_{n_1}(\mathbf{r}_1)\ldots u_{n_M}(\mathbf{r}_M), \tag{2}$$

where $\Psi_{mn_1\ldots n_M}(\mathbf{r})$ is the fast-electron wave function corresponding to the transition of the crystal from the zero state to the m state and to the transitions of M core electrons to the n_1, n_2, $\ldots$, n_M states.

Substituting (1) and (2) into Shrödinger's equation and using the orthogonality properties of eigenfunctions, after transformations, we get a system consisting of equations of the type

$$\left[\left(\hbar^2/8\pi^2 m\right)\nabla^2 - V(\mathbf{r}) + E_{fl_1\ldots l_M}\right]\Psi_{fl_1\ldots l_M}(\mathbf{r})$$
$$= \sum_{m\neq f} S_{fm}(\mathbf{r})\Psi_{ml_1\ldots l_M}(\mathbf{r})$$
$$+ \sum_i \sum_{n_i\neq l_i} H_{l_i n_i}(\mathbf{r})\Psi_{fl_1\ldots n_i\ldots l_M}(\mathbf{r}), \tag{3}$$

where $E_{fl_1\ldots l_M}$ is the energy of an electron incident on the crystal minus losses produced by the corresponding excitations and $V(\mathbf{r})$ is the average potential energy of the electron in the crystal; $S_{fm}(\mathbf{r})$ and $H_{l_i n_i}(\mathbf{r})$ are the matrix elements of operators $\hat{S}'$ and $\hat{H}'_i(\mathbf{r}, \mathbf{r}_i)$.

The intensity of fast electrons at the exit surface of the crystal has the form

$$I(\mathbf{r}) = \int \Phi\Phi^* \, d\mathbf{r}_{c1}\ldots d\mathbf{r}_{cN} d\mathbf{r}_1\ldots d\mathbf{r}_M$$
$$= \sum_{mn_1\ldots n_M} |\Psi_{mn_1\ldots n_M}(\mathbf{r})|^2. \tag{4}$$

The intensity within some interval of energy losses is defined by the sum of the terms that correspond to the system excitations resulting in those losses.

To calculate the inelastic intensity with an energy loss ΔE_v and the transition of an electron of the inner shell to the state $l_i = v$, let us select from (3) an equation describing such an interaction at the ith centre. Taking into account the other processes of inelastic scattering of a fast electron during its movement in the crystal at a distance from the ith centre can be done by introducing a complex increment to the potential energy $V(\mathbf{r})$. To solve the chosen equation, we present the wave function of a fast electron as a superposition of Bloch-wave packages (Borgardt, 1991, 1993)

$$\Psi_{0\ldots l_i\ldots 0}(\mathbf{r}) = \sum_j \sum_g \int \psi^{(j)}_{0\ldots l_i\ldots 0}(z,\mathbf{p}) C^{(j)}_g(\mathbf{p})$$

$$\times \exp\left[2\pi i \mathbf{k}^{(j)}_0 \cdot \mathbf{r}\right] \exp\left(2\pi i \mathbf{g} \cdot \mathbf{r}\right) d\mathbf{p}, \qquad (5)$$

where $\psi^{(j)}_{0\ldots l_i\ldots 0}(z,\mathbf{p})$ is the excitation amplitude of the jth Bloch wave with scattering by the ith centre; $C^{(j)}_g(\mathbf{p})$ and $\mathbf{k}^{(j)}_0$ are the Fourier coefficient of the jth Bloch-wave expansion and the wave vector with components $[p_x, p_y, k^{(j)}_{0z}(\mathbf{p})]$ for an electron with the energy of $E_{0\ldots l_i = v\ldots 0}$; $\mathbf{p}$ is the vector on the $k_x 0 k_y$ plane parallel to the crystal entrance surface.

Substituting (5) into the corresponding equation of the system (3) assuming that all the vectors $\mathbf{g}$ do not possess z components and using Born's first approximation, if $z > z_i$, we get for the amplitude of the Bloch wave

$$\psi^{(j')}_{0\ldots l_i\ldots 0}(z, \mathbf{p}_1) = \left[-2\pi i m / h^2 k^{(j')}_{0z}(\mathbf{p}_1)\right]$$

$$\times \sum_j \sum_g \sum_h \int C^{(j)}_g(\mathbf{p}) C^{(j')*}_h(\mathbf{p}_1)$$

$$\times \psi^{(j)}_{0\ldots 0}(0, \mathbf{p}) \tilde{H}'_{l_i 0}(\mathbf{Q})$$

$$\times \exp\left(-2\pi i \mathbf{Q} \cdot \mathbf{r}_i\right) d\mathbf{p}, \qquad (6)$$

where $\tilde{H}'_{l_i 0}(\mathbf{Q})$ is the Fourier transform of the matrix element $H_{l_i 0}(\mathbf{r})$, which is calculated in the coordinate system centred at the scattering atom with a coordinate $\mathbf{r}_i$, and $\mathbf{Q}$ is the vector with components $[\mathbf{p}_1 + \mathbf{h} - \mathbf{p} - \mathbf{g}, k^{(j')}_{0z}(\mathbf{p}) - k^{(j)}_{0z}(\mathbf{p})]$. The branches of a dispersion surface corresponding to the electron inelastically scattered by the ith centre are indicated with a prime.

Substitution of (6) into (5) permits one to obtain an analytical equation for the wave function $\Psi_{0\ldots l_i\ldots 0}(\mathbf{r})$. To determine the intensities $I_{0,g}(\mathbf{r}, \Delta E_v)$ of electrons with the energy loss ΔE_v, it is necessary to use (4) to obtain a summation with respect to all the atoms where interaction occurs.

In the present experiments, the characteristic angle of inelastic scattering θ_E ($\theta_E = \Delta E_v / 2E_{0\ldots 0}$) is much

smaller than the Bragg angle. It is easy to show that in such cases the intensity of electrons inelastically scattered by both native and uniformly distributed impurity atoms, the Bragg conditions being satisfied for some reflection, is given by the formula

$$I_{0,g}(\mathbf{r}, \Delta E_v)$$

$$\simeq I^{\text{el}}_{0,g}(\mathbf{r}) Nt$$

$$\times \left\{ \left(2\pi m/h^2 k_{0z}\right)^2 \int |\tilde{H}'_{l_i 0}(\mathbf{p}', \Delta k_z) d\mathbf{p}'|^2 \right\}, \qquad (7)$$

where $I^{\text{el}}_{0,g}(\mathbf{r})$ is the intensity of elastic scattering in the direct or diffracted beam, N is the number of atoms in the unit volume, t is the specimen thickness, k_{0z} is the z component of a fast incident electron, $\mathbf{p}'$ is the vector $(\Delta k_x, \Delta k_y)$ and Δk_x, Δk_y, Δk_z are the changes of the wave-vector components as a result of scattering.

Expression (7) accounts for the character of the intensity distribution in Figs. 1(c) and 2(c). If the effect of the crystal on the movement of an ejected electron is neglected, the factor in braces in (7) can be expressed in terms of the scattering cross section of an isolated atom.

The experimental and theoretical results obtained show that the intensity of electrons with small inner-shell energy losses at the exit surface of the crystal is proportional to that of elastically scattered electrons. This effect arises both by inelastic scattering at the atoms forming the regular crystal lattice and by inelastic scattering at impurity atoms occupying random positions.

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