

The theory of electron energy-loss near-edge structure

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ABSTRACT

This paper presents a complete theory of electron energy-loss near-edge structure, which appears near atomic core-electron excitation edges in the energy-loss spectrum of fast electrons transmitted through a thin crystal. In order to extract the maximum information from spectra recorded during microanalysis in the electron microscope, it is necessary to have a full understanding of the dynamical scattering of the transmitted fast electrons as well as the multiple scattering of the ejected core electrons. This is provided within the framework of a unified theory. Also considered are the effects of the 'non-dipole' terms in the electron excitation process, and of a finite electron collection aperture.

§1. INTRODUCTION

In recent years the study of extended X-ray absorption fine structure (EXAFS) has proved to be a very powerful means of revealing the local atomic geometry and coordination around particular atomic sites in solids. Electrons ejected from inner atomic shells by absorption of X-ray photons travel to atoms neighbouring the absorbing atom and are scattered back from them. The interference between the outgoing and the incoming electron waves at the site of the absorbing atom can be either constructive or destructive, and this gives rise to a modulation of the characteristic saw-tooth profile of the free atom's absorption spectrum. In the region beyond about 50 eV from the absorption edge, this modulation is a signature of the radial distribution of scattering matter relative to the absorbing atom, and this radial distribution is easily recovered by Fourier transformation (Stern, Sayers and Lytle 1975, Ashley and Doniach 1975, Lee and Pendry 1975).

In the first 50 eV or so from the absorption edge, the modulation of the free atom's absorption spectrum is known as the X-ray absorption near-edge structure (XANES). In this region the ejected core electron has a large cross-section for elastic scattering from neighbouring atoms, and as a result multiple-scattering effects become important. From the point of view of the study of local crystallography, this has the disadvantage that radial distribution functions are no longer recoverable by Fourier transformation. On the other hand, an analysis of the multiple scattering can yield information on multi-atom correlations and determine the magnitudes of otherwise inaccessible bond angles (Durham, Pendry and Hodges 1981, 1982).

Electrons from inner shells can undergo similar excitations through interactions with a high-energy electron beam, which itself suffers a corresponding energy loss in the process. The cross-sections for such inelastic scattering processes also manifest absorption edges and fine structure modulation. At energy losses greater than about

50 eV the phenomenon is known as extended electron energy-loss fine structure (EXELFS) and is the analogue of EXAFS in X-ray absorption spectra. The fine structure within 50 eV of the absorption edge, electron energy-loss near-edge structure (ELNES), is the corresponding analogue of XANES.

The fine structure in electron energy-loss spectra has been found to be just as characteristic of the local atomic geometry, and its study offers many advantages over that of X-ray absorption spectra. Firstly, the latter spectra usually require the use of inconvenient central radiation sources, such as synchrotrons, while the former require only an electron source, such as that found in common laboratory electron microscopes. Secondly, the region of the sample under study may be imaged simultaneously in the electron microscope, thus ensuring, for instance, that the spectra are obtained from defect-free regions (Disko, Spence, Sankey and Saldin 1986). Thirdly, it is possible to select energy-loss spectra from particular Bloch wave states of the high-energy electrons by suitably orientating the specimen and positioning the collector aperture, and this enables spectra from the same atomic species on inequivalent sites to be distinguished (Taftø and Krivanek 1982). Fourthly, the Coulombic interaction between the beam and crystal electrons make it possible to study non-vertical transitions (Chen and Silcox 1977) and non-dipole transitions (Doniach, Platzman and Yue 1971).

Various aspects of the theory of the excitation of atomic inner-shell electrons by a beam of incident fast electrons have been treated already. Manson (1972) and Leapman, Rez and Mayers (1980) have modelled the excitation of electrons from isolated atoms. Rossouw and Maslen (1984) have treated the full multiple scattering of the incident fast electrons in a crystal and the atomic excitation process, but omitted the effect of the back-scattering of the ejected core electron. Schaich (1984) has treated the back-scattering of the ejected core electron in the single-scattering (or EXELFS) approximation, but omitted the dynamical scattering—and hence the Bloch character—of the fast electrons.

In a previous paper (Saldin and Rez 1987) it was shown how to incorporate an EXAFS-like description (Lee and Pendry 1975) of the inner-shell and ejected electrons in a spherical-wave basis with the conventional Bloch wave treatment of the dynamical scattering of the fast electron. The back scattering of the ejected core electrons was not taken into account, but the detailed structure of an ELNES spectrum is clearly dependent on this. In the present paper the picture is completed by including the effects of the multiple scattering of the fast and crystal electrons within the framework of the same theory, thus providing for the first time a complete description of ELNES. The full theory is presented in §2. This formulation would be capable of describing Bloch wave channelling effects, as well as the energy dependence of the electron absorption cross-section.

Although Bloch wave channelling effects can be used to separate the contributions to an ELNES spectrum from identical atomic species in crystallographically different sites (Taftø and Krivanek 1982), electron energy-loss experiments are frequently performed (see, for example, Disko *et al.* 1986) for directions of incidence of the fast electrons which do not excite strong Bragg reflections in the crystal (as is generally the case with polycrystalline samples). Under such circumstances a kinematic description of the fast-electron scattering is more appropriate, and it is shown in §3 that this may be regarded as a special case of the general theory advanced here.

The partial-wave orbitals of the ejected electrons have a directional character (except for s-waves). Such orbitals are orientated with respect to the fast-electron momentum transfer vector \mathbf{q} which plays the role of the X-ray polarization vector in

XANES. The possibility of selectively orientating \mathbf{q} with respect to particular crystallographic directions has been exploited by Leapman and Silcox (1979), Disko, Krivanek and Rez (1982) and Leapman, Fejes and Silcox (1983) to use the ejected electrons as a sort of 'searchlight' to explore the directional dependence of the local crystallography. For a polycrystalline sample, however, an ELNES signal is an average over all directions of \mathbf{q} with respect to the crystallographic axes. Such an averaging further simplifies the expressions in the present theory and this is demonstrated in §4.

For single-crystal samples, with the detector aperture of the energy-loss electrons placed so as to collect only forward-scattered electrons, a more restricted form of averaging is possible. An azimuthal average is taken of the vector \mathbf{q} , and an integration over the magnitudes of \mathbf{q} is permitted by the aperture. This procedure is performed in §5, and the particularly simple form of the resulting expressions for K-shell excitations is presented.

The conclusions of this paper are discussed in §6.

§2. THEORY

Consider a beam of electrons in a transmission electron microscope, represented by a plane wave of energy E_i and wave-vector \mathbf{K} , incident on a thin parallel-sided foil of thickness t . This beam can interact inelastically with an atomic core electron of wavefunction $u_i(\varepsilon_i)$ and energy ε_i . In the process the core electron is lifted to a higher energy state $u_f(\varepsilon_f)$, of energy ε_f . The beam electron suffers an energy loss and emerges from the exit surface of the foil with energy E_f . The amplitude of a particular plane wave component of wave-vector $\mathbf{K}' + \mathbf{G}$ (where \mathbf{G} is the reciprocal lattice vector of the foil) is capable of being detected by appropriately positioning a collector aperture. The vector \mathbf{G} is introduced here to ensure that the component of the wave-vector \mathbf{K}' parallel to the foil surface, \mathbf{K}'_{\parallel} , is taken to lie within the first Brillouin zone. The calculation of the probability of such an event taking place requires the evaluation of the matrix element

$$\langle \mathbf{K}'_{\parallel} + \mathbf{G}, E_f; u_f(\varepsilon_f) | T | u_i(\varepsilon_i); E_i, \mathbf{K}_{\parallel} \rangle, \quad (1)$$

where the fast-electron states $|E_i, \mathbf{K}_{\parallel}\rangle$ and $|E_f, \mathbf{K}'_{\parallel} + \mathbf{G}\rangle$ are represented by plane waves of the form

$$\exp(i\mathbf{K} \cdot \mathbf{r}), \quad (2)$$

$$\exp[i(\mathbf{K}' + \mathbf{G}) \cdot \mathbf{r}], \quad (3)$$

outside the foil surfaces, and

$$\sum_j C_0^j \langle \mathbf{r} | B^j \rangle, \quad (4)$$

$$\sum_{\mathbf{g}} C_{\mathbf{g}}^i \langle \mathbf{r} | B^i \rangle \exp[i(K_z^i - k_z^i)t], \quad (5)$$

which are linear superpositions of Bloch waves $\langle \mathbf{r} | B^j \rangle$ and $\langle \mathbf{r} | B^i \rangle$, inside the crystal, where

$$\langle \mathbf{r} | B^j \rangle = \sum_{\mathbf{h}} C_{\mathbf{h}}^j \exp[i(\mathbf{k}^j + \mathbf{h}) \cdot \mathbf{r}], \quad (6)$$

$$\langle \mathbf{r} | B^i \rangle = \sum_{\mathbf{g}} C_{\mathbf{g}}^i \exp[i(\mathbf{k}^i + \mathbf{g}) \cdot \mathbf{r}], \quad (7)$$

with \mathbf{h} and \mathbf{g} reciprocal lattice vectors.

The Bloch wave excitation coefficients $C_{\mathbf{h}}^i$ and $C_{\mathbf{g}}^i$ and the z -components of the Bloch wave-vectors k_z^i and k_z^i , are determined by the usual secular equation for fast-electron diffraction (Hirsch, Howie, Nicholson, Pashley and Whelan 1965).

In eqn. (1) the operator T represents the Coulombic interaction between the beam and crystal electrons and may be expressed as

$$e^2/4\pi\epsilon_0|\mathbf{r} - \mathbf{r}_c|, \quad (8)$$

where e is the charge on an electron, ϵ_0 is the vacuum permittivity, and \mathbf{r} and \mathbf{r}_c are position vectors of the beam and crystal electrons, respectively. Evaluation of matrix element (1) leads to the following expression for the angle-resolved differential intensity of electrons inelastically scattered by a crystal by the excitation of atomic inner-shell electrons (see, for example, Rossouw and Maslen 1984, Saldin and Rez 1987):

$$\frac{\partial^2 I(\mathbf{K}' + \mathbf{G}, \mathbf{K}_i)}{\partial \Omega \partial E_f} = \frac{4}{a_0^{*2}} \frac{K_z'}{K_z} \sum_{\beta} \sum_{\mathbf{g}\mathbf{h}\mathbf{g}'\mathbf{h}'} [\text{site}][\text{atom}] \sum_{ijj'} [\text{BW}], \quad (9)$$

where N_i is the number of lattice sites per unit volume, $a_0^* = 4\pi\hbar^2\epsilon_0/me^2$ is the relativistic Bohr radius, m is the mass of the electron, $\hbar (= 2\pi h)$ is Planck's constant, and ϵ_0 is the permittivity of free space. The other quantities in eqn. (9) are given by

$$[\text{BW}] = C_{\mathbf{G}}^i * C_0^i C_{\mathbf{G}}^i C_0^i * C_{\mathbf{h}}^i C_{\mathbf{g}}^i * C_{\mathbf{h}}^i C_{\mathbf{g}}^i X, \quad (10)$$

where

$$X = \frac{\exp [i(k_z^j - k_z^i)t] - \exp [i(k_z^i - k_z^j)t]}{i(k_z^j - k_z^i - k_z^i + k_z^j)}, \quad (11)$$

$$[\text{atom}] = \frac{M_{\beta}(\mathbf{Q}_1) M_{\beta}^*(\mathbf{Q}_2) \rho_{\beta}(e_f)}{Q_1^2 Q_2^2}, \quad (12)$$

$$[\text{site}] = \exp [i(\mathbf{Q}_1 - \mathbf{Q}_2) \cdot \tau_{\beta}], \quad (13)$$

where

$$\mathbf{Q}_1 = \mathbf{q}_{ij'} + \mathbf{h} - \mathbf{g}', \quad (14)$$

$$\mathbf{Q}_2 = \mathbf{q}_{ij'} + \mathbf{g} - \mathbf{h}', \quad (15)$$

$$\mathbf{q}_{ij'} = \mathbf{k}^i - \mathbf{k}^j, \quad (16)$$

$$M_{\beta}(\mathbf{Q}) = \int \phi_i^{\beta*}(\mathbf{r}) \exp (i\mathbf{Q} \cdot \mathbf{r}) \phi_f^{\beta}(\mathbf{r}) d\mathbf{r}. \quad (17)$$

In all these expressions and those that follow, a prime denotes electrons after the inelastic scattering event: τ_{β} and $\rho_{\beta}(e_f)$ are respectively the position vectors and local densities of states of the excited crystal electrons of particular atoms β within each unit cell.

Rossouw and Maslen (1984) quoted a similar formula based on a tight-binding description of the crystal electrons, in which the functions $\phi_i(\mathbf{r})$ and $\phi_f(\mathbf{r})$ in eqn. (17) represent atomic basis functions of the initial and final crystal electron states. They assumed that both these functions were so localized on the atoms that they made no overlap with corresponding functions on any other atom. While this is a good approximation for ϕ_i , it is clearly quite incorrect for ϕ_f . In a previous treatment (Saldin and Rez 1987) the tight-binding representation of the crystal electrons was dispensed with altogether, and ϕ_i and ϕ_f were regarded as independent localized states

on each atom. Several reasons were given to justify this treatment. The excited core electron is ejected from the excited atom as a low-energy electron, with an energy of the order of, for instance, those employed in low-energy electron diffraction (LEED) experiments. It is known from LEED experiments that the mean free path for further inelastic scattering is only of the order of a few interatomic distances. The state ϕ_f must therefore be regarded as a state localized to within a few interatomic distances from the exciting atom, and not as one extending throughout the foil. The inner-shell state ϕ_i remains localized within an atomic radius. The inelastic scattering processes on different atoms are treated incoherently, a result justified even within the tight-binding theory, as shown by Young and Rez (1975) who demonstrated that only diagonal terms (which bear no phase relations to each other) contribute to the lattice sums in expressions for the magnitude of the inelastic scattering.

Here the term [atom] (eqn. (12)) is calculated, using a model of the crystal potential which represents the atomic potential in 'muffin-tin' form with a constant interstitial potential in the regions between atoms. This model has been used with considerable success in the theories of EXAFS (Lee and Pendry 1975) and XANES (Durham *et al.* 1982). We begin by rewriting eqn. (12) as

$$[\text{atom}] = -\frac{1}{\pi Q_1^2 Q_2^2} \int d\mathbf{r} d\mathbf{r}' \phi_i^{\beta*}(\mathbf{r}) \exp(i\mathbf{Q}_1 \cdot \mathbf{r}) \\ \times \text{Im} \langle \mathbf{r} | G^+ | \mathbf{r}' \rangle \exp(-i\mathbf{Q}_2 \cdot \mathbf{r}') \phi_f^\beta(\mathbf{r}'), \quad (18)$$

where $G^+(\epsilon_f)$ is the retarded Green function of electrons of energy ϵ_f . This is the term which takes account of the multiple scattering of the ejected core electrons by the surrounding atoms in the crystal.

If $\phi_i^\beta(\mathbf{r})$ is a core wavefunction characterized by the angular momentum quantum numbers $L \equiv (l, m)$, we may write

$$\phi_i^\beta(\mathbf{r}) = \langle \mathbf{r} | L \rangle, \quad (19)$$

and inserting complete sets of states $|L'\rangle$ and $|L''\rangle$ in eqn. (18), we obtain

$$[\text{atom}] = -\frac{1}{(2l+1)\pi Q_1^2 Q_2^2} \sum_{L'L''m} \langle L | \exp(i\mathbf{Q}_1 \cdot \mathbf{r}) | L' \rangle \\ \times \text{Im} \langle L' | G^+(\epsilon_f) | L'' \rangle \langle L'' | \exp(-i\mathbf{Q}_2 \cdot \mathbf{r}') | L \rangle, \quad (20)$$

where we have averaged over values of the azimuthal quantum number m of the core states, since the degeneracy of such states implies that they all contribute to a given absorption edge.

The term $\langle L' | G^+(\epsilon_f) | L'' \rangle$ is the same quantity as is calculated in the theory of X-ray absorption near-edge structure (XANES) (Durham *et al.* 1982, Vvedensky, Saldin and Pendry 1986), and is related to the scattering path operator $\tau_{L'L''}(\epsilon_f)$ (see, for example, Faulkner and Stocks 1980) by the equation

$$\langle L' | G^+(\epsilon_f) | L'' \rangle = \frac{\tau_{L'L''}(\epsilon_f)}{\sin \delta_{L'}(\epsilon_f) \sin \delta_{L''}(\epsilon_f)}, \quad (21)$$

where

$$\tau_{L'L''}(\epsilon_f) = t_{L'L''}(\epsilon_f) [1 - S(\epsilon_f) t(\epsilon_f)]^{-1}, \quad (22)$$

$\delta_l(\varepsilon_f)$ and $\delta_{l'}(\varepsilon_f)$ are the phase shifts of the exciting atom at energy ε_f and

$$t_{L'L}(\varepsilon_f) = \delta_{L'L} - i \sin \delta_l(\varepsilon_f) \exp(i\delta_{l'}(\varepsilon_f)) \quad (23)$$

are the elements of the (diagonal) atomic t -matrix, and $S(\varepsilon_f)$ is the 'out-in' reflection matrix, expressed in an angular momentum basis, which represents the scattering of the ejected core electron by the near neighbours of the excited atom. For an absorbing atom in free space, G^+ is diagonal in an angular momentum representation, and this corresponds to the approximation employed by Rossouw and Maslen (1984) and Saldin and Rez (1987). A crystalline host destroys any spherical symmetry in the potential experienced by the ejected electrons, which results in the coupling of many different angular momentum channels for these electrons.

Although in theory such couplings are possible in EXAFS and XANES, the dipole nature of the excitation, and the resulting selection rules $\Delta l = \pm 1$ and $\Delta m = 0, \pm 1$, severely restrict the number of values of L' and L'' , and therefore a very limited subset of the elements $\langle L'|G^+|L'' \rangle$ contribute to the observed signal. The lack of such restrictions in the general theory of ELNES and the resulting contribution of so many different elements of $\langle L'|G^+|L'' \rangle$ may give rise to a much richer structure in ELNES spectra.

The excitation matrix elements may be evaluated by taking the polar coordinate representations

$$\langle \mathbf{r}|L \rangle = \phi_{nl}(r) Y_L(\hat{\mathbf{r}}), \quad (24)$$

$$\langle \mathbf{r}|L' \rangle = R_{l'}(\varepsilon_f, r) Y_{L'}(\hat{\mathbf{r}}), \quad (25)$$

$$\langle \mathbf{r}|L'' \rangle = R_{l''}(\varepsilon_f, r) Y_{L''}(\hat{\mathbf{r}}), \quad (26)$$

$$\exp(i\mathbf{Q} \cdot \mathbf{r}) = \sum_{\lambda\mu} 4\pi i^{\lambda} j_{\lambda}(Qr) (-1)^{\mu} Y_{\lambda-\mu}(\hat{\mathbf{r}}) Y_{\lambda\mu}(\hat{\mathbf{Q}}), \quad (27)$$

which yield

$$\langle L|\exp(i\mathbf{Q} \cdot \mathbf{r})|L' \rangle = \sum_{\lambda\mu} 4\pi i^{\lambda} Y_{\lambda\mu}(\hat{\mathbf{Q}}) \langle Y_L Y_{\lambda\mu} | Y_{L'} \rangle F_{nl,\varepsilon_f}^{\lambda}(Q), \quad (28)$$

where

$$F_{nl,\varepsilon_f}^{\lambda}(Q) = \int_0^{\infty} \phi_{nl}(r) j_{\lambda}(Qr) R_{l'}(\varepsilon_f, r) r^2 dr, \quad (29)$$

$$\langle Y_L Y_{\lambda\mu} | Y_{L'} \rangle = \int Y_L^* Y_{\lambda\mu}^* Y_{L'} d\Omega. \quad (30)$$

By using eqns. (21) and (28), eqn. (20) can be rewritten as

$$\begin{aligned} [\text{atom}] = & -\frac{1}{(2l+1)\pi Q_1^2 Q_2^2} \sum_{\substack{L'L''\lambda'\lambda'' \\ \mu'\mu''m}} \left[i^{\lambda'-\lambda''} Y_{\lambda'\mu'}(\hat{\mathbf{Q}}_1) Y_{\lambda''\mu''}^*(\hat{\mathbf{Q}}_2) \langle Y_L Y_{\lambda'\mu'} | Y_{L'} \rangle \right. \\ & \left. \times F_{nl,\varepsilon_f}^{\lambda'}(Q_1) \frac{\text{Im}(\tau_{L'L''}(\varepsilon_f))}{\sin \delta_{l'} \sin \delta_{l''}} F_{nl,\varepsilon_f}^{\lambda''}(Q_2) \langle Y_{L''} | Y_{\lambda''\mu''} | Y_L \rangle \right]. \quad (31) \end{aligned}$$

If this expression for the term [atom] is used in eqn. (9), that equation represents the complete solution of the problem of energy loss from fast electrons by the excitation of inner-shell atomic electrons in crystals. Equation (9) would then give both the energy-loss spectrum and the angular distribution of the fast electrons after energy loss.

The term [BW] in eqn. (9) requires the solution of the typical secular equation for the Bloch wave excitation coefficients $C_{\mathbf{g}}^i$ and the z -components k_z^i of the Bloch wave-vectors of the incident fast electrons and those after energy loss (Hirsch *et al.* 1965). The term [atom] (eqn. (31)) requires the evaluation of the scattering path operator $\tau_{L'L''}(\epsilon_f)$, and this can be performed by using computer programs already developed for XANES (Durham *et al.* 1982, Vvedensky *et al.* 1986). Also required for the term [atom] is the calculation of the matrix elements $F_{nl,el'}^{\lambda'}(\mathbf{Q})$. This has already been done for many free atoms by Leapman *et al.* (1980), using Hermann-Skillman atomic wavefunctions. Alternatively, the matrix elements may be evaluated by a modification of the MUFPO program developed by Pendry and co-workers, which permits the use of atomic wavefunctions which may then be overlapped with wavefunctions from neighbouring atoms to generate atomic potentials, and hence wavefunctions R_r of the emitted electrons reflecting the local atomic arrangements.

§3. KINEMATICAL SCATTERING OF FAST ELECTRONS

Up to this point the theory has been completely general. Under certain easily realizable circumstances, however, the expressions (9)–(17) and (31) may be considerably simplified. If, for example, no strong Bragg reflection is excited by the incident electron beam, only one term of the form [BW] remains significant in eqn. (9). This term is

$$[\text{BW}] = |C_0^{(1)}|^8 X, \quad (32)$$

since all other coefficients of the form $C_{\mathbf{g}}^i$ are negligible. Only one Bloch wave (with index $i = 1$) contributes to eqn. (9), and in this limit (corresponding to the kinematic scattering of the fast electrons):

$$C_0^{(1)} \rightarrow 1, \quad (33)$$

$$X \rightarrow t, \quad (34)$$

$$\mathbf{Q}_1 = \mathbf{Q}_2 = \mathbf{q}, \quad (35)$$

$$[\text{site}] \rightarrow N, \quad (36)$$

where N is the number of atoms per unit cell.

With the relations (32)–(36), eqn. (9) reduces to

$$\frac{\partial^2 I(\mathbf{K}'_{\parallel}, \mathbf{K}_{\parallel})}{\partial \Omega \partial E_f} = \frac{4}{a_0^{*2}} \frac{K'_z}{K_z} N t [\text{atom}], \quad (37)$$

where the term [atom] takes the simplified form

$$[\text{atom}] = - \frac{1}{(2l+1)\pi q^4} \sum_{\substack{L'L''\lambda'\lambda'' \\ \mu'\mu''m}} \left[i^{\lambda'-\lambda''} Y_{\lambda'\mu'}(\mathbf{q}) Y_{\lambda''\mu''}(\mathbf{q}) \langle Y_L Y_{\lambda'\mu'} | Y_L \rangle \right. \\ \left. \times F_{nl,el'}^{\lambda'}(q) \frac{\text{Im}(\tau_{L'L''}(\epsilon_f))}{\sin \delta_{l'} \sin \delta_{l''}} F_{nl,el''}^{\lambda''}(q) \langle Y_{L''} | Y_{\lambda''\mu''} Y_L \rangle \right]. \quad (38)$$

§4. AVERAGING OVER MOMENTUM TRANSFER VECTORS

The direction of the momentum transfer vector \mathbf{q} is defined with respect to the orientation of the crystal. For a polycrystalline sample we can follow Schaich (1984) in

assuming that the observed ELNES signal is an average over all directions of \mathbf{q} . For this purpose we need consider only the term [atom]. By making use of the relation

$$\int Y_{\lambda'\mu'}(\mathbf{q})Y_{\lambda''\mu''}(\mathbf{q})d\mathbf{q} = \delta_{\lambda'\lambda''}\delta_{\mu'\mu''}, \quad (39)$$

eqn. (38) can be written (after averaging) as

$$\begin{aligned} [\text{atom}] = & -\frac{1}{(2l+1)\pi q^2} \sum_{L'L'\lambda'} \left[\langle Y_L Y_{\lambda'\mu'} | Y_L \rangle \frac{F_{nl,\epsilon_f l'}^{\lambda'}}{q} \right. \\ & \left. \times \frac{\text{Im}(\tau_{L'L'}(\epsilon_f))}{\sin \delta_{l'} \sin \delta_{l'}} \frac{F_{nl,\epsilon_f l'}^{\lambda''}}{q} \langle Y_{L'} | Y_{\lambda'\mu'} Y_L \rangle \right]. \end{aligned} \quad (40)$$

The matrix element (29) can be written in terms of Clebsch-Gordon coefficients as

$$\begin{aligned} \langle Y_L Y_{\lambda'\mu'} | Y_{L'} \rangle = & \left[\frac{(2l+1)(2\lambda'+1)(2l'+1)}{4\pi} \right]^{1/2} \\ & \times \begin{pmatrix} l & \lambda' & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & \lambda' & l' \\ -m & -\mu' & m' \end{pmatrix} (-1)^{m+\mu}. \end{aligned} \quad (41)$$

By making use of the orthogonality condition,

$$\sum_{m\mu'} \begin{pmatrix} l & \lambda' & l' \\ -m & -\mu' & m' \end{pmatrix} \begin{pmatrix} l & \lambda' & l'' \\ -m & -\mu' & m'' \end{pmatrix} = \frac{1}{(2l'+1)} \delta_{l'l''} \delta_{m'm''}, \quad (42)$$

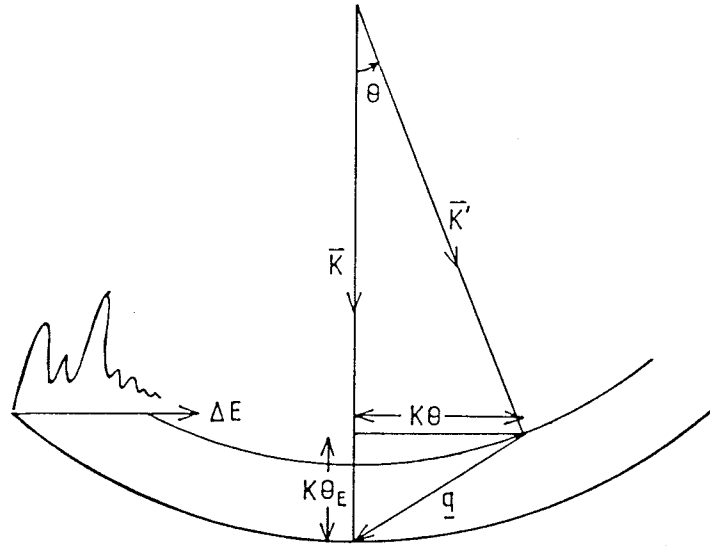
eqn. (40) is further simplified to

$$\begin{aligned} [\text{atom}] = & -\frac{1}{\pi q^2} \sum_{L'\lambda'} \left[\left(\frac{F_{nl,\epsilon_f l'}^{\lambda'}}{q} \right)^2 \frac{\text{Im}(\tau_{L'L'}(\epsilon_f))}{\sin^2 \delta_{l'}} \right. \\ & \left. \times (2\lambda'+1) \begin{pmatrix} \lambda' & l' & l \\ 0 & 0 & 0 \end{pmatrix}^2 \right]. \end{aligned} \quad (43)$$

The value of the quantity $F_{nl,\epsilon_f l'}^{\lambda'}/q$ tends to the value of the corresponding dipole matrix element for small q . However, in a typical ELNES experiment the value of q may be chosen by the experimenter by moving a small collector aperture away from the forward-scattering direction. For values of q large enough for qr_c to become a significant fraction of π (where r_c is the radius of the core wavefunction), or for large collection apertures, the dipole selection rule for the atomic excitation process ceases to apply, and the core state becomes coupled to ejected electron states of many different angular momentum values l' . As a result many more elements of the matrix $\tau_{L'L'}$ contribute to the ELNES signal. The effects of these 'non-dipole' terms in the matrix elements on ELNES spectra have not received much attention to date.

§ 5. SINGLE-CRYSTAL SAMPLES—INTEGRATION OVER THE COLLECTION APERTURE

For single-crystal samples, the scattering kinematics in electron transmission geometry (see the figure) indicates that when a collection aperture of semi-angle (θ_c) typically 10 to 20 mrad is used, the measured ELNES signal at a particular value of the energy loss does not involve an isotropic integral over all directions of the momentum transfer vector \mathbf{q} . On the contrary, since the maximum scattering angle $\theta = \theta_c$ is small, \mathbf{q} may be regarded as a vector sum of its components parallel and



Scattering kinematics for a plane wave electron beam of incident wave-vector \mathbf{K} , scattered wave-vector \mathbf{K}' and total momentum transfer vector \mathbf{q} . The magnitudes of the components of \mathbf{q} parallel and perpendicular to \mathbf{K} (for small θ) are shown. The resulting energy-loss spectrum is suggested schematically.

perpendicular to the wave-vector \mathbf{K} of the incident electrons of magnitudes $K\theta_E$ and $K\theta$ respectively, where

$$\theta_E = \Delta E/2E_0, \quad (44)$$

with ΔE the energy loss and E_0 the relativistically corrected kinetic energy of the fast electrons. This implies that the magnitude of the energy loss (ΔE) determines the component of \mathbf{q} parallel to \mathbf{K} , and that the effect of a finite collection aperture may be modelled by an integration over values of \mathbf{q} perpendicular to \mathbf{K} . This involves an azimuthal integral over the directions of \mathbf{q} and a suitably weighted integral over θ , which yields

$$\begin{aligned} \frac{dI}{dE_f} = & \frac{8\pi}{K^2 a_0^{*2}} \frac{K'_z}{K_z} Nt \int_0^{\theta_c} \frac{\theta d\theta}{(\theta^2 + \theta_E^2)} \sum_{L'L''} \left[i^{\lambda' - \lambda''} \langle Y_{\lambda'0} Y_{L'} | Y_L \rangle \right. \\ & \left. \times \frac{F_{nl,\epsilon_f}^{\lambda'}(q)}{q} \frac{\text{Im}(\tau_{L'L''}(\epsilon_f))}{\sin \delta_{L'} \sin \delta_{L''}} \frac{F_{nl,\epsilon_f}^{\lambda''}(q)}{q} \langle Y_L | Y_{\lambda''0} Y_{L''} \rangle \right]. \end{aligned} \quad (45)$$

For small q quantities of the form

$$F_{nl,\epsilon_f}^{\lambda'}(q)/q \quad (46)$$

may be taken as independent of q , and the integral over θ performed analytically to give

$$\begin{aligned} \frac{dI}{dE_f} = & \frac{4\pi}{K^2 a_0^{*2}} \frac{K'_z}{K_z} Nt \ln \left(1 + \frac{\theta_c^2}{\theta_E^2} \right) \sum_{L'L''} \left[i^{\lambda' - \lambda''} \langle Y_{\lambda'0} Y_{L'} | Y_L \rangle \right. \\ & \left. \times \frac{F_{nl,\epsilon_f}^{\lambda'}(q)}{q} \frac{\text{Im}(\tau_{L'L''}(\epsilon_f))}{\sin \delta_{L'} \sin \delta_{L''}} \frac{F_{nl,\epsilon_f}^{\lambda''}(q)}{q} \langle Y_L | Y_{\lambda''0} Y_{L''} \rangle \right]. \end{aligned} \quad (47)$$

Note, however, that the assumption that $F_{nl, \epsilon_f l'}^{l'}/q$ is independent of q is equivalent to the dipole approximation, and under such circumstances the selection rule $l' = l \pm 1$ obtains.

For the excitation of K-shell electrons with $L = (0, 0)$, eqn. (47) simplifies further to yield

$$\frac{dI}{dE_f} = \frac{4\pi}{K^2 a_0^*{}^2} \frac{K_z'}{K_z} Nt \ln \left(1 + \frac{\theta_c^2}{\theta_E^2} \right) \left(\frac{F_{10, \epsilon_f 1}^1(q)}{q} \right)^2 \frac{\text{Im}(\tau_{10, 10}(\epsilon_f))}{\sin^2 \delta_1}, \quad (48)$$

which is now in a form that can easily be handled by a computer. It is of the same form as the expression used in the analysis of XANES, and justifies the use of XANES calculations for the interpretation of ELNES (Lindner, Sauer, Engel and Kambe 1986, Disko *et al.* 1986) where no strong Bragg reflection is excited by the fast electrons, and where a small aperture is used to collect forward-scattered electrons.

§6. CONCLUSIONS

A full solution of the problem of electron energy-loss near-edge structure has been presented, taking into account the multiple scattering of both fast and slow electrons. The special case of kinematic scattering of the fast electrons has been examined, and the effect of a finite collection aperture has been included in a realistic manner. Simplified expressions have been derived for the common case of K-shell excitations, and the 'XANES' limit derived. Expressions have also been presented for the more general situation where the so-called 'non-dipole' terms in the excitation matrix elements are retained.

Attempts have previously been made to simulate ELNES spectra by means of XANES calculations (Lindner *et al.* 1986, Disko *et al.* 1986), with some success, but some remaining discrepancies. The question of whether these discrepancies are resolved by the additional 'non-dipole' terms and the inclusion of dynamical effects in the fast-electron scattering awaits numerical studies, which could be based on the equations presented in this paper.

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