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Diffraction and absorption of x-rays by 3d transition ions: the 1s \rightarrow 3d process*

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Abstract. The resonant scattering length for K-shell absorption and an E2 transition is calculated for 3d transition ions, on the basis of an atomic model. It is applied to the evaluation of the intensity of x-rays Bragg reflected from a magnetic salt, e.g. NiO, and the circular dichroic signal in the attenuation coefficient. The information which can be extracted from these quantities relates to the orbital properties of the 3d valence shell. An exception is the s-state ion 3d⁵, for which the leading-order effect is zero. For the 3d⁵ ion it is shown that inclusion of core polarization in the calculation leads to a weak effect which contains the spin magnetic moment.

1. Introduction

Recently Hill *et al* (1997) reported the first observation of the elastic diffraction of x-rays enhanced by the E2 (electric quadrupole) absorption at the K edge of a transition ion, in a magnetic salt. The experiment was performed on a large crystal of NiO, which is a type II antiferromagnet at a temperature less than 523 K. With a primary energy $E = 8333$ eV ($\equiv 1.49$ Å), just less than the position in energy of the maximum in the absorption, a twofold resonant enhancement of the signal at two magnetic Bragg settings was observed. As Hill *et al* (1997) point out, their observation opens a rich seam of investigations of 3d magnets.

Using an atomic model of a 3d transition ion, we offer an interpretation of the E2 (1s \rightarrow 3d) resonance-enhanced diffraction amplitude, and the dichroic signal in the attenuation coefficient. The measured signals are sensitive to the orbital magnetic moment in the 3d valence shell, since the 1s core state is not split by the spin-orbit interaction. If need be in the future, polarization of the core state by the exchange field can be accounted for. At the moment, the relatively low energy resolution applied in diffraction experiments does not warrant inclusion of this and other small effects.

Sections 2 and 3 summarize a theoretical framework for the scattering length enhanced by an E2 resonance at the K edge of a 3d transition ion. Thereafter, in sections 4 and 5, the focus is on contributions to the scattering length observed at magnetic Bragg reflections from an antiferromagnet, and the dichroic signal in the attenuation coefficient picked out by circular polarization. Salient points are gathered in section 6, together with a treatment of the ion 3d⁵ which is a special case on account of having $L = 0$.

* The paper is dedicated to the memory of M C M O'Brien.

2. The resonant scattering length

When the energies of the primary x-ray beam, $E = \hbar c q$, and the absorption edge, Δ , almost match the elastic scattering length per unit cell $\langle f \rangle$ is, to a good approximation, given by

$$\langle f \rangle = -(eq)^2 \left\{ E - \Delta + \frac{i}{2} \Gamma \right\}^{-1} \sum_{\mathbf{d}} \exp\{i\mathbf{k} \cdot \mathbf{d} - W_d(\mathbf{k})\} \langle Z(\mathbf{d}) \rangle. \quad (2.1)$$

Here, $\mathbf{k} = \mathbf{q} - \mathbf{q}'$ is the scattering vector, the sum on \mathbf{d} is over all resonant ions in the magnetic cell, and $\exp\{-W_d(\mathbf{k})\}$ is the Debye–Waller factor. For 3d transition ions the total decay width $\Gamma \sim 1$ eV. In the following section we offer an account of the amplitude factor $\langle Z(\mathbf{d}) \rangle$ suitable for 3d transition ions and an E2 absorption event.

In arriving at (2.1) one has taken into account that the scattering length is to be used in calculations of the cross-section for Bragg diffraction or the attenuation coefficient. Both quantities refer to the bulk state of the target sample, so the relevant scattering lengths are an average over all degenerate variables required to define the equilibrium, or time-averaged, state of the sample. The average includes an average over the phase factor of each ion separately. Phase factors arise from the wave functions used to calculate the atomic matrix elements in the scattering length for the entire sample f ; the wave functions are essentially defined only to within an arbitrary phase factor, which is different for each ion. The scattering cross-section is proportional to $|f|^2$ averaged over all degenerate variables. The part of the cross-section proportional to $|\langle f \rangle|^2$, where $\langle f \rangle$ is the average value of the scattering length, for crystals can give rise to Bragg scattering where translational symmetry sets a strict geometric condition on the allowed values of \mathbf{k} . For the case of resonance-enhanced Bragg scattering it is notable that the average over the phase factors of the ions means that $\langle f \rangle$ is a sum of matrix elements from individual ions only, which is necessary to obtain the Bragg condition, of course, although f includes cross-terms of the matrix element of the current operator for ions at different positions in the sample.

3. The amplitude factor

For an E2 absorption event, the factor $\langle Z \rangle$ in (2.1) is expressed as a sum of five terms labelled by the rank, K , of two spherical tensors. One tensor, denoted by \mathbf{T}^K , describes the valence shell which accepts the photo-emitted electron. The condition of a beam of x-rays is described by its wave vector and polarization vector. These quantities for the primary and secondary beams are grouped to form a tensor $\mathbf{H}^{(K)}$. Full details on $\mathbf{H}^{(K)}$ are found in papers by Lovesey (1996) and Lovesey *et al* (1998). (For an E1 event the tensor that corresponds to $\mathbf{H}^{(K)}$, being independent of the wave vectors for the primary and secondary beams, is much simpler, as shown by Lovesey and Balcar (1996).)

Since the scattering length is a scalar object the two tensors, one for the valence shell and one for the x-ray beams, appear in $\langle Z \rangle$ in the form of a scalar product. From Lovesey (1996) one finds, for an E2 absorption event and a valence shell with angular momentum $l = 2$,

$$\langle Z(\mathbf{d}) \rangle = \frac{1}{5} \Phi \sum_K (2K + 1)^{1/2} \langle \mathbf{T}^K \rangle_{(xyz)} \cdot \mathbf{H}^{(K)} \quad (3.1)$$

where $K = 0, \dots, 4$, and the E2 radial integral $\langle R^2 \rangle$ appears in (for elastic scattering $q = q'$)

$$\Phi = \frac{1}{6} \{q \langle R^2 \rangle\}^2 \left\{ \frac{3l(l-1)}{2(2l-1)} \right\} = \frac{1}{6} \{q \langle R^2 \rangle\}^2. \quad (3.2)$$

The subscripts (x, y, z) on the atomic tensor in (3.1) denote that it is evaluated in the frame of reference for the experiment, the frame in which $\mathbf{H}^{(K)}$ is evaluated. If the local principal axes of the ion are defined relative to this frame by Euler angles α, β and γ (Judd 1975) and $\langle \mathbf{T}^K \rangle$ is the value of the tensor with respect to these axes,

$$\langle T_{m_0}^K \rangle_{(xyz)} = \sum_Q \langle T_Q^K \rangle \mathcal{D}_{Qm_0}^{(K)}(-\gamma, -\beta, -\alpha) \quad (3.3)$$

where $\mathcal{D}^{(K)}$ is an element of the rotation matrix. For all configurations of the magnetic moments other than a ferromagnet the Euler angles will depend on \mathbf{d} , the position of the ion in the unit cell. In simple models $\langle T_Q^K \rangle$ is zero for all Q different from zero, i.e. the atomic tensor is diagonal in the local principal axes. On setting $Q = 0$ on the right-hand side of (3.3) one finds

$$\langle T_{m_0}^K \rangle_{(xyz)} = \langle T_0^K \rangle C_{m_0}^{(K)}(\beta, \alpha) \quad (3.4)$$

where $C_{m_0}^{(K)}(\beta, \alpha)$ is a spherical harmonic normalized to give $C_0^{(0)}(\beta, \alpha) = 1$.

Table 1. Values of the reduced-matrix element of the unit tensor operator $V(K)$ are given for 3d transition ions and $K = 2, 3$ and 4. The configuration of the valence shell is determined from Hund's rules, and θ is an abbreviation for the atomic quantum numbers S, L and ν . Entries are adapted for holes from tables prepared by Nielson and Koster (1963).

Ion	$\langle \theta V(2) \theta \rangle$	$\langle \theta V(3) \theta \rangle$	$\langle \theta V(4) \theta \rangle$
3d ¹ , 2D	$-\sqrt{5}$	$\sqrt{7}$	-3
3d ² , 3F	$-(\frac{6}{5})^{1/2}$	$-(\frac{21}{5})^{1/2}$	$3(\frac{11}{5})^{1/2}$
3d ³ , 4F	$(\frac{6}{5})^{1/2}$	$-(\frac{21}{5})^{1/2}$	$-3(\frac{11}{5})^{1/2}$
3d ⁴ , 5D	$\sqrt{5}$	$\sqrt{7}$	3
3d ⁶ , 5D	$-\sqrt{5}$	$\sqrt{7}$	-3
3d ⁷ , 4F	$-(\frac{6}{5})^{1/2}$	$-(\frac{21}{5})^{1/2}$	$3(\frac{11}{5})^{1/2}$
3d ⁸ , 3F	$(\frac{6}{5})^{1/2}$	$-(\frac{21}{5})^{1/2}$	$-3(\frac{11}{5})^{1/2}$
3d ⁹ , 2D	$\sqrt{5}$	$\sqrt{7}$	3

The notation $\langle \dots \rangle$ used in (3.1) denotes an expectation, or mean, value of the enclosed atomic operator for the ground state of the valence shell. In general, the mean value is a sum of matrix elements, expressed in terms of Racah unit tensors $\langle \theta || V(K) || \theta \rangle$ with θ shorthand for the quantum numbers S, L and ν . If n_h is the number of holes in a shell, with angular momentum $l = 2$,

$$\langle \theta || V(0) || \theta \rangle = n_h \left\{ \frac{1}{5}(2L + 1) \right\}^{1/2} \quad (3.5)$$

and

$$\langle \theta || V(1) || \theta \rangle = \left(\frac{1}{10} \right)^{1/2} (L || L || L) \quad (3.6)$$

where the reduced-matrix element $(L || L || L) = \sqrt{\{L(L + 1)(2L + 1)\}}$. Other special cases are: for $n_h = 1$,

$$\langle \theta || V(K) || \theta \rangle = (2K + 1)^{1/2} \quad \text{for all } K \quad (3.7)$$

and for $K > 0$ and $n_h = (4l + 1)$,

$$\langle \theta || V(K) || \theta \rangle = (-1)^{1+K} (2K + 1)^{1/2}. \quad (3.8)$$

The remaining values of $\langle \theta || V(K) || \theta \rangle$ for 3d transition ions are listed in table 1. For $K > 0$, $n_h = 5$ and $L = 0$ all the matrix elements are zero. (Results for the jj -coupling scheme applied to the valence shell are given by Lovesey (1996).)

A matrix element of $T_{m_0}^K$ is

$$\begin{aligned} \langle M_s M_L \theta | T_{m_0}^K | M'_s M'_L \theta \rangle &= \left(\frac{1}{2K+1} \right)^{1/2} \delta_{M_s, M'_s} \langle \theta || V(K) || \theta \rangle \\ &\times (-1)^{L-M_L} \begin{pmatrix} L & K & L \\ -M_L & m_0 & M'_L \end{pmatrix}. \end{aligned} \quad (3.9)$$

Here, the $3j$ -symbol is possibly non-zero for $m_0 = M_L - M'_L$. Setting $K = 1$ in (3.9) and using (3.6) shows that

$$\langle M_s M_L \theta | T_{m_0}^1 | M'_s M'_L \theta \rangle = \left(\frac{1}{30} \right)^{1/2} \langle M_s M_L \theta | L_{m_0} | M'_s M'_L \theta \rangle \quad (3.10)$$

where L_{m_0} is a spherical component of the operator for angular momentum. It might be convenient to couple S and L and use atomic states $|\theta JM\rangle$. In this instance,

$$\langle \theta JM | T_{m_0}^K | \theta' J' M' \rangle = (-1)^{J-M} \begin{pmatrix} J & K & J' \\ -M & m_0 & M' \end{pmatrix} \langle \theta J || T(K) || \theta' J' \rangle \quad (3.11)$$

and the reduced-matrix element is

$$\delta_{s,s'} (-1)^{L'+J+S+K} \left\{ \frac{(2J+1)(2J'+1)}{2K+1} \right\}^{1/2} \begin{Bmatrix} J' & L' & S \\ L & J & K \end{Bmatrix} \langle \theta || V(K) || \theta' \rangle. \quad (3.12)$$

The expressions (3.9)–(3.12) apply for $l = 2$, and are the essential building blocks; they enable one to calculate the mean value $\langle T_{m_0}^K \rangle$ with a ground-state wave function for a 3d ion of any degree of complexity created by, e.g., covalency, the spin-orbit interaction, the crystal field, and full multiplet calculations.

4. Odd-order Bragg reflections and circular dichroism

The configuration of the magnetic moments in the ordered state is often such that the unit-cell amplitude factor contains only $K = 1$ and 3, e.g. a collinear antiferromagnet. More generally, these two contributions to $\langle Z \rangle$ appear at odd-order satellite reflections, and $K = 0$, 2 and 4 appear at even-order satellite reflections. Thus, it is worth revisiting the expression for the amplitude factor to consider its form when the sum on K is restricted to the odd values.

One can show that, for an E2 absorption event and a valence shell with orbital angular momentum l , the terms in the sum on K in the right-hand side of (3.1) with $K = 1$ and 3 are

$$\langle Z(\mathbf{d}) \rangle = \left(\frac{2}{5} \right)^{1/2} \Phi \frac{1}{l(2l+1)} \left\{ \langle \mathbf{L} \rangle_{(xyz)} \cdot \mathbf{H}^{(1)} + \frac{1}{(l-1)(2l-1)} \langle \mathbf{\Lambda} \rangle_{(xyz)} \cdot \mathbf{H}^{(3)} \right\}. \quad (4.1)$$

In (4.1), $\langle \mathbf{L} \rangle$ is the mean value of the orbital angular momentum and its appearance was anticipated in (3.10). The second operator in (4.1), $\mathbf{\Lambda}$, is of rank three and has the reduced-matrix element

$$\begin{aligned} \langle \mu || \mathbf{\Lambda} || \mu' \rangle &= \left(\frac{1}{2} \right) \langle \mu || \sum_j \{ l_0(5l_0^2 - 3l(l+1) + 1) \}_j || \mu' \rangle \\ &= \frac{1}{2} (l || l || l) \{ (l-1)(2l-1)(l+2)(2l+3) \}^{1/2} \langle \mu || T(3) || \mu' \rangle \end{aligned} \quad (4.2)$$

in which l_0 ($\equiv l_z$) is the diagonal orbital operator. The reduced-matrix element in the second equality is calculated from (3.9) or (3.12). Note that $\langle \Lambda \rangle$ does not depend on the spin operator, so the atomic character of (4.1) is exclusively about the orbital properties of the valence shell.

The expression (4.1) also determines the circular dichroic signal in the attenuation coefficient. If the signal is defined as the difference in the amplitude factors for equal and opposite values of the mean helicity in the x-ray beam, P_2 , and $\langle \Lambda \rangle$ is diagonal in the local principal axes one finds ($l = 2$)

$$\Delta Z(C) = -\frac{1}{50} \Phi P_2 \cos \varphi \left\{ \langle L_0 \rangle - \left(\frac{5}{3} \cos^2 \varphi - 1 \right) \langle \Lambda_0 \rangle \right\} \quad (4.3)$$

where φ is the angle enclosed by the principal axis and the direction of the beam. For a simple antiferromagnet the dichroic signal, being the sum of (4.3) evaluated at φ and $\varphi + \pi$, is zero. Suitably normalized, equation (4.3) is the analogue for E2 events of the sum rule for E1 events proposed by Thole *et al* (1992). For reference, the standard normalization factor applied to the dichroic signal is $3\Phi n_h/50$. Evaluated for $f^{13} 2F_{7/2}$, the expressions (4.1) and (4.2) reproduce the dichroic signal used by Giorgetti *et al* (1995) in the interpretation of their data collected for Yb^{3+} . Should $\langle \Lambda \rangle$ not be diagonal in the principal axes the complete version of the circular dichroic signal is obtained from the results for $\mathbf{H}^{(3)}$ given by Lovesey (1996) and (4.1).

Table 2. The components of $\mathbf{C}^{(K)}(\beta, \alpha) \cdot \mathbf{H}^{(K)}$ are shown for $K = 1$ and 3, see (3.4) and (5.1). For each K there are two components labelled by the state of polarization in the secondary beam, namely, σ' and π' (σ - and π -polarizations are, respectively, perpendicular and parallel to the plane defined by the primary and secondary beams of x-rays). The primary beam is purely σ -polarization. In the far left column in round brackets is a factor that is common to the two components. The beam of x-rays is deflected through an angle θ (=twice the Bragg angle).

	$\sigma' \sigma$	$\pi' \sigma$
$K = 1$ ($i/(2\sqrt{10})$)	$\sin \theta \cos \beta$	$-\sin(\frac{3}{2}\theta + \alpha) \sin \beta$
$K = 3$ ($-i/(8\sqrt{10})$)	$\sin \theta (3 \cos \beta + 5 \cos 3\beta)$	$\frac{3}{4} \sin(\frac{3}{2}\theta + \alpha) (\sin \beta + 5 \sin 3\beta)$ $+ \frac{5}{4} \sin(\frac{1}{2}\theta + 3\alpha) (3 \sin \beta - \sin 3\beta)$

5. Examples

The results in the previous section are illustrated by considering two examples. In both examples the mean values of \mathbf{L} and Λ are diagonal in the local principal axes. Using (3.4),

$$\langle \mathbf{L} \rangle_{(xyz)} \cdot \mathbf{H}^{(1)} = \langle L_0 \rangle \mathbf{C}^{(1)}(\beta, \alpha) \cdot \mathbf{H}^{(1)} \quad (5.1a)$$

and

$$\langle \Lambda \rangle_{(xyz)} \cdot \mathbf{H}^{(3)} = \langle \Lambda_0 \rangle \mathbf{C}^{(3)}(\beta, \alpha) \cdot \mathbf{H}^{(3)} \quad (5.1b)$$

and for the two examples we give values for $\langle L_0 \rangle$ and $\langle \Lambda_0 \rangle$. The geometric factors in (5.1) are listed in table 2. The dichroic signal is obtained using (4.3). In the remaining part of this section the focus is on the diffracted signal.

5.1. $Ni^{2+}({}^3F)$ in NiO

Recent surveys of the electronic structure of transition-metal oxides are found in Corti *et al* (1997), Tjernberg *et al* (1997), and references therein. In the paramagnetic phase of NiO the 3d ion is subjected to a crystal field with cubic symmetry. Below the Néel temperature a contraction along $\langle 111 \rangle$, which increases with decreasing temperature, brings the symmetry of the environment to rhombohedral. The ground-state orbital wave function is non-degenerate and purely real:

$$|\Gamma_2\rangle = \frac{i}{\sqrt{2}} \{|2\rangle - |-2\rangle\}$$

where $|2\rangle \equiv |L = 3, M_L = 2\rangle$, etc. To this wave function the spin-orbit interaction adds contributions from states higher in energy. Keeping to diagonal terms in the interaction and the first state, of Γ_5 symmetry, one finds (Abragam and Bleaney 1970)

$$|\psi\rangle = |S = 1, M_s\rangle \left\{ |\Gamma_2\rangle + \frac{i}{4}(g - 2)M_s|\Gamma_5\rangle \right\} \quad (5.2)$$

where $g = 2.23$ is the gyromagnetic factor and $g - 2$ is proportional to the strength of the spin-orbit interaction. With (5.2) one finds, of course,

$$\langle L_0 \rangle = \langle \psi | L_0 | \psi \rangle = (g - 2)\langle S \rangle. \quad (5.3a)$$

At zero temperature, $\langle S \rangle = 0.81$. Using entries in table 1,

$$\langle \Lambda_0 \rangle = \langle \psi | \Lambda_0 | \psi \rangle = \frac{3}{2}\langle L_0 \rangle. \quad (5.3b)$$

Anisotropy of the form $\mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$ leaves the easy axis aligned with $[1, 1, -2]$.

Consider an antiferromagnetic configuration of the moments with the easy axis perpendicular to the plane of scattering, defined by the primary and secondary beams of x-rays. From table 2 for the geometric factors in (5.1) one learns that, for pure σ -polarization in the primary beam, and $\beta = 0$ and π , the $\pi'\sigma$ -channel is zero. A short calculation reveals the same result for the $\sigma'\sigma$ -channel, since the contributions to the amplitude factor for $K = 1$ and 3 are equal in magnitude and opposite in sign; cf. section 5.2. These two results lead to the conclusion that, when the easy axis is perpendicular to the plane of scattering the Bragg intensity is zero.

As a second case, let the easy axis lie in the plane of scattering, for which $\beta = \pi/2$. The $\sigma'\sigma$ -channel is still zero, and for the $\pi'\sigma$ -channel

$$\langle Z(\mathbf{d}) \rangle = \frac{-i}{80} \Phi(g - 2)\langle S \rangle \sin(\theta + 2\alpha) \cos\left(\frac{\theta}{2} - \alpha\right). \quad (5.4)$$

Here, α is the angle enclosed by the easy axis and the x -axis (the scattering geometry is fully described by Lovesey and Collins 1996), and θ is the angle through which the beam is deflected. The unit-cell amplitude factor is constructed from (5.4) and the spatial phase factors. It will be useful to confirm by experiments the polarization selection rules that we have established, and the angular dependence of the intensity in the $\pi'\sigma$ -channel, equation (5.4).

5.2. $Cu^{2+}({}^2D)$ in an octahedral crystal field

The wave function in this example is derived by diagonalizing a Hamiltonian that contains the spin-orbit interaction, a crystal-field interaction of O_h symmetry and a Zeeman energy

created by a magnetic field along the [001] axis of the crystal field (Saintavit *et al* 1995). In terms of states $|J, M\rangle$, with $J = \frac{3}{2}$ and $\frac{5}{2}$, the wave function of the ground state is

$$|\psi\rangle = \sin\phi \left| \frac{3}{2}, \frac{3}{2} \right\rangle + \frac{1}{\sqrt{6}} \cos\phi \left\{ \left| \frac{5}{2}, \frac{3}{2} \right\rangle + \sqrt{5} \left| \frac{5}{2}, -\frac{5}{2} \right\rangle \right\}. \quad (5.5)$$

The mixing angle ϕ is fixed by the ratio of the strengths of the spin-orbit and crystal-field interactions.

The mean values of $\langle L \rangle$ and $\langle \Lambda \rangle$ are diagonal. For the diagonal components one finds

$$\langle L_0 \rangle = \frac{1}{15} (27 \sin^2 \phi - \sqrt{6} \sin 2\phi - 22 \cos^2 \phi) \quad (5.6a)$$

and

$$\langle \Lambda_0 \rangle = \frac{1}{5} (6 \sin^2 \phi - 3\sqrt{6} \sin 2\phi - 16 \cos^2 \phi). \quad (5.6b)$$

If the spin-orbit interaction is set to zero, $\sin\phi = -(2/5)^{1/2}$. For this value of the mixing angle, $\langle L_0 \rangle = \langle \Lambda_0 \rangle = 0$, results which reflect the fact that the Γ_3 orbital is non-magnetic (Abragam and Bleaney 1970). In the opposite extreme of an infinite spin-orbit interaction, $\phi = 0$ and

$$\langle L_0 \rangle = \frac{11}{24} \langle \Lambda_0 \rangle = -\frac{22}{15}.$$

Let us consider an antiferromagnetic configuration of the moments and the easy axis perpendicular to the plane of scattering. In contrast to the first of our two examples the diffracted signal in the $\sigma'\sigma$ -channel can be different from zero. One finds ($\beta = 0$ and π)

$$\langle Z(\mathbf{d}) \rangle = \frac{i}{300} \Phi \sin\theta \cos\beta (3 \sin^2 \phi + \sqrt{6} \sin 2\phi + 2 \cos^2 \phi). \quad (5.7)$$

The amplitude factor increases with increasing order of the Bragg reflection. For arbitrary α and β the amplitude factor is constructed from the entries in table 2 and (5.6).

In an expansion of (5.7) in powers of the ratio of the strengths of the spin-orbit and crystal-field interactions the leading term is quadratic in the ratio. This finding shows that (5.7) for Cu^{2+} and the corresponding null result for the model of Ni^{2+} are consistent, since the latter model is valid only up to terms linear in the spin-orbit interaction.

Polarization in the diffracted beam can be calculated using formulae given by Lovesey *et al* (1998).

6. Conclusions and discussion

On the basis of the atomic picture of 3d transition ions, the scattering length has been calculated for a primary energy tuned to the K edge of an ion and an E2 (quadrupole) absorption event. The scattering length is used to examine the amplitude of Bragg diffracted x-rays, and the circular dichroic signal in the attenuation coefficient. A parallel study for an E1 absorption event has been reported by Lovesey and Grimmer (1997).

The scattering length is determined by the orbital angular momentum of the valence shell and, also, a trivial entry proportional to the number of holes in the shell. For K-shell absorption and the level of approximation deployed in calculating the scattering length, no information is available on the spin state of the valence shell. Set against this finding, Hill *et al* (1997) ascribe the signal measured by diffraction from NiO to the spin moment of the nickel ion. Formulae given here permit the scattering length to be calculated for a ground-state wave function of an arbitrary degree of complexity. The easy axis of the

resonant 3d transition ion can be at any orientation with respect to the frame of reference established by the experiment.

In one example calculation, suitable for NiO, the orbital moment in the ground state is created by the action of the spin-orbit interaction within the states of the crystal field. Using a standard treatment, by perturbation theory, the amplitude factor is shown to be proportional to the induced orbital moment $(g - 2)\langle S \rangle$, where g is the principal gyromagnetic factor and $\langle S \rangle$ is the mean value of the spin (even at zero temperature $\langle S \rangle < S$ due to zero-point spin fluctuations in an antiferromagnet). The second example calculation does not treat the spin-orbit interaction by perturbation theory, and thus one can explore the amplitude factor as a function of the strength of the interaction. The symmetry is Γ_3 , which is non-magnetic, and for zero spin-orbit interaction the amplitude factor is also zero.

Both examples display selection rules for the polarization of the primary and secondary beams, which might usefully be exploited in experiments. Different selection rules apply depending on the orientation of the easy axis of magnetization relative to the plane of scattering, and the formalism offered allows these to be derived for the general case.

Our theory applied to the ion $3d^5$ with $L = 0$ yields a null value for the E2 scattering length, $\langle f \rangle$. A value of $\langle f \rangle$ for this ion different from zero is predicted if splitting of the 1s core state is allowed for. Referring to (2.1), one now has $\Delta = \Delta(\bar{M}) = \bar{M}\Delta_0$ where Δ_0 is the size of the exchange interaction, the core-level magnetic quantum number $\bar{M} = \pm\frac{1}{2}$ and the energy of the adsorption edge is chosen as the origin of the energy scale. Following Lovesey *et al* (1998), the scattering length is found to be

$$\langle f \rangle = -(eq)^2 \sum_{\bar{M}} \left\{ E - \Delta(\bar{M}) + \frac{i}{2}\gamma \right\}^{-1} \sum_{\mathbf{d}} \exp\{i\mathbf{k} \cdot \mathbf{d} - W_d(\mathbf{k})\} \langle Z(\mathbf{d}) \rangle_{\eta}$$

and for the ion $3d^5$ the amplitude factor

$$\langle Z(\mathbf{d}) \rangle_{\eta} = \frac{1}{20} \Phi(\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon}) \cos \theta \left\{ 1 + \frac{4}{5} \langle S \rangle \bar{M} \cos \beta \right\}.$$

In this expression, $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}'$ are the polarization vectors of the primary and secondary beams, respectively. In the cross-section for Bragg diffraction we use the expression

$$(\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon})^2 = \frac{1}{2} (1 + \cos^2 \theta + P_3 \sin^2 \theta)$$

where P_3 is the component of the Stokes vector that measures the linear polarization in the primary beam, and for pure σ -polarization, nearly realized with a synchrotron source, $P_3 = 1$. It is notable that $\langle f \rangle$ is zero in the channels of scattering in which the primary polarization is rotated, and for pure σ -polarization it is proportional to $\cos \theta$ and thus decreases in size with increasing order of the Bragg reflection. For a collinear antiferromagnet $\cos \beta$ alternates in sign between ions in the unit cell, labelled by \mathbf{d} , and $\langle f \rangle$ is proportional to the spin magnetic moment and Δ_0 . A calculation of Δ_0 for $3d^5$ by van der Laan (1997) shows that it is very small, so $\Delta_0 \ll \gamma$. The attenuation coefficient is proportional to the imaginary part of $\langle f \rangle$ evaluated with $\mathbf{k} = 0$. The predicted attenuation coefficient, being independent of the primary polarization, does not contain a dichroic signal, unlike the diffraction cross-section.

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