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The importance of the magnetic dipole term in magneto-circular x-ray absorption dichroism for 3d transition metal compounds

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Abstract. The application of the magneto-circular x-ray absorption dichroism (MCXD) spin sum rule for 3d transition metal compounds faces two problems: the unknown value of the magnetic dipole operator T_z and the division between the L_2 and L_3 edges. A systematic study of the order of magnitude of the T_z -operator for $3d^n$ ions is presented. The variation of the T_z -values with temperature is described and analysed, for all cases from d^1 to d^9 cations in two different situations. Firstly the perfect octahedral case is considered. It is shown that T_z is non-zero for low temperature; but, as it originates only from d-electron spin-orbit splitting, it is washed out at room temperature. Secondly, a model of the surface situation is considered. In this case T_z originates mainly from the crystal-field splitting. It then exhibits quite large values at any temperature and can by no means be neglected when applying the sum rule. The error introduced in the sum rule due to the mixing of L_2 and L_3 edges has been estimated.

1. Introduction

In the past few years, thanks to technological advances in synchrotron radiation facilities, there has been much activity in the study of the magnetic properties of materials using photon beams. X-ray magnetic dichroism is one of the new tools for investigating the magnetism of transition metal systems [1, 2, 3]. In 1975 Erskine and Stern [4] predicted the occurrence of dichroism in x-ray absorption spectroscopy (XAS). Both linear and circular dichroism can exist in XAS. In the first case, a difference in absorption for two different linear polarizations of light is measured while magneto-circular x-ray dichroism (MCXD) measures the difference in absorption between left- and right-polarized light sources. This paper is concerned only with this latter kind of dichroism. For $L_{2,3}$ edges of 3d transition metal compounds and $M_{4,5}$ edges of rare-earth compounds the MCXD spectra can be interpreted with sum rules established by Thole and Carra [6, 7] which relate the dichroic spectra to the magnetic moments of the valence shell probed by the absorption process. In the case of $L_{2,3}$ absorption edges of transition elements, the 2p XAS spectrum is dominated by dipole-allowed transitions to d final states (it is known that the s channel can be neglected, compared to the d channel, in this dipolar process [5]). The orbital sum rule relates the dichroic spectrum area to the value of the orbital magnetic moment L_z in the initial state before the x-ray absorption process has occurred [6]:

$$\frac{-1}{2n_h} \langle L_z \rangle = \int_{L_{2,3}} (\mu^+ - \mu^-) dE / \int_{L_{2,3}} (\mu^+ + \mu^0 + \mu^-) dE.$$

The denominator of the right-hand side of this expression is the isotropic XAS spectrum area formed by the sum of the right (μ^+), left (μ^-) and linear (μ^0) polarization absorption cross sections for the z -axis, the numerator being the dichroic spectrum area. In the left-hand side n_h and $\langle L_z \rangle$ appear; these denote the number of holes in the d shell and the thermal average value of the orbital moment for the d shell, both of these quantities being defined for the ground state before the absorption process has occurred.

Due to the spin-orbit coupling of the 2p core level, the 2p XAS spectrum is divided into two parts, namely the L_2 and L_3 edges. Based on the measurement of the MCXD spectrum areas for the two edges, the spin sum rule enables an estimation to be made of the spin magnetic moment S_z in the initial state before the x-ray absorption process has occurred [7]:

$$R_S = \frac{2}{3n_h} \langle S_z \rangle + \frac{7}{3n_h} \langle T_z \rangle$$

$$= \left(\int_{L_3} (\mu^+ - \mu^-) dE - 2 \int_{L_2} (\mu^+ - \mu^-) dE \right) / \int_{L_{2,3}} (\mu^+ + \mu^0 + \mu^-) dE. \quad (1)$$

The denominator of the right-hand side of this expression is the isotropic XAS spectrum area formed by the sum of the right (μ^+), left (μ^-) and linear (μ^0) polarization for the z -axis. In this expression T_z appears, which is analogous to a magnetic dipole operator:

$$T = \sum_i t_i = \sum_i s_i - 3 \frac{\mathbf{r}_i(\mathbf{r}_i \cdot \mathbf{s}_i)}{r_i^2}.$$

The total operator T corresponds to a summation, with index i , over the d electrons of a one-electron operator t . In the z -direction, $t_z = s_z(1 - 3 \cos^2(\theta))$. In equation (1) $\langle S_z \rangle$ and $\langle T_z \rangle$ refer to the thermal average values of the spin and magnetic dipole operators for the d shell in the ground state.

The expressions given above are written for the electric dipolar approximation for the spectral shape. We just mention the existence of an extension of the sum rules including electric quadrupolar transitions [8].

These two sum rules are of considerable interest for the study of magnetism. Indeed they enable an element- and shell-specific measure of the orbital and spin orbital moments to be obtained (in the present case of $L_{2,3}$ edges the d shell of the transition metal is probed). Moreover the orbital and orbital moment are estimated separately. Unfortunately the effective application of the rules faces several drawbacks. Firstly the experiments are not very easy to handle and present specific problems that we shall not discuss in the present paper; for an example of a description of an experiment, see [9]. Secondly the determination of the isotropic spectrum and of the number of holes in the ground state n_h is often problematic. However, the orbital angular momentum sum rule is usually admitted, and this rule tends to be commonly used. Indeed both theoretical [10] and experimental [11] checking confirms its applicability. In contrast, the applicability of the spin sum rule is still debated as it raises two specific problems.

Firstly the problem of the L_2 - and L_3 -edge separation should be treated cautiously. Indeed Carra *et al* indicate [7] that the sum rule is written with the following assumption: the L_2 and L_3 parts of the spectrum are sufficiently separated that the mixing of the two edges by core-valence interactions is negligible. For the early-transition-metal cations of the first series this is obviously not the case, as the L_2 and L_3 edges cannot be distinguished in the spectral shape. In [7] the authors consider that at the end of the first transition series the error induced is smaller than 5%.

Secondly the T_z -term that appears in the sum rule is regarded as troublesome. Indeed one usually wishes, with this rule, to determine the value of the spin momentum. It is therefore better to study conditions in which this term is negligible. In [7] it is claimed that, in 3d transition metal compounds for O_h cation site symmetry, the T_z -part can be neglected, the reason being that only spin-orbit coupling can produce a non-zero T_z and that this coupling is small enough to allow the neglect of T_z within an accuracy of 15%. This is indeed the case for transition metals such as iron, cobalt or nickel. This has been demonstrated by band-structure calculations, in which a T_z/S_z ratio of less than 1% is expected [12]. We can, however, note that, even for metals, Wu *et al* [10] expect large values for T_z if the surrounding of the metallic atoms deviates from the perfect octahedral situation of the bulk.

For rare-earth or transition metal compounds (oxides or halides for instance) the situation appears much less clear. Indeed a calculation made by Arrio *et al* [13] for a d^9 ion in octahedral symmetry shows that at zero temperature, T_z can be quite large and even larger than S_z . Not knowing the value of T_z often makes the rule inapplicable (see, for example, [14]). This difference between transition metals and transition metal compounds can be tracked in the huge difference in electronic structure between these two kinds of material. In transition metal compounds band-structure effects are much less important than in transition metals, in which they play a leading role. In contrast, the electronic structure of the d orbitals of the cations in transition metal compounds is dominated by local effects, the two major ones being intracationic electronic interactions and crystal-field splitting induced by the oxygen anions.

We present in this paper a study of the two specific problems of the spin sum rule in the case of transition metal compounds (as opposed to transition metals). To estimate the importance of the T_z -term for transition metal compounds we address the question of the orders of magnitude of the T_z -operator through the 3d transition series. We show calculations of T_z -values in two typical situations: perfect octahedral surroundings of the cation and an example of a surface case. We highlight, for a given ion and geometry, the variation of the T_z -values with temperature. Our goal there is not to produce tables of T_z -values for direct use, but to exhibit trends and orders of magnitude for different temperatures and d^n configurations.

Secondly we tackle briefly the problem of the separation of the L_2 and L_3 edges.

The next section presents our calculation method. Then we present and discuss our results for T_z in the octahedral situation and in the surface situation. The last section deals with the separation of the L_2 and L_3 edges.

2. Calculation method

Our calculations are based on a configuration interaction (CI) semi-empirical cluster approach already used in [15, 16]. We recall briefly the characteristics of our method. We consider a cluster made up of a transition metal cation surrounded by its oxygen first neighbours. The d and 2p orbitals of the cation are considered. The calculation is made in the ionic limit so that no hybridization occurs between the cations and the oxygen ions. The Hamiltonian acting on the cation takes into account the crystal-field splitting in a point charge model, the intracationic electronic repulsions (i.e. d-electron interactions and electron-core-hole interactions), and spin-orbit coupling of 2p and d orbitals of the cation. This Hamiltonian is written in a multielectronic basis made up of Slater determinants.

In order to study the values of T_z through the first transition series we considered one example of a cation for each d^n configuration from $n = 1$ to $n = 9$ (see table 1). Only one type of cation was considered for each configuration, as it is known that the differences

Table 1. d^n cations used in the calculations.

| d^n | Cation |
|-------|-----------|
| d^1 | V^{3+} |
| d^2 | V^{2+} |
| d^3 | Cr^{3+} |
| d^4 | Cr^{2+} |
| d^5 | Mn^{2+} |
| d^6 | Fe^{2+} |
| d^7 | Co^{2+} |
| d^8 | Ni^{2+} |
| d^9 | Cu^{2+} |

between the parameters of the different d^n cations produce only small differences in XAS spectra [17, 18]. The Slater integrals appearing in intracationic elements of the Hamiltonian were taken from Hartree–Fock *ab initio* calculations [17], but these values obtained by the one-electron method should be reduced to account for intra-atomic correlation effects before use in configuration interaction calculations [19]. We chose a multiplicative factor of 80%. The spin–orbit coupling parameters are taken from the same Hartree–Fock calculations [20].

In our point charge model the crystal-field splitting, for a given set of atomic positions, depends on two parameters $\overline{r^2}$ and $\overline{r^4}$. See [21] for details of the crystal-field calculations. In the particular case of O_h symmetry, only $\overline{r^4}$ acts on crystal-field splittings. The crystal-field splitting was taken to be $10Dq = 1.5$ eV. This corresponds, for the cation–oxygen distance we chose (2 Å), to $\overline{r^4} = 1.0$ Å⁴.

We have chosen the z -axis of quantization along a cation–oxygen direction. A supplementary term in the Hamiltonian can be introduced to mimic the effect of a magnetic or interatomic exchange field in this direction. In the present work, in order to reproduce a magnetic arrangement, we introduced an exchange field which splits the up and down electrons by an energy V_H . We chose $V_H = 0.05$ eV as this is the value used in the original paper by Carra *et al* [7].

At 0 K the cation is in the ground state, i.e. only the eigenvectors corresponding to the lowest eigenvalue of the Hamiltonian are populated. The ground state is either non-degenerate, in which case it is represented by one vector, or degenerate, in which case it is represented by an equally distributed set of orthogonal eigenvectors forming a basis of the ground-state eigenspace. At non-zero temperature, higher-energy eigenvectors are populated. The distribution weights of the eigenvectors of the Hamiltonian in the equilibrium state follow a Maxwell–Boltzmann law.

The calculation of S_z and T_z develops as follows: consider Φ , an eigenvector of the Hamiltonian. Φ is expressed as a linear combination of Slater determinants:

$$|\Phi\rangle = \sum_i a_i |(d^n)_i\rangle.$$

In the summation, i runs over the Slater determinants of the d^n configuration of the ion.

Let O_z be a mono-electronic operator acting on the d electrons of the cation, namely S_z or T_z . The mean value of O_z in the Φ state is given by $\langle O_z \rangle = \langle \Phi | O_z | \Phi \rangle$. O_z , being a summation over d electrons of the mono-electronic operator o_z , can be expressed in the framework of second quantization as

$$O_z = \sum_{\alpha\beta} (o_z)_{\alpha\beta} C_\alpha^+ C_\beta$$

where α and β run over the d spin orbitals and $(o_z)_{\alpha\beta}$ is the matrix element of o_z connecting α - and β -orbitals. In order to calculate this expression, one has to calculate the o_z -matrix in the basis of one-electron d functions.

We used the usual $t_{2g}-e_g$ d-orbital basis set made up of $d_{x^2-y^2}$, $d_{3z^2-r^2}$, d_{xy} , d_{zx} and d_{yz} for the orbital part; the spin part, indicated by m_s , equals up or down.

Table 2. Top: the T_z -matrix in the spherical harmonics basis set. Bottom: the T_z -matrix in the $t_{2g}-e_g$ basis set.

| | $-2 \uparrow$ | $-1 \uparrow$ | $0 \uparrow$ | $1 \uparrow$ | $2 \uparrow$ | $-2 \downarrow$ | $-1 \downarrow$ | $0 \downarrow$ | $1 \downarrow$ | $2 \downarrow$ |
|------------------------|----------------------|----------------------------------|----------------------------------|----------------|-----------------|------------------------|------------------|---------------------------------|---------------------------------|-----------------|
| $-2 \uparrow$ | 2/7 | | | | | | -3/7 | | | |
| $-1 \uparrow$ | | -1/7 | | | | | | $\frac{1}{7}\sqrt{\frac{3}{2}}$ | | |
| $0 \uparrow$ | | | -2/7 | | | | | | $\frac{1}{7}\sqrt{\frac{3}{2}}$ | |
| $1 \uparrow$ | | | | -1/7 | | | | | | 3/7 |
| $2 \uparrow$ | | | | | 2/7 | | | | | |
| $-2 \downarrow$ | | | | | | -2/7 | | | | |
| $-1 \downarrow$ | -3/7 | | | | | | 1/7 | | | |
| $0 \downarrow$ | | $-\frac{1}{7}\sqrt{\frac{3}{2}}$ | | | | | | 2/7 | | |
| $1 \downarrow$ | | | $-\frac{1}{7}\sqrt{\frac{3}{2}}$ | | | | | | 1/7 | |
| $2 \downarrow$ | | | | 3/7 | | | | | | -2/7 |
| | $x^2 - y^2 \uparrow$ | $z^2 \uparrow$ | $xy \uparrow$ | $zx \uparrow$ | $yz \uparrow$ | $x^2 - y^2 \downarrow$ | $z^2 \downarrow$ | $xy \downarrow$ | $zx \downarrow$ | $yz \downarrow$ |
| $x^2 - y^2 \uparrow$ | 2/7 | | | | | | | | -3/14 | -3i/14 |
| $z^2 \uparrow$ | | -2/7 | | | | | | | $-\sqrt{3}/14$ | $i\sqrt{3}/14$ |
| $xy \uparrow$ | | | 2/7 | | | | | | 3i/14 | -3/14 |
| $zx \uparrow$ | | | | -1/7 | | -3/14 | $-\sqrt{3}/14$ | 3i/14 | | |
| $yz \uparrow$ | | | | | -1/7 | -3i/14 | $i\sqrt{3}/14$ | -3/14 | | |
| $x^2 - y^2 \downarrow$ | | | | -3/14 | 3i/14 | -2/7 | | | | |
| $z^2 \downarrow$ | | | | $-\sqrt{3}/14$ | $-i\sqrt{3}/14$ | | 2/7 | | | |
| $xy \downarrow$ | | | | -3i/14 | -3/14 | | | -2/7 | | |
| $zx \downarrow$ | -3/14 | $-\sqrt{3}/14$ | -3i/14 | | | | | | 1/7 | |
| $yz \downarrow$ | 3i/14 | $-i\sqrt{3}/14$ | -3/14 | | | | | | | 1/7 |

In this basis the operator S_z is, of course, diagonal. We give in table 2 the t_z -matrix, both for the spherical harmonics basis and the $t_{2g}-e_g$ basis.

As we now have the o_z -matrix, $\langle \Phi | O_z | \Phi \rangle$ can be calculated using the usual second-quantization techniques.

The expectation value of O_z in the ground state (in the equilibrium state) is then the weighted summation over the Φ eigenvectors of $\langle \Phi | O_z | \Phi \rangle$ for each eigenvector Φ contributing to the ground state (the equilibrium state).

In the last part of this paper we present some checking of the MCXD spin sum rule involving calculations of polarized XAS spectra. In the dipolar approximation for which the sum rules are written, according to the Fermi Golden Rule, the absorption cross section is given by:

$$\sigma(E) \propto \sum_F |\langle \Phi_G | \epsilon \cdot \mathbf{r} | \Phi_F \rangle|^2 \delta(E_G + h\nu - E_F)$$

where F runs over the final states.

The dipolar operator $\epsilon \cdot \mathbf{r}$ can be developed in terms of spherical harmonics Y_1^m :

$$\epsilon \cdot \mathbf{r} = r(uY_1^{-1} + vY_1^1 + wY_1^0).$$

The polarized spectra μ^+ , μ^- and μ^0 correspond to the case where $\epsilon \cdot r$ is proportional to Y_1^{-1} , Y_1^1 and Y_1^0 respectively. This leads to three sets of transition probabilities from 2p core states to d orbitals. The spectra are calculated for each of these cases. The integrations over the spectra appearing in the sum rules can then be calculated.

3. T_z in O_h symmetry

In this part we deal with the specific case of the O_h symmetry for the cation site. So we consider a central cation surrounded by six oxygen ions in perfect octahedral positions around the central cation.

We first recall the fact that in O_h symmetry $T_z = 0$ for all d^n cases when d-orbital spin-orbit coupling is set to zero [7]. A sketch of the explanation, for high-spin configurations, can be obtained by looking at the t_z -matrix in the t_{2g} - e_g basis. The exchange field introduced tends to align the spins in the z -direction. When the number of electrons on the cation is lower than five, they are all either up or down. If they are all down only the right-hand lower corner of the t_z -matrix comes into play for the calculation of T_z . This 5×5 matrix is diagonal. So the value of T_z is only the summation of t_z for all occupied orbitals in the states forming the ground state. In the d^1 case the ground state is made up of three vectors with the same probability: Φ_1 , Φ_2 and Φ_3 in which d_{xy} , d_{zx} and d_{yz} are occupied respectively. The value of T_z in this state is therefore the sum of the values of T_z for Φ_1 , Φ_2 and Φ_3 which are the values of t_z for d_{xy} , d_{zx} and d_{yz} respectively. This summation leads to $T_z = 0$. Another example is the d^3 case in which the ground state is made up of one single vector Φ with d_{xy} , d_{zx} and d_{yz} occupied. Then $T_z(\Phi) = t_z(d_{xy}) + t_z(d_{zx}) + t_z(d_{yz}) = 0$. Complete calculations of cation ground states show in the same way that T_z is zero for any d^n configuration for an octahedral cation site when d-orbital spin-orbit coupling is neglected.

Table 3. S_z - and T_z -values for O_h symmetry sites from d^1 to d^9 . In the first column the spectroscopic crystal-field terms of the ground state in an octahedral field but without d spin-orbit coupling are indicated [23]. The second column gives the energy difference between the ground state and the first excited state for the complete calculation including spin-orbit coupling. The S_z - and T_z -values are given at $T = 0$ K, 80 K and 300 K in third, fourth and fifth columns respectively.

| | Δ | $T = 0$ K | | $T = 80$ K | | $T = 300$ K | |
|---------------------|--------------------------|-----------|-----------------------|------------|-----------------------|-------------|----------------------|
| | | S_z | T_z | S_z | T_z | S_z | T_z |
| d^1 (2T_2) | 6.6×10^{-3} eV | -0.500 | 0.137 | -0.481 | 1.3×10^{-2} | -0.361 | -2×10^{-3} |
| d^2 (3T_1) | 1.31×10^{-2} eV | -0.999 | -0.131 | -0.983 | -7.9×10^{-2} | -0.818 | -8×10^{-3} |
| d^3 (4A_2) | 5.00×10^{-2} eV | -1.499 | 3×10^{-5} | -1.499 | 3×10^{-5} | -1.332 | 2×10^{-6} |
| d^4 (5E) | 1.4×10^{-3} eV | -1.999 | 0.301 | -1.998 | 3.0×10^{-2} | -1.830 | 7×10^{-3} |
| d^5 (6A_1) | 5.00×10^{-2} eV | -2.499 | 2×10^{-4} | -2.499 | 2×10^{-4} | -2.330 | 2×10^{-4} |
| d^6 (5T_2) | 2.27×10^{-2} eV | -1.937 | -6.4×10^{-2} | -1.937 | -5.5×10^{-2} | -1.805 | 9×10^{-4} |
| d^7 (4T_1) | 4.29×10^{-2} eV | -1.364 | 3.1×10^{-2} | -1.364 | 3.1×10^{-2} | -1.256 | 1.1×10^{-2} |
| d^8 (3A_2) | 4.99×10^{-2} eV | -0.997 | -1×10^{-3} | -0.996 | -2×10^{-3} | -0.836 | -2×10^{-3} |
| d^9 (2E) | 2.1×10^{-4} eV | -0.498 | -0.260 | -0.495 | -6×10^{-3} | -0.369 | -3×10^{-3} |

In contrast, d-orbital spin-orbit coupling is fully considered in our calculations (see the preceding section). Our results will thus enable us to assess the importance of spin-orbit coupling for the T_z -value. Its variation with temperature is illustrated by the three cases that

were considered: the ground state (at 0 K) and the equilibrium states at 80 K and 300 K. The values of S_z (showing the alignment of the spins in the direction of the exchange field) and T_z , in units of \hbar , for the ground state and equilibrium states are indicated in table 3.

To explain the values of table 3 one should consider spin-orbit splittings of the ground state from a perturbative point of view. In order to have a non-zero T_z for a state Φ , there should be some spin-orbit coupling in this state. Let Φ_0 be the ground state without spin-orbit coupling. When spin-orbit coupling is turned on, Φ_0 will sustain an energy change and possibly a splitting due to the supplementary interaction. This change can be of either first order or second order in ζ_d (where ζ_d is the d-electron spin-orbit coupling constant). The perturbative effect of spin-orbit coupling on Φ_0 is explained in [22]. It can be summed up by saying that the conditions for an octahedral crystal-field term to be split to first order are: the spin should be non-zero; and the orbit has to be degenerate (otherwise there is only a second-order energy change without splitting) with the exception of E which does not split to first order.

In order to support our analysis, we have also indicated in table 3 the spectroscopic crystal-field term of the ground state for each d^n ion in an octahedral field but without d spin-orbit coupling [23]. The second column gives Δ , defined as the energy difference between the ground state and the first excited state (for the complete calculation including spin-orbit coupling).

Three situations can be distinguished.

(1) The d^3 (4A_2), d^5 (6A_1) and d^8 (3A_2) cases. The orbital part of the crystal-field term on Φ_0 is not degenerate. Thus there is no first-order term of spin-orbit coupling. There is a second-order correction energy but this correction does not split Φ_0 . T_z is then zero to first order and appears only as a second-order term. In this situation T_z is very small at any temperature. The energy difference Δ is large because, as Φ_0 is not split, Δ measures a zero-order energy difference close to the energy difference between Φ_0 and Φ_1 first excited states without spin-orbit coupling.

(2) The d^1 (2T_2), d^2 (3T_1), d^6 (5T_2) and d^7 (4T_1) cases. The conditions for a first-order spin-orbit splitting are fulfilled. Thus T_z is non-zero to first order. Indeed, at $T = 0$, T_z is found to be large. T_z decreases when all spin-orbit-split sublevels tend to be equally populated with increasing temperature. The energy difference between these levels being of first order (as can be seen from the values of Δ), T_z decreases slowly when temperature is raised (see $T = 80$ K). Still, room temperature is large enough to effectively quench T_z . Note that for d^6 and d^7 configurations the spins are only partially aligned with the exchange field which leads to smaller T_z -values (see S_z - and T_z -values at 0 K). This is only due to the arbitrary choice of the exchange field and does not provide evidence of any particular behaviour.

(3) The d^4 (5E) and d^9 (2E) cases. In these two cases, spin-orbit interaction splits Φ_0 but only at second order. But the quenching of first-order values of $\mathbf{L} \cdot \mathbf{S}$ for E terms does not imply that the first-order values of T_z are quenched. Indeed in the present case the second-order $\mathbf{L} \cdot \mathbf{S}$ splitting produces for each split vector a large, first-order, value for T_z . Then T_z is large at $T = 0$ K. However, as the energy splitting between the spin-orbit-split levels is of second order (Δ is indeed small), they are quickly populated with increasing temperature. And so T_z decreases quickly with temperature (see $T = 80$ K).

This classification accounts well for the values of T_z at $T = 0$ and for the trends of variation with increasing temperature. Whatever the case may be, in all situations T_z is close to zero at room temperature.

Concerning the MCXD spin sum rule, Carra *et al* [7] claimed that T_z could be neglected

in octahedral symmetry. They expected that the effect of the T_z -term was to introduce an error of not more than 15% in the S_z -value. Our calculations show that at room temperature, the values of T_z are indeed very small and thus can be neglected. But, at very low temperature the error introduced by neglecting T_z can be much larger. This is enhanced by the fact that the T_z -value appears in the expression for the sum rule with a multiplicative factor of 7/2 compared to the S_z -value. In this case the T_z -contribution cannot be neglected. This is evidence of the importance of d-orbital spin-orbit coupling—responsible for the non-nullity of T_z . However small, it proves non-negligible in this case. At room temperature, however, its effect is hidden by thermal effects.

Table 4. S_z - and T_z -values in the surface site from d^1 to d^9 , at $T = 0$ K and $T = 300$ K. In the last column the results for calculations without spin-orbit coupling at $T = 0$ K are given.

| | $T = 0$ K | | $T = 300$ K | | $T = 0$ K, $\zeta_d = 0$ |
|-------|-----------|---------------------|-------------|---------------------|--------------------------|
| | S_z | T_z | S_z | T_z | T_z |
| d^1 | -0.499 | 0.134 | -0.373 | 0.107 | 0.1429 |
| d^2 | -0.996 | 0.268 | -0.827 | 0.222 | 0.2531 |
| d^3 | -1.499 | -4×10^{-3} | -1.328 | -3×10^{-3} | 0 |
| d^4 | -1.999 | 0.294 | -1.835 | 0.270 | 0.2857 |
| d^5 | -2.499 | -4×10^{-3} | -2.330 | -4×10^{-3} | 0 |
| d^6 | -1.998 | -0.146 | -1.858 | -0.132 | -0.1428 |
| d^7 | -1.481 | -0.217 | -1.214 | -0.178 | -0.2498 |
| d^8 | -0.994 | -9×10^{-3} | -0.827 | -8×10^{-3} | 0 |
| d^9 | -0.499 | -0.266 | -0.372 | -0.199 | -0.2857 |

4. T_z in a surface case

The contribution of T_z is expected to be larger when the cation site symmetry is lower than O_h [10], as may occur for some compounds for bulk cation sites. A symmetry reduction also appears when a surface site is considered. To illustrate this point, we analyse the situation of a cation surrounded by five oxygen ions, 2 Å distant from the cation, occupying all but one of the six positions of the perfect octahedral surroundings. The oxygen ions in these positions correspond to the first neighbours of a cation in a (100) surface of rock-salt structure. In this symmetry the crystal-field splitting depends on both $\overline{r^2}$ and $\overline{r^4}$. For $\overline{r^4}$ we used the same value as before: 1 Å⁴. For $\overline{r^2}$ we chose 0.43 Å², which leads to the following splittings of d orbitals:

$$\begin{aligned}
 E(d_{zx}) = E(d_{yz}) &= -0.65 \text{ eV} & E(d_{xy}) &= -0.2 \text{ eV} \\
 E(d_{3z^2-r^2}) &= +0.2 \text{ eV} & E(d_{x^2-y^2}) &= 1.3 \text{ eV}.
 \end{aligned}$$

We have calculated the values of S_z and T_z in the ground state and at $T = 300$ K (table 4).

Compared to the octahedral situation, the most striking change is the remanence of the large value of T_z at large temperature. The ground-state values are of the same order as the octahedral case values, but they barely decrease with increasing temperature. Note the d^3 , d^5 and d^8 cases where T_z is small as in the octahedral case. This arises simply from the fact that the filling of the orbitals is the same as in the octahedral case until the crystal field is large enough for a low-spin ground state to be obtained.

To highlight the difference between the surface and the octahedral situation we made calculations without spin-orbit coupling for the surface case (see the last column of table 4).

In the octahedral situation T_z would always be zero. In contrast, surface calculations exhibit large values for the d^1 , d^2 , d^4 , d^6 , d^7 and d^9 cases. The obvious conclusion is that, in the surface situation, spin-orbit coupling is not the only factor acting on T_z . The non-zero T_z -values come indeed from the particular crystal-field splitting. Consider for instance the d^1 case where the d electron occupies either the d_{zx} or the d_{yz} orbital, these two lying lowest in energy. The value of t_z in both of these orbitals is $1/7$ (see the t_z -matrix in the t_{2g} - e_g basis). The calculated T_z -value corresponds exactly to this value. In O_h symmetry T_z lowers to zero as the d_{xy} orbital, with a value of $-2/7$ for t_z , and d_{zx} or d_{yz} become equally populated.

Comparing the situations with and without spin-orbit coupling, one can see that its influence is relatively small, the leading effect being that of the crystal field. In the d^3 , d^5 and d^8 cases the crystal-field influence is quenched by the filling of t_{2g} or e_g orbitals. In these cases only, T_z is driven by spin-orbit coupling. But as in the octahedral situation they correspond to very small T_z -values.

The remanence of the large T_z -values at room temperature is directly related to the crystal-field origin of the non-zero values for T_z . Indeed the energy differences due to crystal-field splittings (a few tenths of an eV) are large, so they are not washed out at room temperature.

The effects that create non-zero values for T_z are thus very different in the surface case and in the octahedral situation. In the latter, only spin-orbit coupling can produce non-zero T_z . This interaction, being small, is easily screened by temperature, and so T_z is small at room temperature. In contrast, in the surface situation the crystal-field splitting is responsible for non-zero T_z -values. As the energy splittings are much larger, T_z remains important at room temperature.

The results of this surface example indicate that for transition metal compounds with low-symmetry surface or bulk cation sites, one could expect similar large and remanent values of T_z .

For the MCXD spin sum rule, our calculations show that when the spectrum includes a large signal arising from the surface cations, as happens in the ion-yield detection mode and Auger detection mode, the T_z -factor can by no means be neglected.

Should the case arise in the study of a specific case where the structure of the surface is known, crystal-field calculations in our framework would allow a guess to be made of the expected T_z -values.

The situation in transition metal compounds can be compared with what happens for rare-earth compounds. In these latter, the spin-orbit couplings are larger than the crystal-field splittings. So the large T_z originates mainly from spin-orbit coupling. For instance, in [9] Collins *et al* make an estimation of T_z -values in uranium sulphide, US. They show that it originates from f-electron spin-orbit coupling and that the effect of the crystal field can be effectively neglected. One can probably expect in this case a larger remanence of T_z with increasing temperature compared to what we calculate for spin-orbit-induced T_z -values in the octahedral situation in transition metal compounds. Indeed the rare-earth f-electron spin-orbit coupling is larger than that of 3d electrons in transition metal compounds.

5. L_2 and L_3 splitting

The fact that T_z can be non-zero does not make the spin sum rule useless. It introduces a supplementary factor in the expression for the rule. The splitting of L_2 and L_3 edges can be a more crucial problem. It is known that when 2p-core-hole spin-orbit coupling is weak, the L_2 and L_3 edges are mixed due to d-electron-2p-core-hole interactions. This is

obvious for the early 3d transition metals in which the L_2 and L_3 edges cannot be separated in the spectra. But as soon as the spin-orbit coupling constant ζ_{2p} is somewhat larger than 6 eV, the separation of the spectra into two parts is apparent [17]. When ζ_{2p} is very large these two parts correspond exactly to the excitation of an electron of the $2p_{3/2}$ (L_3 -edge) and $2p_{1/2}$ (L_2 -edge) levels.

In order to make an estimation of the error induced by L_2 - L_3 mixing, we calculated the dichroic and isotropic spectra for cations in octahedral sites for d^4 to d^8 configurations at $T = 300$ K. Note that for d^9 ions there is no possible mixing of L_2 and L_3 edges as the d shell is filled in the XAS final state, $2p^5d^{10}$. The XAS spectrum then presents only two peaks, one for each core-hole state. In this case the sum rules apply perfectly.

Table 5. Application of the MCXD spin sum rule: ground-state calculated and expected spectrum values of $2S_z + 7T_z$ in the octahedral situation at $T = 300$ K. In the last column the discrepancy between the two figures is given.

| | Calculated $2S_z + 7T_z$ | Expected $2S_z + 7T_z$ | Discrepancy |
|---------------------|--------------------------|------------------------|-------------|
| d^4 (Cr^{2+}) | -3.61 | -1.58 | 56% |
| d^5 (Mn^{2+}) | -4.66 | -3.36 | 28% |
| d^6 (Fe^{2+}) | -3.60 | -3.25 | 10% |
| d^7 (Co^{2+}) | -2.43 | -2.19 | 10% |
| d^8 (Ni^{2+}) | -1.68 | -1.53 | 9% |

The values of $2S_z + 7T_z$ were estimated from the spectra by applying the sum rule. These are to be compared with the values obtained from calculated values of S_z and T_z for the initial state appearing in the right-hand column of table 3 (see table 5). The agreement, very poor in the Cr^{2+} (d^4) and Mn^{2+} (d^5) cases, tends to be better for heavier atoms. Nevertheless the differences are important even for compounds at the end of the transition series. These results show that even at the end of the first transition series the separation between the L_2 and L_3 edges is not fully achieved and that the mixing of the two edges can affect the results for all of the elements in the first transition series.

The cases of the cations in the middle of the series deserve special stress. Indeed in these compounds the $L_{2,3}$ spectra can be divided in two parts; the L_2 and L_3 edges seem then to be separated. In fact they still mix in the sense that not all of the peaks from the low-energy part of the $L_{2,3}$ edge correspond to purely $2p_{3/2}$ (L_3 -edge) core holes; in the same way not all of the peaks from the high-energy part of the spectra correspond to purely $2p_{1/2}$ (L_2 -edge) core holes. Even if a separation of the spectra into two parts is apparent, these compounds do not fulfil the conditions of applicability defined by Carra *et al* [7]. The application of the sum rule would lead for these compounds to large errors for $2S_z + 7T_z$.

6. Conclusions

The application of the MCXD spin sum rule to cation $L_{2,3}$ edges in transition metal compounds faces two problems: the value of the magnetic dipole operator T_z and the division between the L_2 and L_3 edges. In order to study the importance of the magnetic dipole term T_z at different temperatures, we have calculated the value of the T_z -operator for all d^n cations (from d^1 to d^9) in O_h symmetry and for a model of the surface situation. For the octahedral situation non-zero values of T_z originate only from spin-orbit coupling. We have shown that this small effect leads to important T_z -values at low temperature. Nevertheless they are rapidly quenched when temperature is raised, and so the T_z -part of

the sum rule can be neglected at room temperature. In contrast, in the surface case, non-zero T_z -values originate mainly from crystal-field splittings. As these splittings are large, T_z remains important even at room temperature. It can by no means be neglected in this case.

The error introduced in the sum rule due to the mixing of L_2 and L_3 edges has been estimated. This error decreases with spin-orbit coupling of the core hole but we have highlighted that even when L_2 and L_3 edges seem to be separated in the spectrum the error introduced by their mixing can still be large. This is in particular the case for the transition cations in the middle of the first transition series.

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