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The accuracy of the spin sum rule in XMCD

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Abstract The effective spin sum rule is reviewed with a detailed analysis of the various sources for errors and deviations of this widely used X-ray Magnetic Circular Dichroism (XMCD) tool. The simulations confirm that the final state effects of the core level spin-orbit coupling and the core-valence exchange interactions (multiplet effects) are linearly related with the effective spin sum rule error. Within the ligand field multiplet approach, we have analyzed these effects, in combination with the interactions affecting the magnetic ground state, including the crystal field strength and the 3d spin-orbit coupling. We find that for the late transition metal systems, the error in the effective spin moment is between 5 and 10%. Because of the potentially large $<T_z>$ value, the spin moment can not reliably be determined for all systems other than Ni. The error for $3d^4$ systems is very large, implying that, without further information, the derived effective spin sum rule values for $3d^4$ systems have no meaning.

1. Introduction

The X-ray Magnetic Circular Dichroism (XMCD) sum rules have been introduced by Thole et al. who showed that the integral over the XMCD signal of a given edge allows for the determination of the ground state expectation values of the orbital moment $<L_z>$[1]. Carra et al introduced a second sum rule for the effective spin moment $<SE_z>$[2]. The sum rules apply to a transition between two well-defined shells, for example the transition from a 2p core state to 3d valence states in transition metal systems, where these 3d valence states are assumed to be separable from other final states. The XMCD sum rules have been reviewed in a number of recent publications[3-6].

The spin sum rule gives the expectation value of the effective spin $<SE_z>$ as a function of the difference between in absorption between left circular polarized, positive helicity, X-rays (μ_{+1}) and the absorption of right circular polarized, negative helicity, X-rays (μ_{-1}), both divided over the L_3 and L_2 edge:

$$\langle SE_z \rangle = \langle S_z \rangle + \tfrac{7}{2}\langle T_z \rangle = \frac{\int_{L_3} (\mu_{+1} - \mu_{-1}) - 2\int_{L_2} (\mu_{+1} - \mu_{-1})}{\int \mu} \cdot \frac{3}{2} \cdot \langle N_h \rangle$$

$<T_z>$ is the spin-quadrupole coupling. If this sum rule is used to determine the spin moment $<S_z>$ one has to assume that $<T_z>$ is zero or $<T_z>$ must be known from other experiments or theoretically approximated. The effective spin rule makes an additional approximation that the L_3 and the L_2 edge are not mixed and well separated. The edges must be well separated in energy because otherwise there is no clear method to divide the spectrum into L_3 and L_2. Moreover, the two edges must be pure $2p_{3/2}$ and $2p_{1/2}$. Throughout this paper we will discuss two different sum rule errors: (a) The error in the spin moment $\langle S_z \rangle$ and (b) The error in the effective spin moment $\langle SE_z \rangle$. The error in the effective spin moment $\langle SE_z \rangle$ is, as will show below, caused by the mixing of the L_3 and L_2 edges. The error in the spin moment $\langle S_z \rangle$ has, in addition, the effect of $7/2\langle T_z \rangle$.

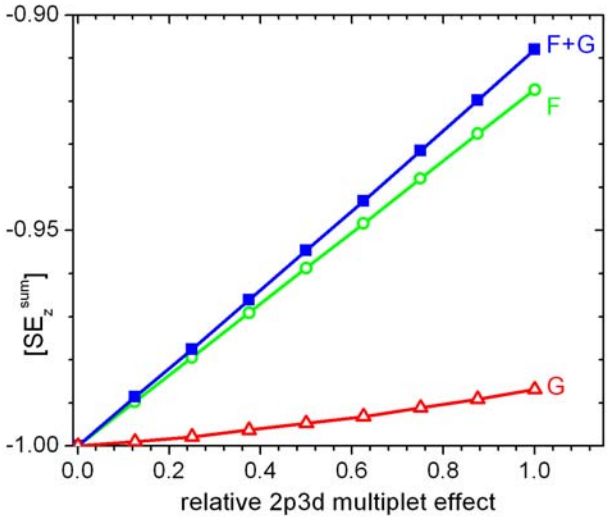

Figure 1 - The sum rule derived value [SE_z^{sum}] expectation value for Ni^{2+} (d^8) as a function of the relative 2p3d multiplet interactions (F_{2p3d} and G_{2p3d}), where 1.0 refers to the atomic Slater integral values. Three curves are given, respectively for only G_{2p3d} (red), only F_{2p3d} (green) and for the combined effect of G_{2p3d} and F_{2p3d}. (blue)

Van der Laan et al[7] use the ratio of the G_1(pd) Slater integral and the core hole spin-orbit coupling to estimate the purity of the L_2 and L_3 edges and as such the accuracy of the effective spin sum rule. This trend is confirmed in figure 1, which shows that if the 2p3d multiplet interactions F_{2p3d} and G_{2p3d} in Ni^{2+} are modified from zero to their atomic values, this decreases the sum rule value from its calculated value of -1.0 to value of approximately -0.90. The atomic values of the Slater integrals yield a 10% error. There is no error in $\langle SE_Z \rangle$ for a calculation without 2p3d multiplet effects and the relation between the 2p3d multiplet effects and the sum rule value [SE_z^{sum}] is approximately linear. An interesting observation is that the error is almost completely due to the F^2_{2p3d} Slater integral, in other words due to the dipole-dipole interactions between the 2p and 3d holes. The exchange terms (G^1_{2p3d} and G^3_{2p3d}) have little effect on the error, as is indicated by the red line. In addition, it can be shown that [SE_z^{sum}] is a function of the inverse 2p spin-orbit coupling ($1/\zeta'$), where ζ' is normalized to the atomic value of the core hole spin-orbit coupling (ζ_{ATOM}) as $\zeta'=\zeta/\zeta_{ATOM}$. In conclusion, it can be stated that if $\zeta_{2p}/\langle F_{2p3d} \rangle$ is large, the error in $\langle SE_z \rangle$ can be neglected. This also implies that the L edges of the 4d, 5d and 4f elements will have errors in $\langle SE_z \rangle$ close to zero, at least due to the multiplet and spin-orbit induced effects.

The other aspects that determine the actual error in $\langle SE_Z \rangle$ are the factors that determine the magnetic ground state, i.e. the crystal field strength, charge transfer effects, the 3d spin-orbit coupling and the magnetic (exchange) field. The effective spin sum rule has been theoretically simulated and tested by Teramura et al.[8]. They calculated the expectation values of the effective spin $\langle SE_z \rangle$, and compared them with simulated effective spin sum rule values [SE_z^{sum}]. Crocombette et al.[9] also tested the effective spin sum rule theoretically. They focus on the role of the $\langle T_z \rangle$ operator and found that in octahedral symmetry, the value of $\langle T_z \rangle$ is determined by the 3d spin-orbit coupling. Because the spin-orbit coupling is small, the value of $\langle T_z \rangle$ is close to zero at room temperature. $\langle T_z \rangle$ reaches larger values at temperatures where the 3d spin-orbit coupling causes an uneven distribution over the states. At lower symmetry the value of $\langle T_z \rangle$ is essentially given by the occupation of the respective 3d orbitals and essentially unaffected by the 3d spin-orbit coupling[9]. Van der Laan et al.[10] also discuss the role of $\langle T_z \rangle$ and its large value for small crystal field values. Wu and Freeman[11, 12] calculated the value of $\langle T_z \rangle$ for both bulk and surface 3*d* transition metals using DFT based band structure

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calculations. They find large values of $<T_z>$ at the surface, yielding $<S_z>$ errors up to 50% for the Ni(001) surface, solely due to the value of $<T_z>$. Within this approximation, the error in $<SE_z>$ is found to be small.

2. Procedure to determine the theoretical sum rule values.

In case of the 3d metal $L_{2,3}$ edges, the agreement between one-electron codes and the x-ray absorption spectral shape is, in general, poor. The reason for this discrepancy is that one does not observe the density of states in such X-ray absorption processes, due to the strong overlap of the core wave function with the valence wave functions. In the final state of an X-ray absorption process one finds a partly filled core state, for example, a $2p^5$ configuration. In case one studies a system with a partly filled 3d-band, for example a $3d^8$ system, the final state will have an incompletely filled 3d-band, which after the 2p3d transition can be approximated as a $3d^9$ configuration. The 2p-hole and the 3d-hole have radial wave functions that overlap significantly. This wave function overlap is an atomic effect that can be very large. It creates final states that are found after the vector coupling of the 2p and 3d wave functions. This effect is well known in atomic physics and actually plays a crucial role in the calculation of atomic spectra. Experimentally it has been shown that while the direct core hole potential is largely screened, these so-called multiplet effects are hardly screened in the solid state. This implies that the atomic multiplet effects are of the same order of magnitude in atoms and in solids. Ligand field theory is a model that is based on a combination of these atomic effects and the role of the surrounding ligand, approximated with an effective electric field. The starting point of the crystal field model is to approximate the transition metal as an isolated atom surrounded by a distribution of charges that should mimic the system, molecule or solid, around the transition metal. Charge transfer effects can be added to this approach, by mixing the $3d^n$ configuration with $3d^{n+1}\underline{L}$, etc[13, 14].

Within the ligand field multiplet calculations, the transition metal ion is defined with one configuration $3d^n$. The ground state expectation values of $<L_z>$, $<S_z>$ and $<T_z>$ are calculated. These ground state expectation values are affected by the 3d3d Slater integrals, the 3d spin-orbit coupling and the ligand field splitting. The 2p X-ray absorption and XMCD spectra are calculated. The spectral shape is, in addition to the ground state interactions mentioned above, determined by the 2p core hole spin-orbit coupling and the 2p3d Slater integrals. The orbital sum rule and the effective spin sum rules are applied to the calculated spectra. This theoretical sum rule calculation uses the following assumptions:

i. the division of the spectrum into its L_3 and L_2 components similar as one would use for an experimental spectrum
ii. the addition of the calculated, unbroadened, stick values for both the L_3 and the L_2 edge.
iii. the application of the effective spin sum rule. This yields the theoretical sum rule-derived value for $<SE_z>$, defined as $[SE_z^{sum}]$. The theoretical sum rule derived value for the orbital moment is defined as $[L_z^{sum}]$.
iv. The sum-rule values are compared with the calculated ground state values to determine the ratio $[SE_z^{sum}]:<SE_z>$ and $[L_z^{sum}]:<L_z>$.
v. The value of $[L_z^{sum}]:<L_z>$ is equal to one for all calculations performed, confirming the theoretical validity of the orbital moment sum rule.

3. Results

The effective spin moment sum rule has been tested theoretically for $3d^4$ Mn^{3+}, $3d^5$ Fe^{3+}, $3d^6$ Fe^{2+}, $3d^7$ Co^{2+}, $3d^8$ Ni^{2+} and $3d^9$ Cu^{2+}. The procedure we use calculates for a given ground state their spin $<S_z>$, orbital $<L_z>$ and spin-quadrupole $<T_z>$ expectation values and compares them with the sum rule values that have been derived from the multiplet simulations. The value of $<SE_z>$ is then given as

$<S_z> + 7/2<T_z>$. The calculated value for $<L_z>$ is found to be always exactly equal to the derived sum rule value. This confirms the validity of the $<L_Z>$ sum rule. Because this sum rule integrates the complete L edge, the internal structure of the L edge due to spin-orbit coupling and multiplet effects has no effect on the integrated value. The effect of temperature is not considered in the simulations here presented. All simulations were done at zero Kelvin.

In this paper, we discuss only the crystal field effects on the effective spin moment sum rule for $3d^4$ Mn^{3+}, $3d^6$ Fe^{2+} and $3d^8$ Ni^{2+}. A more complete discussion, including all other 3dn systems (for n=4 to 9), charge transfer effects and variations in the magnetic (exchange) field will be published separately.

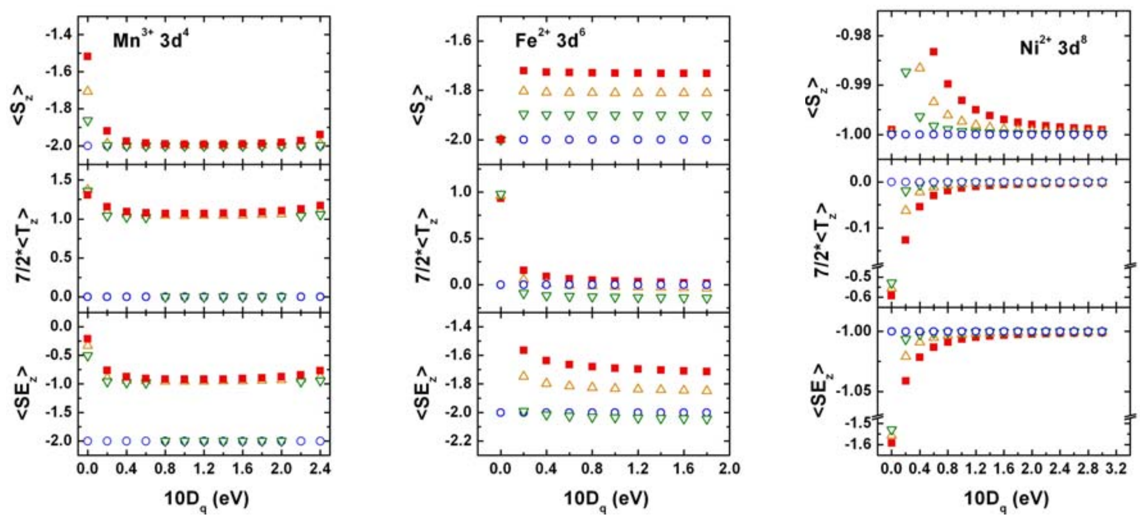

Figure 2 - The expectation values of $<S_z>$, $7/2<T_z>$ and $<SE_z>$ are given as a function of the cubic crystal field splitting 10Dq. Given are (left) Mn^{3+} $3d^4$, (middle) Fe^{2+} $3d^6$ and (right) Ni^{2+} $3d^8$. The symbols indicate calculations with: atomic 3d spin-orbit coupling (filled square, red), 60% of the atomic value (up triangle, orange), 30% of the atomic value (down triangle, green) and no 3d spin-orbit coupling (open circle, blue).

Figure 2 gives the expectation values of the spin $<S_z>$, the spin-quadrupole contribution to the sum rule $7/2<T_z>$ and the theoretical value of the effective spin $<SE_z>$ as a function of the cubic crystal field splitting 10Dq. Different curves indicate calculations with distinct magnitudes for the 3d spin-orbit coupling. Analyzing figure 1 it is seen that in case the atomic 3d spin-orbit coupling is zero (open circles), the value of $<T_z>$ is zero and $<S_z>$ is given by -0.5 times the number of unpaired electrons. A zero value for $<T_z>$ also implies that $<SE_z> = <S_z>$. For all cubic $3d^6$ and $3d^8$ systems with a crystal field above 0.5 eV, the value of 7/2 $<T_z>$ is between -0.1 and 0.1. The contribution of $<T_z>$ is therefore small and $<SE_z>$ is very close to $<S_z>$. The $3d^4$ systems present a special case with respect to the values of $<T_z>$. One can observe that there are essentially two options for $<T_z>$, (1) a value close to zero, or (2) a value close to 1.0. The origin for the value of 1.0 is that the 3d spin-orbit coupling creates a small energy difference between the $3d_{x2-y2}$ and $3d_{z2}$ states. If only the $3d_{z2}$ state is occupied, the value of $<T_z>$ is +1. In real systems, there often will be a distortion in the $3d^4$ ground state implying a $<T_z>$ value of -1 or +1.

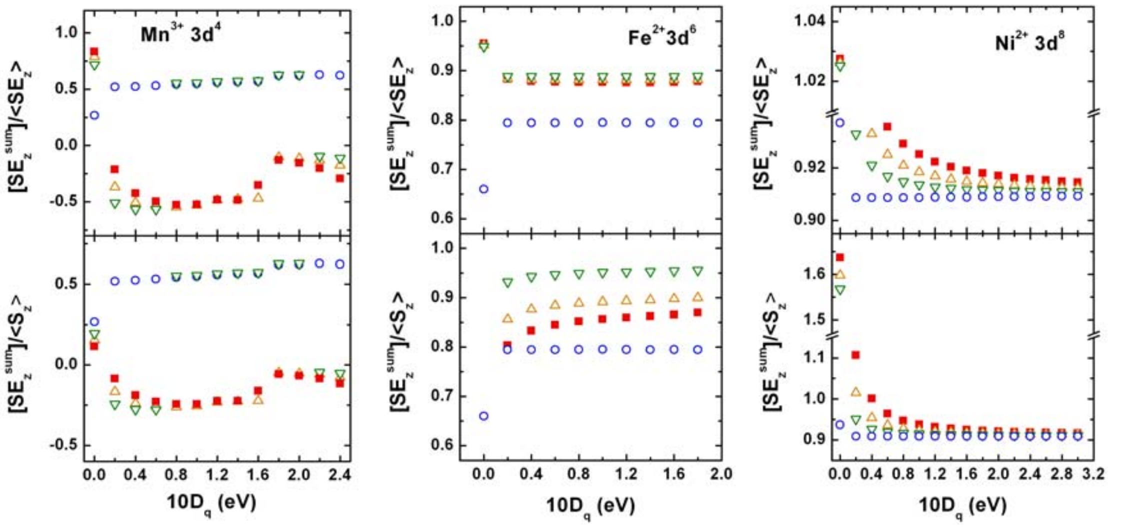

Figure 3 - The ratio of the sum rule value [SE^{sum}] with <SE_z> (top panels) and <S_z> (bottom panels) for (left) Mn^{3+} $3d^4$, (middle) Fe^{2+} $3d^6$ and (right) Ni^{2+} $3d^8$. The symbols indicate calculations with: atomic 3d spin-orbit coupling (filled square, red), 60% of the atomic value (up triangle, orange), 30% of the atomic value (down triangle, green) and no 3d spin-orbit coupling (open circle, blue).

Figure 3 gives the ratio [SE_z^{sum}]/<SE_z> (top panels) and [SE_z^{sum}]/<S_z> (bottom panels). A value of 1.0 implies that the sum rule value [SE_z^{sum}] is equal to the expectation values, respectively for <SE_z> and <S_z>. The error in the effective spin sum rule is given by [SE_z^{sum}]/<SE_z>, but the ratio with <S_z> is also given as the experimental quantity that one usually attempts to determine is <S_z>. In case of $3d^8$ Ni^{2+}, the values for [SE_z^{sum}]/<SE_z> and [SE_z^{sum}]/<S_z> are close to 0.90, except for the atomic calculations and calculations with very small crystal fields. This implies that for $3d^8$ systems one finds an underestimation in <S_z> of approximately 10%. The case of $3d^6$ Fe^{2+} shows a [SE_z^{sum}]/<SE_z> value of 0.8 without spin-orbit coupling and a value at ~0.88 with spin-orbit coupling. In case of [SE_z^{sum}]/<S_z>, the values vary between 0.80 and 0.96. This implies a <S_z> error between 4% and 20% dependent on the values of 10Dq and the 3d spin-orbit coupling.

In case of $3d^4$ Mn^{3+}, there is little relation between the sum rule value and the <SE_z> and <S_z> expectation values. In systems where 7/2<T_z>=0, the value of [SE_z^{sum}]/<SE_z> and [SE_z^{sum}]/<S_z> are approximately 0.5, implying an underestimation of 50% by the sum rule. If the 3d spin-orbit coupling and/or a symmetry distortion, splits the two lowest states, the [SE_z^{sum}]/<SE_z> value lies between -0.2 and -0.5 and the value of [SE_z^{sum}]/<S_z> lies between 0.0 and -0.3. This implies that the sum rule gives next to an underestimation of 50% to 80%, also the wrong sign for the <SE_z> (and <S_z>) value. For actual $3d^4$ systems, it is not a priori known if the ground state is degenerate or split, and one does not know if the error of the effective spin sum rule is 50% or -50%, so one is not even sure of the sign of the (effective) spin, from the derived sum rule value.

Although there are several XMCD studies on Mn^{3+} systems, the spin sum rule has been applied in only a few cases. Terai et al have measured the XMCD spectra $CaMn_1{-}xRu_xO_3$ thin films[15]. They apply a sum rule correction of 58%, based on the Mn^{4+} correction factor provided by Teramura et al. As we have shown, Mn^{3+} systems do not have a constant correction factor that ranges from +50% to -50%. Matsumoto et al. have measured $Mn_{2.97}Co_{0.03}GaC$ and they determine the spin moment without any correction and by assuming that <T_z> is zero, reaching good agreement with band structure calculations for the <L_z>/(<L_z>+2<S_z>) moment ratio[16]. Given the large corrections and potentially large <Tz> values this good correspondence seems fortuitous. Moroni et al have measured a Mn_{12}-acetate molecular superparamagnet, which is a mixed valence system containing Mn^{3+} and Mn^{4+} ions[17]. This system is compared with reference systems for the Mn^{3+} and Mn^{4+} ions and these reference systems have been analyzed with crystal field multiplet simulations. The spin moment has been calculated for the determined ground states, similar as discussed in this paper. This procedure effectively avoids the spin sum rule and its associated errors.

Concluding remarks

The simulations confirm that the final state effects of the 2p3d multiplet effects and the core hole 2p spin-orbit coupling are linearly related with the effective spin sum rule error, that is the error scales exactly with $\langle F_{2p3d} \rangle/\zeta_{2p}$, in agreement with previous results. The effective spin sum rule error for the $3d^4$ to $3d^9$ systems as a function of (1) the crystal field effects and (2) the 3d spin-orbit coupling show errors of 5 to 10% for $3d^8$ Ni^{2+} and 5 to 20% for $3d^6$ Fe^{2+}. For the case of a $3d^4$ Mn^{3+} ground state, the error is very large and varies between -50% to +50%. This implies that, without further information, the derived effective spin sum rule values for $3d^4$ Mn^{3+} has essentially no meaning. The $3d^4$ ground state is strongly affected by the Jahn-Teller distortion, which is strongly linked with the magnitude of the $\langle T_z \rangle$ value.

The $3d^5$, $3d^7$ and $3d^9$ systems as well as the effects of the inclusion of charge transfer effects and the effects of the variation of the magnetic (exchange) field will be studied in a separate paper. This paper will also discuss various routes that are suggested to correct the effective spin sum rule errors.

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