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# X-ray magnetic circular dichroism spectra and distortions at $Fe^{2+}$ $L_{2,3}$ edges

Xin Wang [a], Frank de Groot [b] and Stephen P. Cramer [a]

[a]Department of Applied Science, University of California, Davis, CA 95616
[b]Solid State Physics, University of Groningen, The Netherlands

We have shown from ligand field multiplet calculations that the shape of X-ray magnetic circular dichroism (XMCD) spectra changes drastically with the distortion parameter Ds. The temperature dependence study of XMCD makes it possible to determine both Ds and spin-orbit coupling.

## 1. INTRODUCTION

X-ray magnetic circular dichroism (XMCD) is a new experimental technique with promising future for site-specific characterization of metals in complex. By observing the XMCD signal, we can investigate the magnetic and electronic structure of 3d transition metals and rare earth compounds. XMCD was predicted theoretically by Thole *et al.* (1) using ligand field multiplet calculations, and experimentally then demonstrated at the $L_3$ and $L_2$ edges of transition metals (2-3). XMCD spectra of transition metal ions have been calculated in $O_h$ symmetry (4). There are several powerful sum rules being developed (5) which allow determination of the average values for $<S_z>$ and $<L_z>$.

In this paper, we demonstrate that the shape of XMCD spectra changes drastically not only with a crystal field, exchange field and spin-orbit interactions, but also with the presence of distortion for a certain ground state. When the distortion is in the same order of the spin-orbit interaction, the ground state character changes with the distortion parameter Ds, and some excited states cross the ground state. In some cases the energy splitting is very small, causing the XMCD spectra shape to be very sensitive to temperature.

## 2.GROUND STATE CHARACTER OF TETRAGONAL DISTORTIONS

The effect of distortion on XMCD spectra is studied for high-spin $Fe^{2+}$ $L_{2,3}$ edges. In the ligand field multiplet calculations, the transition channels for $d^6$ L edge can be approximated as $2p^6 3d^6 \text{->} 2p^5 3d^7$. The ground state $^5D_4$ in spherical symmetry $O(s)$ is reduced to $^5T_2$ in the presence of a crystal field with octahedral symmetry $O_h$. A magnetic field along the z axis lower the symmetry futher to C4 and the exchange field is included by a Zeeman term in the Hamiltonian. As shown in Fig 1, which represents the single particle picture, the 3d orbitals are split into $t_{2g}$ and $e_g$ levels with an energy difference of 10 Dq. When there is a weak field along the z axis and stronger field along the x and y axes, the octahedron is elongated along the z axis, and the degeneracy of $t_{2g}$ ($d_{xy}$, $d_{yx}$, $d_{xz}$) and eg ($d_{z^2}$, $d_{x^2-y^2}$) are removed. The distortion is represented


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by the ligand field parameter Ds. The $T_2$, E, $T_1$, $A_1$, $T_1$ and $T_2$ levels which derive from the $^5T_2$ configuration through spin-orbit interaction (6) will split futher, and each state gives different XMCD spectra. When Ds changes sign, the elongated shape changes into a compressed one, and the energy level ordering of the xy and xz, yz orbitals reverses, therefore the ground state symmetry changes from $e_g$ to $b_2$.

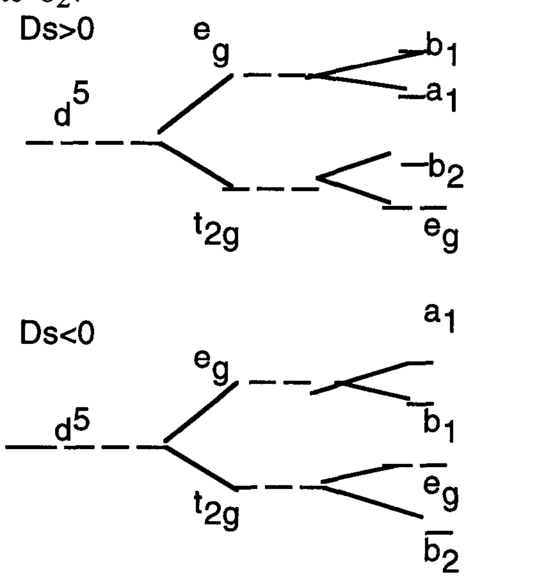


Figure 1. Ground state symmetry with the presence of tetrogonal distortions.

## 3. RESULTS AND DISCUSSIONS

The XMCD spectra calculated with different Ds values at T=0K are presented in Figure 2. All the coulomb interaction and exchange integrals are scaled to 80%. The exchange field is included by a term $g\mu_B HS$ in the Hamiltonian with $\mu_B H$=0.001 eV. The crystal fields of 10Dq=1.0 eV and Dt=0.0 eV were used to simplify the analysis. The core hole lifetime was taken into account by broadening the spectra with a Lorentzien width of 0.3 eV and a Gaussian width of 0.2 eV.

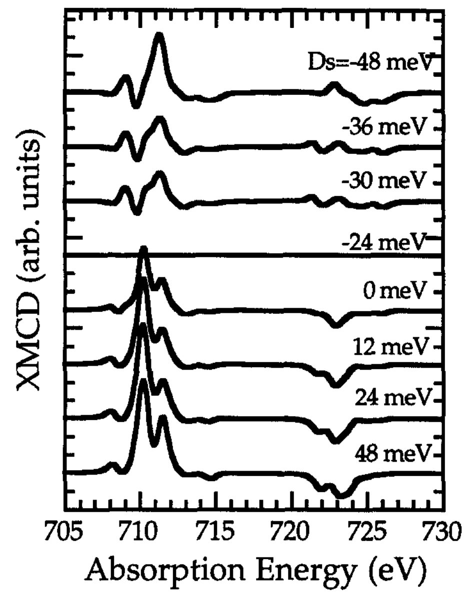


Figure 2. XMCD spectra as a function of distortion Ds.

Both the XMCD spectra shape and intensity change drastically with Ds. For Ds=-24 meV, there is no observable MCD effect at 0 K. With an increase of negative Ds, the $L_3$ edge shows a larger MCD effect around 711 eV and a well separated small peak around 709 eV. The intensity increase is almost 50% at the $L_3$ when changing Ds from -30 meV to -48 meV, and $L_2$ becomes much broader. For positive Ds, the XMCD spectra are very different. The $L_3$ peaks are much sharper around 710 eV, which is about 1 eV lower energy than the $L_3$ peak for negative Ds. There is also a shoulder on 1.5 eV higher energy side. From Ds=0 to 48 meV, the MCD effect at $L_3$ gradually increases and becomes more distinguishable at the $L_2$ edge.

Figure 3 presents the energy level diagram for square planar symmetry. The number shown on the top gives the approximate expectation values of <Sz> except for Ds=0, where <Sz>=-1 and 1 should be respectively -1.53 and 1.52.

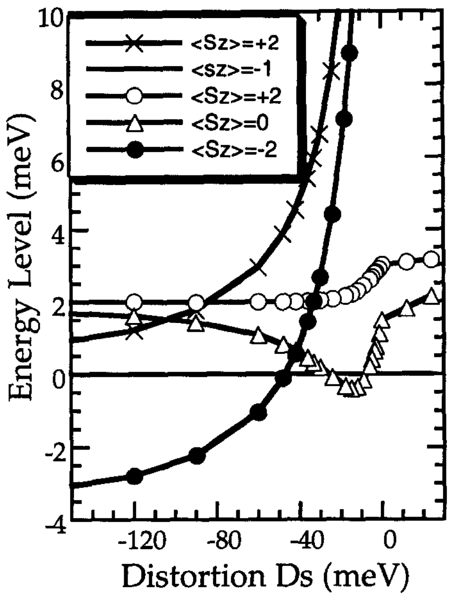


Figure 3. Five lowest energy level diagram as a function of Ds.

For positive Ds, the lowest energy level remains lowest, which is consistant with that there is no "sudden" changes in the XMCD spectra. For negative values of Ds, there are three clear transitions, one near -8 meV, one around -24 meV and the last one at -42 meV . At Ds =-8 meV, the $<S_Z>=0$ line crosses the $<S_Z>=-1$ line and becomes the ground state due to the coupling of the ground states to the excited states. At Ds=-24 meV, the $<S_Z>= 0$ line crosses $<S_Z>=-1$ again and $<S_Z>=-1$ is the ground state. At Ds=-42 meV, a phase transition occurs where a 'spin-orbit' excited state with $<S_Z>=-2$ becomes the ground state. This is a similiar effect as the high-spin low-spin crossings in the Tanabe-Sugano diagrams, which comparing 'Couloumb exchange' and cubic crystal field instead of 'spin-orbit' and 'Ds'.

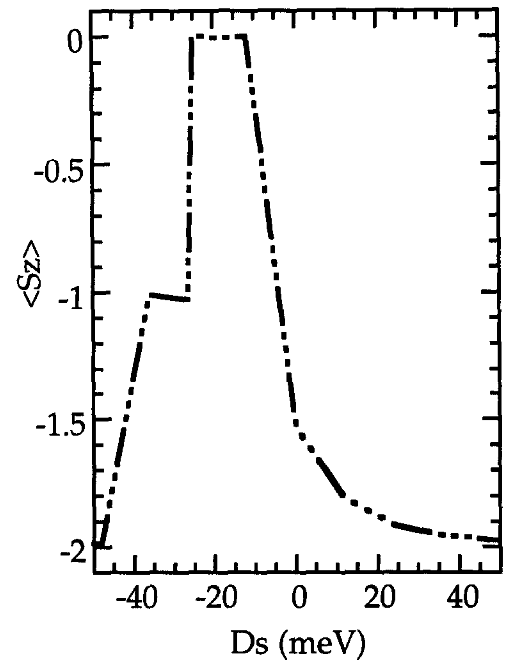


Figure 4. Ground state expectation value $<S_Z>$ as a function of Ds.

In Figure 4, we show the expectation values of the spin moment in the z direction $<S_Z>$ at the ground state. When the two lowest states cross, there is a jump in $<S_Z>$ at 0 K. The ground state $<S_Z>$ shows a strong dependence on Ds: between -8 meV and -24 meV, <Sz>=0 is the ground state, therefore no MCD effect will be observed for such a system. The strongest dichroic effect is not observed at 0K here, as shown in Figure 5 and 6. Mixing of higher energy levels with higher $<S_Z>$ values will give larger MCD. For Ds=-26 meV, half of the dichroic effect of $<S_Z>=-2$ ground state is expected since $<S_Z>=-1$ is the grounds state. For Ds=-48 meV, the ground state is almost $<S_Z>=-2$. Increase of positive Ds values gradually shift the ground state into a pure $<S_Z>=-2$ state.

Figure 5 and 6 illustrate the

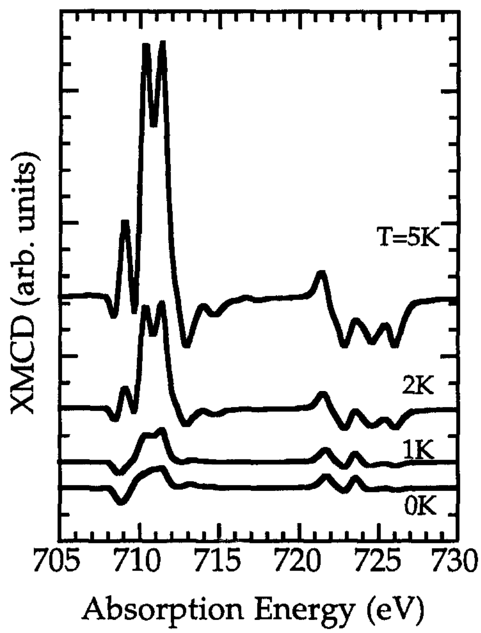


Figure 5. Temperature dependence of XMCD spectra at Ds=-12 meV.

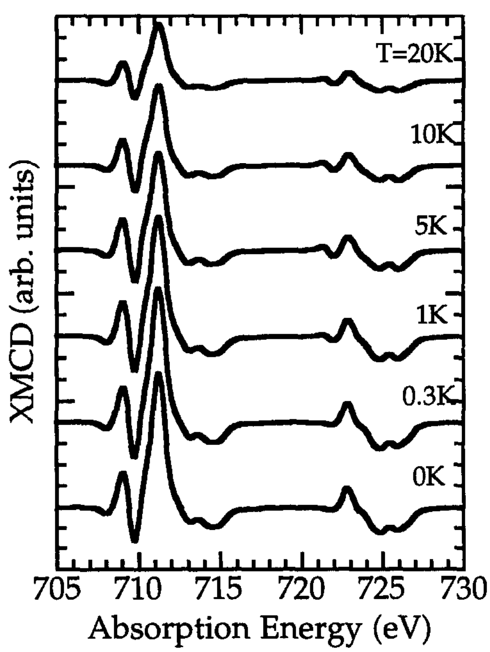


Figure 6. Temperature dependence of XMCD spectra at Ds=-48 meV.

temperature dependence of the XMCD spectra for a given value of Ds. For Ds=-12 meV, as shown in Figure 5, there is almost no dichroic effect at 0K, but with an increase of temperature to 5K, a weak MCD spectrum is expected. When Ds=-48 meV, higher temperature reduces the MCD, as the higher levels are with lower $<S_z>$ values. The temperature dependent XMCD study makes it possible to determine both spin-orbit coupling and Ds values.

## 4. CONCLUSIONS:

From ligand field multiplet calculations, we have shown that for the high-spin $d^6$, the XMCD spectra shape changes drastically with the presence of distortions. The character of the ground state changes when Ds changes sign, and mixings of different states could yield no dichroic effect at 0K for certain distortions. XMCD spectra also show a strong temperature dependence which allows determination of both spin-orbit coupling and Ds values. This calculation can be genaralized to all 3d transition metals.

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