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The X-ray Dichroic Signal from a Two-iron Cluster (Ferredoxin)

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Abstract

A calculation of the circular dichroic signal for a two-iron cluster (Fe^{3+} and Fe^{2+} antiferromagnetically coupled in reduced *c. pastorianum*) is used to demonstrate the potential ability of soft X-ray absorption spectroscopy to give quantitative information very directly on its orbital magnetism and gyromagnetic factor.

1. Introduction

The absorption of X-rays by a material depends on its magnetic properties. A particularly useful effect is the variation of the attenuation coefficient with respect to the handedness of circular polarization in the primary beam of X-rays, because this dichroic effect, as it is often called, is directly related to the net magnetic polarization of the material. Thus, there is no dichroic effect for an antiferromagnet or a paramagnet, in the absence of an applied field inducing a net magnetic polarization. Applications of the dichroic effect to investigate properties of concentrated magnetic materials are reviewed by Lovesey and Collins (1996).

Here, prompted by findings from a recent experimental study by van Elp et al. (1996), we investigate the dichroic effect from a cluster of two iron atoms. The dinuclear cluster contains a ferric (Fe^{3+}, $3d^5$) atom and a ferrous (Fe^{2+}, $3d^6$) atom. The atoms are believed to be coupled by an antiferromagnetic exchange interaction that has a magnitude of about 25 meV, and to occupy sites at which the electrostatic fields of the ligand atoms have an almost tetrahedral point-group symmetry (properties of magnetic clusters are reviewed by Bencini and Gatteschi 1990 and Kahn 1993). In the experiments, the paramagnetic clusters were aligned by a magnetic field of 6T, and the sample was held at a temperature of 1.5K. Dichroic signals were measured at the L_2 and L_3 absorption edges of the atoms, which are separated in energy by about 12 eV. The principal empirical findings we address are (a) at the L_3 absorption edge the dichroic signal from the Fe^{2+} atom is zero (b) the dichroic signals from the cluster at the L_2 and L_3 edges are of opposite sign, and (c) the magnitude of the dichroic signal from the cluster at the L_3 edge is larger than the signal at the L_2 edge.

Our theoretical investigation of the dichroic signal from a two-iron cluster is based on the following properties of the atoms; an antiferromagnetic alignment of the two spins, to form a total spin $S = \frac{1}{2}$, a ferric atom in a pure ^6S atomic state, and a ferrous atom in an intermediate crystal-field state with a high spin. The wave function for the latter state is a product of a spin state, with a multiplicity = 5, and a linear combination of two orbital states $| z^2 \rangle$ and $| x^2 - y^2 \rangle$, in the Γ_3 (or e) space of a tetrahedral crystal-field, plus a small amount of the orbital $| xy \rangle$, in the Γ_5 (t_2) space. The admixture of states from Γ_3 and Γ_5 is created by the spin-orbit interaction. In the ground-state orbital of Fe^{2+} the coefficient of $| xy \rangle$ is

proportional to $(g_0 - 2) > 0$ where g_0 is the gyromagnetic factor, i.e. the ratio of the mean values of the orbital and spin moments of the ferrous atom is $(g_0 - 2)$. Our assumed properties for the two iron atoms are different from those put forward by van Elp et al. (1996), and similar to those used by Bertrand and Gayda (1979) and Bertrand et al. (1985) in their successful analysis of data for EPR signals.

For the moment, though, we make one observation not reliant on the detailed theoretical investigation we report. In their discussion of the data van Elp et al. (1996) make no mention of a magnetic moment due to orbital angular momentum. Yet their findings, (b) and (c) above, indicate that the total dichroic signal of a cluster from the L_2 and L_3 edges is different from zero and this result alone is an unmistakable signature of the existence of a *net* orbital magnetic moment.

In the next section we discuss the resonant contribution to the scattering length, which is the instrument used by Lovesey and Balcar (1996) (hereafter referred to as L & B) in their formulation of absorption and resonance-enhanced scattering of X-rays by magnetic materials. A matrix element of the scattering length suitable for a description of a 3d-atom is described in §3. The wave functions for our model of the cluster are the subject of §4, and the corresponding dichroic signal is given in §5. Our interpretation of the data and the one put forward by van Elp et al. (1996) are discussed in §6, and §7 gives our main conclusions.

2. Attenuation coefficient

The resonant contribution to the scattering length for one cluster is denoted by f. The corresponding attenuation coefficient is proportional to the imaginary part of the mean value of f evaluated for a geometry of forward scattering, and averaged over the states of polarization in the primary beam of X-rays (Lovesey and Collins 1996). Here, and throughout the remainder of the paper, we label the ferric and ferrous atoms by the numbers 1 and 2, respectively. Thus, $f = (f_1 + f_2)$.

The two atomic wave functions are taken to be,

$$|S_1 M_1\rangle|L_1\rangle \equiv |S_1 M_1, L_1\rangle, \text{ and, } |S_2 M_2\rangle|L_2\rangle \equiv |S_2 M_2, L_2\rangle, \tag{2.1}$$

and the wave function of the cluster of two atoms is constructed to have a total spin $= S$, namely,

$$\sum_{M_1 M_2} (S_1 M_1 S_2 M_2 | SM) |S_1 M_1, L_1\rangle |S_2 M_2, L_2\rangle, \tag{2.2}$$

in which the Clebsch-Gordan coefficient is defined following Edmonds (1957) and Bencini and Gatteschi (1990). In the orbital contributions to the wave functions (2.1) we do not display the orbital magnetic quantum numbers for, in general, the orbital wave functions are a linear combination of components labelled by these quantum numbers, with coefficients determined by the (ligand) crystal-field, spin-orbit interaction, etc. From (2.2), we find for the mean value of f the value,

$$\langle f \rangle = \sum_{M_1 M_2} \sum_{M_1' M_2'} (S_1 M_1 S_2 M_2 | SM)(S_1 M_1' S_2 M_2' | SM)$$

$$\left\{ \delta_{M_2, M_2'} \langle S_1 M_1, L_1 | f_1 | S_1 M_1', L_1 \rangle + \delta_{M_1, M_1'} \langle S_2 M_2, L_2 | f_2 | S_2 M_2', L_2 \rangle \right\} \tag{2.3}$$

$$= \sum_{M_1 M_2} (S_1 M_1 S_2 M_2 | SM)^2 \left\{ \langle S_1 M_1, L_1 | f_1 | S_1 M_1, L_1 \rangle + \langle S_2 M_2, L_2 | f_2 | S_2 M_2, L_2 \rangle \right\}.$$

Because $\langle f \rangle$ is a diagonal matrix element, the ordering of the spin quantum numbers for the two atoms in the Clebsch-Gordan coefficients does not influence $\langle f \rangle$.

For the matrix elements of f_1 and f_2 in (2.3) we use the theoretical formulation developed by L & B. In this case, the spectrum of energies of the transitions between the ground state of an atom and the many, non-equilibrium, intermediate states in the resonant process is modelled by an energy spectrum that contains two components which are identified by the total angular momentum of the hole transferred from the valence shell to the core-state, $\bar{J} = \bar{l} \pm \frac{1}{2}$. Using μ and μ' as abbreviations for several quantum labels, a matrix element is,

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$$\langle \mu | f_1 | \mu' \rangle = - \left(\frac{2\pi e}{\lambda} \right)^2 \left\{ E - \Delta_1 + \tfrac{i}{2} \Gamma_1 \right\}^{-1} Z(\mu; \mu':1). \tag{2.4}$$

The matrix element $Z(\mu; \mu':1)$ is a product of factors for the core-hole and the description of the ground state of the atomic valence electrons, in terms of Racah unit spherical tensors. Other qualities in (2.4) are, the energy of the primary X-rays $E = (2\pi \hbar c/\lambda)$, and the mean energy and width, Δ_1 and Γ_1, of the absorption edge labelled by the value of $\bar{J}$.

Let us denote by ΔZ the change in the mean value of Z caused by reversing the handedness of the circular polarization in the primary beam, from right to left-handed. The dichroic signal is here defined as the corresponding change in the attenuation coefficient, for which we get the expression,

$$\Delta \gamma = (2\pi)^3 \, (n_o e^2 / \lambda) \left\{ \Delta Z_1 \, \delta(E - \Delta_1) + \Delta Z_2 \, \delta(E - \Delta_2) \right\}, \tag{2.5}$$

where n_o is the density of atoms in the sample. In arriving at (2.5) the energies Γ_1 and Γ_2 are assumed to be vanishingly small. The quantities ΔZ_1 and ΔZ_2, apart from a simple factor, admit the interpretation as the integrated intensities of the dichroic signals from the two atoms. For two different ionic states of an element a chemical shift means $\Delta_1 \neq \Delta_2$.

3.   Matrix element

The L_2 and L_3 absorption edges are formed with electric-dipole (E1) events. In this case, the theoretical formulation developed by L & B gives an expression for the matrix element $Z(\mu; \mu')$ – for the moment we drop the label for the type of atom – that is a sum of three tensors. Just one of these is married to the helicity in the primary beam of X-rays. So, in forming an expression for the circular dichroic-signal, which is a difference signal for opposite handedness in the primary beam, only this one tensor survives for the others cancel in taking the difference. The surviving tensor in the dichroic signal is of rank one, as might be anticipated.

For a given value of the total angular momentum of the hole in the core state, $\bar{J}$, the matrix element is a sum of three contributions. One contribution is purely orbital, one is purely spin and the other is a mixture of spin and orbital character. The latter two contributions have opposite signs for $\bar{J} = \bar{l} - \frac{1}{2}(L_2)$ and $\bar{J} = \bar{l} + \frac{1}{2}(L_3)$. Hence, the sum of the intensities of the dichroic signals at the L_2 and L_3 absorption edges is a measure of the orbital character in the wave function of the valence electrons.

We work in this paper with matrix elements of Z in the SL basis, because it is more convenient to handle 3d-atoms in this basis than in the SLJ basis. An effect of the Wigner-Eckart theorem is that the spin magnetic quantum numbers in $Z(\mu;\mu')$ appear as,

$$(-1)^{S_1 - M_1} \begin{pmatrix} S_1 & a & S_1 \\ -M_1 & m & M_1' \end{pmatrix},$$

and for the case in hand $a = 0$ or 1. If $a = 0$ then $m = M_1 - M'_1 = 0$. For $a = 1$, in (2.3) we are led to consider,

$$\sum_{M_1 M_2} \sum_{M_1'} (S_1 M_1 S_2 M_2 | SM)(S_1 M_1' S_2 M_2 | SM) \, (-1)^{S_1 - M_1} \begin{pmatrix} S_1 & 1 & S_1 \\ -M_1 & m & M_1' \end{pmatrix}$$

$$= \delta_{m,0} (-1)^{1+S+S_1+S_2} \frac{M(2S+1)}{(S\|S\|S)} \begin{Bmatrix} S & S_1 & S_2 \\ S_1 & S & 1 \end{Bmatrix}. \tag{3.1}$$

The same formula can be used for atom-2 after replacing S_1 by S_2 and S_2 by S_1 in the 6j-symbol. The reduced matrix element $(S\|S\|S) = \{S(S+1)(2S+1)\}^{1/2}$.

From the work by L & B a matrix element used to calculate ΔZ_1, say, for $l = 2$, $\bar{l} = 1$ and $\bar{J} = \bar{l} \pm \frac{1}{2}$ is proportional to $\langle R_1 \rangle^2 P_2$ where, $\langle R_1 \rangle$ is the E1 radial-integral, and P_2 is the mean helicity in the primary beam. The definition of P_2 follows Lovesey and Collins (1996); $|P_2| \le 1$, and $P_2 > 0$ is right-handed and $P_2 < 0$ is left-handed circular polarization. The radial integrals of the ferric and ferrous atoms, roughly, are in the ratio 5:4 (private communication from Dr. G. van der Laan).

4. Wave functions

The atomic configurations of the ferric and ferrous atoms are ^6S and ^5D, respectively. To a first approximation, because the ferric atom is an orbital singlet with an exceptionally large pairing energy its local environment will not change the state of the valence electrons and the wave function is that of a free atom, viz., $|S_1 M_1\rangle|L_1\rangle$ with $S_1 = 5/2$ and $L_1 = 0$ (Carlin 1986).

The situation with regard to the influence of the environment on the ferrous atom is quite different, since the orbital of the extra electron outside the half-filled close shell of the ferric atom is perturbed by the crystal-field. We assume the ligands have a fourfold coordination, and the crystal-field has almost tetrahedral symmetry. The strength of the crystal-field is taken to be small enough for the atom to be in a high-spin state. An argument to support this view is given by Huheey (1983) figure (9.13).

For pure tetrahedral symmetry the ground-state orbitals are degenerate and in the Γ_3 space. (A feature of fourfold tetrahedral symmetry is that the metal atom is not a centre of inversion symmetry, but this feature has no direct bearing on our model calculations, cf. Bertrand and Gayda 1979.) In terms of $|L_2 = 2, M_L\rangle = |M_L\rangle$ the two purely real orbitals are,

$$|z^2\rangle = |0\rangle, \text{ and } |x^2 - y^2\rangle = (|2\rangle + |-2\rangle)/\sqrt{2}. \tag{4.1}$$

With a distortion away from the tetrahedral symmetry the degeneracy of the two Γ_3 states is not only lifted but the states are also admixed (Bertrand and Gayda 1979), so the ground state is of the form,

$$\alpha|z^2\rangle + \beta|x^2 - y^2\rangle, \tag{4.2}$$

where the real coefficients satisfy $\alpha^2 + \beta^2 = 1$. The corresponding mean value of the orbital angular momentum is zero, so the crystal-field acts to quench the orbital magnetic moment.

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In other words, the gyromagnetic factor of the ferrous atom calculated with (4.2) is the same as for the spin-only ferric atom. However, empirical data for ferrous atoms show that g_0 is larger than the spin-only value (Low and Weger 1960, and Ohlam and Tinkham 1961).

This finding is attributed, at least in part, to the effect of the spin-orbit interaction between states of Γ_3 and Γ_5 (the spin-orbit interaction does not connect $|z^2\rangle$ and $|x^2 - y^2\rangle$). Let us keep to the diagonal component of the spin-orbit interaction which connects $|x^2 - y^2\rangle$ and one state in the Γ_5 space, namely,

$$|xy\rangle = -\mathrm{i}\left(|2\rangle - |-2\rangle\right)/\sqrt{2}. \tag{4.3}$$

The corresponding ground-state orbital of the ferrous atom is,

$$\left|L_2\right\rangle = \alpha\left|z^2\right\rangle + \beta\left|x^2 - y^2\right\rangle + \left(\frac{\mathrm{i}}{2\beta}\right)\left(g_0 - 2\right)\left|xy\right\rangle. \tag{4.4}$$

Using $\alpha^2 + \beta^2 = 1$ the normalization of $|L_2\rangle$ is preserved up to the first order of smallness in $(g_0 - 2)/\beta$.

No account of zero-field splittings is made, on the grounds that the single-site anisotropy constant (typically 1 - 2 meV) is smaller than the spin-orbit parameter, and the exchange interaction. It is to be noted that, the off-diagonal, or perpendicular, components of the gyromagnetic factor have values found for a spin-only atom. As shown by Bertrand and Gayda (1979), deviations of the off-diagonal components from the spin-only value are caused by mixing the ground-state, through the spin-orbit interaction, with $|zx\rangle$ and $|yz\rangle$, and the deviations are very small compared with $(g_0 - 2)$ because these two states are at a much higher energy than $|xy\rangle$.

5. **Dichroic signal**

We use the results of §§2-4 to calculate the dichroic signal of a two-iron cluster. The value of the total spin of the cluster S is taken to be $\frac{1}{2}$. Physically this means the exchange

interaction aligns the spins of the atoms in opposite directions. The choice $M = -S$ is valid because the temperature of the sample is low. At a relatively high temperature it would be necessary to take for M its thermal average value $\langle S \rangle$, made with respect to the intermolecular exchange interaction and the applied magnetic field; see, for example, Bencini and Gatteschi (1990).

Because the ferric atom is an orbital singlet only the pure-spin contribution to the matrix element is different from zero. We find,

$$\Delta Z_1 = \mp \tfrac{28}{135} \left\langle R_1 \right\rangle^2 P_2 \hat{q}_0 \langle S \rangle, \tag{5.1}$$

where $\hat{q}_0$ is the projection of the unit vector that defines the direction of propagation of the beam, $\hat{\mathbf{q}} = (\mathbf{q} / q)$, on the axis of quantization for the magnetic state of the cluster. In (5.1) the upper (lower) sign corresponds to the L_3 (L_2) absorption edge.

For the ferrous atom we adopt the wave function (4.4). In this case, each of the three contributions to ΔZ_2 are different from zero. Matrix elements calculated with $|L_2\rangle$ involve differences in the magnetic quantum numbers $\Delta M_L = 0, \pm 2$ and ± 4. However, the dichroic signal for E1 events is formed with a tensor of rank one and this restricts the non-zero contributions to the signal to matrix elements with $\Delta M_L = 0$ and ± 1. In consequence, the dichroic signal from the ferrous atom is diagonal with respect to the orbital magnetic quantum number. The result is,

$$\Delta Z_2 = \tfrac{8}{45} \left\langle R_2 \right\rangle^2 P_2 \hat{q}_0 \langle S \rangle \left[\tfrac{1}{4}(2\bar{J}+1)(g_0 - 2) \pm \tfrac{1}{3}(2 + \alpha^2 - \beta^2) \right], \tag{5.2}$$

and the upper (lower) sign is for the L_3 (L_2) absorption edge with $\bar{J} = \tfrac{3}{2}(\tfrac{1}{2})$. Notice that the spin-dependent contributions to ΔZ_1 and ΔZ_2 are opposite in sign, which is due to the 6j-symbol in (3.1) having opposite signs for atom-1 (positive) and atom-2 (negative). Moreover, the third term in (5.2), a mixture of spin and orbital character, contributes to ΔZ_2 two parts with opposite signs. The relative signs are attributed to the spatial properties of the orbitals $\alpha|z^2\rangle$ and $\beta|x^2 - y^2\rangle$ in $|L_2\rangle$; the weight of $|z^2\rangle$ is predominantly along the z-axis and

aligned with the spin, whereas the weight of $|x^2 - y^2\rangle$ is in the plane of x and y. Not surprisingly, any weight from the orbital $|xy\rangle$ adds to weight from $|x^2 - y^2\rangle$, while $|zx\rangle$ or $|yz\rangle$ each add weight to $|z^2\rangle$, e.g. if we add to the wave function (4.4) a term proportional to $(g_x - 2)\, |yz\rangle$ then α^2 is increased by,

$$1 + \tfrac{3}{8}(g_x - 2).$$

In fact, this is the only change to ΔZ_2 made by a term in the wave function which arises by taking account of the leading-order departure of the off-diagonal component of the gyromagnetic factor from the spin-only value. Hence, the sum of the dichroic signals from the L_2 and L_3 absorption edges is not influenced by non-zero values for $(g_x - 2)$ and $(g_y - 2)$.

The dichroic signals of the ferric and ferrous atoms have the same temperature dependence, which is found in the common factor $\langle S \rangle$. It is to be noted that, the pure-orbital contribution to ΔZ_2 has this temperature dependence because in the model used for the ferrous atom the orbital magnetic moment is proportional to the spin moment.

Let us consider the values for ΔZ_2 obtained with a reasonable set of parameters. From the analysis reported by Bertrand et al. (1985) we deduce β^2 is $\tfrac{3}{8}$ or thereabouts, and the same source of information suggests we take -0.08 for the ratio of the spin-orbit interaction parameter (a negative quantity for an atom with an electron shell more than half filled) to the separation in energy of the Γ_5 state from the ground state. The value -0.08 corresponds to a spin-orbit parameter -10.0 meV, which allows for a reduction by covalency, and an energy separation for $|xy\rangle$ of 0.12 eV, which is probably at least a factor of two smaller than for an octahedral symmetry. Using these values one finds $(g_0 - 2) = \tfrac{1}{4}$, and we note that it is in agreement with the value of the gyromagnetic factor observed by Low and Weger (1960) for ferrous atoms in tetrahedral ZnS. Turning now to the result (5.2) for ΔZ_2 the quantities in the square bracket add up to 1 $(-\tfrac{5}{8})$ at the L_3 (L_2) absorption edge, and so ΔZ_1 and ΔZ_2 have opposite signs at the two edges.

To estimate the dichroic signal for a cluster we shall assume that the radial integrals of the ferric and ferrous atoms are the same. In this case, ΔZ_1 and ΔZ_2 have as a common factor,

$$\langle R \rangle^2 \, P_2 \hat{q}_0 \langle S \rangle \, .$$

The numerical factor in $\Delta Z = \Delta Z_1 + \Delta Z_2$ is $-\frac{4}{135}(\frac{13}{135})$ at the $L_3(L_2)$ edge. Hence, for these parameters, the magnitude of the dichroic signal is largest at the L_2 edge. This result can be reversed, together with the relative sign, if the signal from the ferric atom is reduced, e.g. if ΔZ_1 is reduced by a factor $\frac{1}{2}$ then ΔZ is $\frac{10}{135}(-\frac{1}{135})$ at $L_3(L_2)$ edge, while for the extreme case $\Delta Z_1 = 0$ one finds ΔZ is $\frac{8}{45}(-\frac{1}{9})$ at $L_3(L_2)$.

6.   Spin-only models

As we mentioned in §1, van Elp et al. (1996) attempt to explain their findings in terms of models based on atomic spins, and no allowance for orbital angular momenta. In their favoured model the ferrous atom is a spin-singlet and the ferric atom has spin magnetic quantum numbers $= \pm \frac{1}{2}$. (These spin states are realized when the single-site anisotropy constants are large compared to the magnitude of the exchange interaction, while the reality is that the reverse applies.) Their empirical finding (a) is then accounted for in the model by the assumption that ΔZ_2 is proportional to $M_2 = 0$. In contrast to this explanation, in §5 we argue that ΔZ_2 (and ΔZ_1) is proportional to the mean value of the total spin, and in the conditions which apply in the experiment this quantity is close to its saturation value $= -\frac{1}{2}$.

In this section we calculate the energies and ground-state wave functions of a two-spin cluster taking account of the exchange interaction, single-site anisotropies, and an applied magnetic field. We confirm that, realistic values of these quantities give a ground-state wave function little different from the wave function of two spins $S_1 = \frac{5}{2}$ and $S_2 = 2$ coupled, antiferromagnetically, to give a total spin $S = \frac{1}{2}$. The corresponding dichroic signals are obtained by keeping the pure-spin contribution, i.e. the second of the three contributions. For the ferric atom the result is (5.1). The dichroic signal for a fictitious spin-only ferrous atom is similar to this, as can be verified from (5.2) by setting $g_0 = 2$ and $\alpha^2 = \beta^2$, and it is different from zero. Of course, for a spin-only model the *total* dichroic signal for a cluster is zero, since for each atom the dichroic signals at the two absorption edges are of opposite sign.

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Following Kahn (1993), the Hamiltonian of two spins coupled by an isotropic exchange interaction with a strength J_{ex} is,

$$H = -J_{ex}(\mathbf{S}_1 \cdot \mathbf{S}_2) + D_1(S_1^z)^2 + D_2(S_2^z)^2 + g\mu_B B(S_1^z + S_2^z). \qquad (6.1)$$

Here, D_1 and D_2 are the single-site anisotropy constants, and the magnetic field B is applied along the z-axis. The eigenvalues and wave functions of the cluster are obtained by diagonalization. To this end we introduce column vectors for the spins, e.g. for the ferrous atom,

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \dots \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{pmatrix},$$

where the one defines the value of M_2. The matrix contains 5 x 6 = 30 spin states. Each coupled spin-state Φ (M_2, M_1) is an eigenstate of the corresponding Ising model. The wave functions of the Heisenberg model (6.1) are denoted by $\Psi(S,M)$ and they are provided as linear combinations of Φs.

We consider several sets of parameters. First, set $J_{ex} = B = 0$. The two data sets $D_1 = 0$, $D_2 > 0$ and $D_1 > 0$, $D_2 = 0$ reproduce the zero-field splittings for the model favoured by van Elp et al. (1996) and the splittings are depicted in their figure 4.

Next, we turn to the realistic case in which $J_{ex} \neq 0$. With $J_{ex} < 0$ the two spins are aligned antiferromagnetically. The energy level diagram for $J_{ex} = -200\text{cm}^{-1}$ and $D_1 = D_2 = B = 0$ is shown in figure 1, and the wave function is,

$$\Psi(\tfrac{1}{2}, \pm \tfrac{1}{2}) = \mp 0.258 \, \Phi (\pm 2, \mp \tfrac{3}{2}) \pm 0.365 \, \Phi (\pm 1, \mp \tfrac{1}{2}) \mp 0.447 \, \Phi (0, \pm \tfrac{1}{2})$$

$$\pm 0.516 \, \Phi (\mp 1, \pm \tfrac{3}{2}) \mp 0.577 \, \Phi (\mp 2, \pm \tfrac{5}{2}).$$

(6.2)

This wave function is the same as the one quoted by van Elp et al. (1996).

In the last two cases we include the single-site anisotropies together with the exchange interaction. Taking the values proposed by van Elp et al. (1996) (NB 1 meV = 8.07 cm^{-1}), namely $D_1 = 2$ cm^{-1} and $D_2 = 10$ cm^{-1}, the magnitudes of the five coefficients in (6.2), reading from left to right, are replaced by 0.264, 0.383, 0.466, 0.520 and 0.544, and the corresponding energy level diagram is shown in figure 2. Evidently, the coefficients in the wave function change very little as a result of including the single-site anisotropies. Furthermore, we have demonstrated that, independent of the signs of D_1 and D_2 the variations in the coefficients in (6.2) are no more than 6% for $|D_1|$ and $|D_2|$ in a range up to 10 cm^{-1}, i.e. zero-field splittings do not significantly modify the ground-state wave function if their magnitudes are small compared to the strength of the exchange interaction.

Finally, we add an external magnetic field. As shown in figure 2, a field of 6T leads to Zeeman splittings ~ 1 cm^{-1}. The variation to the coefficients in the wave function (6.2) is less than 0.1%.

7. Conclusions

Our calculation for the dichroic signal from a reduced ferredoxin has demonstrated that, the technique of soft X-ray absorption is potentially valuable to better understand the properties of magnetic clusters. For the one case we have studied, the signal is directly relevant to a determination of the wave function of the ground-state and the gyromagnetic factor. The range of questions and samples which might be addressed with the technique are summarized by Bertrand et al. (1985).

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Captions

Figure 1. The energy level diagram of a cluster of two spins with $S_1 = \frac{5}{2}$ and $S_2 = 2$ coupled by an exchange interaction $J_{ex} = -J$ with $J = 200$ cm^{-1} $\equiv 24.78$ meV. (NB the Hamiltonian (6.1) has an exchange energy $-J_{ex}\, \mathbf{S}_1 \cdot \mathbf{S}_2$ whereas some authors include an extra factor of two in the exchange, e.g. Bertrand and Gayda 1979.) The total spin S and the energy separations, in units of J, are shown.

Figure 2. The influences of the single-site anisotropies and a magnetic field on the energy levels of a two-spin cluster. The exchange anisotropy constants and magnetic field are appropriate to the discussion made by van Elp et al. (1996).

Dimer

9/2

9/2·J

single
ion
S=2

7/2

7/2·J

single
ion
S=5/2

5/2

5/2·J

3/2

3/2·J

S=1/2

Energy (cm^{-1})

$J_{ex} = -200$ cm^{-1}

$D_1 = 2$ cm^{-1}
$D_2 = 10$ cm^{-1}

$B = 6$ T

1000

0

-1000

9/2

7/2

5/2

3/2

1/2

2