RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 37, NUMBER 11 15 APRIL 1988-I

Multiplet structure in the $L_{2,3}$ x-ray-absorption spectra: A fingerprint for high- and low-spin Ni^{2+} compounds

G. van der Laan, B. T. Thole, and G. A. Sawatzky
Materials Science Center, Nijenborgh 18, 9747 AG Groningen, The Netherlands

M. Verdaguer
Laboratoire de Spectrochimie des Elements de Transition, Université de Paris-Sud, 91405 Orsay Cédex, France

(Received 19 October 1987)

High-resolution x-ray absorption spectra of high- and low-spin compounds have been analyzed using a newly developed general crystal-field computer program. The calculations show clearly that the gross features of the multiplet structure at the $L_{2,3}$ absorption edge can be used to determine the spin state of the $3d^8$ configuration in Ni and Cu compounds.

In this Rapid Communication we introduce a new method to determine the local spin state of $3d$ transition metals in their compounds. The method uses the details of the multiplet structure in $L_{2,3}$ x-ray absorption spectroscopy (XAS), which can be resolved due to the recent advances in soft x-ray monochromators. The multiplet structure arises from the transition $3d^n \rightarrow 2p^5 3d^{n+1}$, where the dipole selection rules confine the subset of final states that can be reached from the ground state. In the low-spin ground state the electrons pair up in the orbitals with the lowest energy, while in the high-spin ground state higher orbitals are also occupied with the spins parallel. Thus these states do not only differ in spin but also in orbital character. In the two-particle case of $3d^8$ this results in distinctly different types of XAS spectra which can be used as a fingerprint for high spin or low spin. For the other $3d$ metals such a simple fingerprint may not always exist, but a unique spectrum is generally obtained for each choice of physical parameters in a crystal-field calculation. In those cases a limited search through the parameter space will permit an unambiguous determination of the spin state.

To illustrate our method we will give a detailed crystal-field analysis of the multiplet structure for the Ni $3d^8$ configuration in a D_{4h} environment. The square planar D_{4h} geometry has the property that just one d orbital (x^2-y^2) is directed towards the ligands while all the others are not, which is favorable for obtaining a singlet ground state. Another reason for studying divalent Ni compounds is that they are a model for trivalent Cu compounds, which is of interest for the high-T_c superconductors.[1,2]

XAS spectra were measured with synchrotron radiation emitted by the Anneau de Collisions d'Orsay (ACO) using a double-crystal beryl monochromator which resulted in a resolution of 0.4 eV at 850 eV.[3] Freshly ground samples pressed onto Scotch tape in a vacuum of 10^{-7} Torr were measured by electron yield detection. There was no time dependence in the spectra, not even after several hours.

A typical triplet spectrum, that of Ni oxalate, is given in Fig. 1(a). The $2p$ spin-orbit interaction splits the spectrum roughly into two parts, the $2p_{3/2}$ (L_3) and the $2p_{1/2}$ (L_2) structures. Both consist of a double peak. Similar spectral shapes with a double-peak structure are observed for Ni dihalides and NiO.[4] The peak splittings in these compounds vary with the covalency of the Ni ligand bond.

The low-spin compound K_2Ni dithio-oxalate (NiDTO) in Fig. 2(a) shows a rather different type of spectrum.

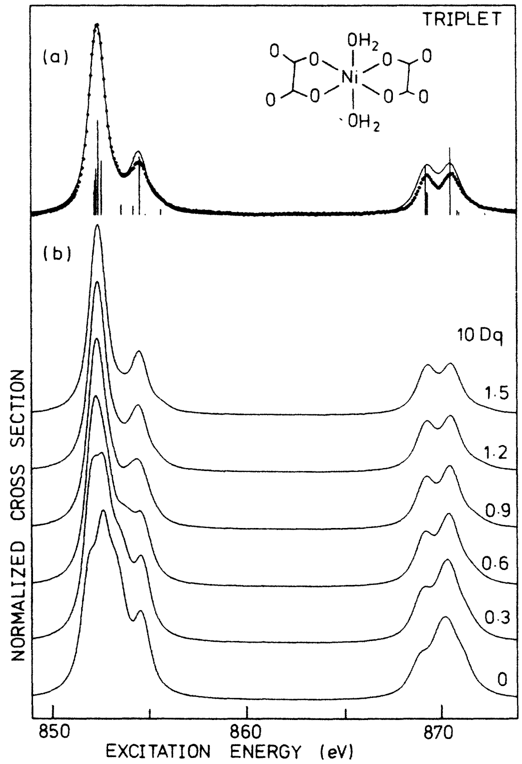

FIG. 1.(a) Experimental $L_{2,3}$ absorption spectrum of Ni oxalate (dots), together with a calculation (lines) where $10Dq$ is 1.5 eV. (b) Calculated $L_{2,3}$ multiplet spectra for a $^3B_1$ ground state in D_{4h} symmetry with different values of $10Dq$ (eV), $Ds=Dt=0$. For all calculations: Slater integrals (unscaled) $F^2=12.2$, $G^1=5.8$ and $G^3=3.3$ eV, $\kappa=0.85$, $\zeta_{2p}=11.5$ eV. Convolution by a Gaussian $\sigma=0.15$ and a Lorentzian $2\Gamma=0.80$ (1.10) eV for L_3 (L_2).

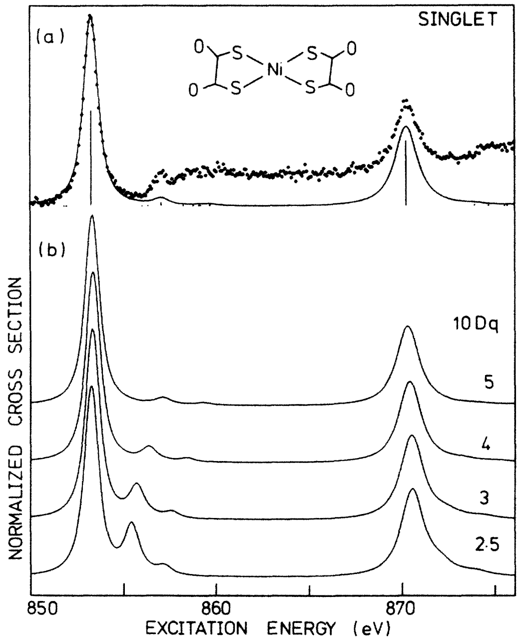

FIG. 2.(a) Experimental $L_{2,3}$ absorption spectrum of K_2Ni dithio-oxalate (dots), together with a calculation (lines) using orbital energies as given in Table I. (b) Calculated multiplet spectra for a $^1A_1(b_1^2)$ ground state in D_{4h} symmetry with different values of $10Dq$ (eV), $Ds = 10Dq/7$, and $Dt = 6Dq/7$. Convolution by a Gaussian $\sigma = 0.15$ and a Lorentzian $2\Gamma = 0.80$ (1.40) eV for L_3 (L_2).

Both the L_3 and L_2 edge consist of a strong, narrow line with a full width at half maximum (FWHM) less than 0.8 and 1.5 eV, respectively. There is a small satellite with about 10% intensity at 3.8 eV above the L_3 main line. It is situated at the leading edge of the $4s$ continuum. The spectrum of the low-spin square planar compound Ni phthalocyanine (NiPC) which has been recorded with ~0.8 eV resolution by Koch, Jugnet, and Himpsel[5] is similar, except that the satellite is larger and closer to the main peak.

The basis for an interpretation of the $2p \rightarrow 3d$ multiplet structure is the behavior of the $3d$ orbitals in the presence of the ligands. In an octahedral environment the two degenerate e_g orbitals have the highest energy and they contain the two holes with parallel spin in order to gain exchange energy. This is the high-spin $^3B_1$ ground state (in D_{4h} notation, where for brevity we omit the parity). If in the sixfold-coordinated octahedral complex both ligands along the z axis are removed giving a square planar D_{4h} environment then $e(O_h)$ splits into b_1 and a_1. The $b_1(x^2-y^2)$ orbital is directed towards the ligands and has the highest energy. The $a_1(z^2)$ orbital will decrease in energy and in the fourfold-coordinated complex it is usually even below the $e(xz,yz)$ and $b_2(xy)$ orbitals. If the energy difference between a_1 and b_1 becomes larger than ~1.5 eV, energy can be gained by pairing the holes in b_1 resulting in a $^1A_1(b_1^2)$ ground state. The $^3B_1$ and $^1A_1$ states are in practice about the only possible ground states although mathematically other ground states may be produced by a suitable choice of parameters.

In order to analyze the experimental data we performed a large number of crystal-field calculations using the chain of groups approach exposed by Butler.[6] This approach starts with the calculation of the reduced matrix elements of all necessary operators in the spherical group, which can be done using Cowan's atomic multiplet program.[7] The Wigner-Eckart theorem is then applied to obtain the reduced matrix elements in any desired point group. Butler's point-group program[6] calculates the necessary isoscalar factors, using modern group-theoretical results[8] to obtain a consistent set of coefficients. The advantage over standard methods[9] is that a general program could be developed which treats all point groups in a uniform way. The program can calculate the transition probabilities between any two configurations in x-ray absorption, photoemission, or inverse photoemission spectroscopy.

In Fig. 1(b) we give the calculated spectra for the $^3B_1$ state as a function of $10Dq$, taking the tetragonal distortion to be zero. These results agree with previous calculations performed in octahedral symmetry.[4,9] It is seen from the figure that when $10Dq$ is less than 0.6 eV the doublet structures are distorted because the low-energy peak of L_3 and the high-energy peak of L_2 are broad. Increasing $10Dq$ above 0.6 eV narrows these peaks without shift in energy, giving the clearly resolved doublets. Introduction of D_{4h} distortions small enough to maintain a triplet ground state broadens all peaks, but the typical doublet structures still remain. It is emphasized that $^3B_1$ is a pure state and that therefore the spectrum does not depend on the parameters of the ground-state configuration, as long as $^3B_1$ remains the ground state. As a consequence, only the parameters of the excited configuration can be obtained from the spectrum. Thus the splittings in the doublets are almost exclusively determined by the value of the $2p$-$3d$ exchange interaction in the $2p^5 3d^9$ configuration. We calculated that for the L_3 and L_2 the splitting is 2.5κ and 1.1κ eV, respectively, where κ is the scaling factor for the exchange interaction. In covalent compounds reduction of the electrostatic interaction is caused by the mixing of the d orbitals with the ligand band, where κ can be used as a measure for the covalent mixing;[4] e.g., κ in NiF_2 is ~1.0, while in $NiBr_2$ κ is ~0.6. Ni oxalate with κ equal to ~0.85 is an intermediate case.

The analysis for the singlet spectrum in Fig. 2 is quite different. In the absence of Coulomb and exchange interactions the ground state is a pure b_1^2 state from which only transitions are allowed to $p_j b_1$ ($j = \frac{1}{2}, \frac{3}{2}$) final states. This causes the two main peaks. In the presence of electrostatic interactions the b_2^2, e^2, and a_1^2 states mix into the ground state and $p_j b_1$ mixes into the $p_j b_2$, $p_j e$, and $p_j a_1$ states giving rise to small satellites. In first order, the satellite distances are given by the b_2, e, and a_1 orbital energies with their intensities decreasing with the square of the satellite distances. The theoretical spectra in Fig. 2(a) are calculated by a choice of the D_{4h} parameters Dq, Ds, and Dt, such that the b_2, e, and a_1 orbital energies are degenerate at $10Dq$ below the b_1 ($Ds = 10Dq/7$ and $Dt = 6Dq/7$). We consider this as a model for a typical fourfold-coordinated D_{4h} complex. Because of Coulomb interactions the originally degenerate final-state levels are spread over ~2 eV.

The theoretical spectrum for NiDTO in Fig 2(a) is calculated with the more realistic parameter values $Dq = 0.43$, $Ds = 0.91$, and $Dt = 0.47$ eV. The orbital energies corresponding with these parameter values are given in Table I and they agree globally with the *ab initio* numerical values of Blomberg and Wahlgren.[10] The spectrum is practically equal to the model spectrum of $10Dq = 5$ eV. The D_2 perturbation in the Ni complex will broaden the spectrum by splitting all lines without changing the overall shape. From the width of the experimental L_3 line we derived that in the case of NiDTO the perturbation of the orbital energies must be less than 0.3 eV. The additional width of the L_2 line is due to interaction with the L_3 continuum.[11]

For NiDTO the theoretical satellite intensity cannot be made as large as the experimental value if we constrain the ligand field parameters of the initial- and final-state configurations to be the same. We did not release this constraint because the defect could, e.g., be due to the fact that the $b_1(x^2-y^2)$ mixes more strongly with the ligands orbitals than the other orbitals do. This cannot be treated explicitly in a crystal-field approach, another more complicated approach would be required.[4]

While NiDTO is rather extreme with $10Dq = \sim 5$ eV, the spectrum of NiPC (Ref. 5) displays the other extreme with $10Dq = \sim 2.5$ eV where $^1A_1$ and $^3B_1$ are nearly degenerate. A lower $10Dq$ will result in a triplet ground state if the exchange interactions are not reduced.

In summary, we have found that the $L_{2,3}$ edge structure in XAS can be used to distinguish between the $3d^8$ high-spin and low-spin configuration because the gross features in the spectrum are only weakly influenced by the choice of parameters (Figs. 1 and 2). In the high-spin spectrum the amount of covalent mixing can be determined from the splitting in the peak structures, whereas the detailed shape allows an estimate of $10Dq$. In the D_{4h} low-spin spectrum precise information on the crystal-field splittings can be obtained from the position and intensity of the weak satellites.

TABLE I. $3d$ orbital energies of NiDTO in D_{4h} symmetry.

Orbital	$b_1(x^2-y^2)$	$b_2(xy)$	$e(xz,yz)$	$a_1(z^2)$
Energy (eV)	0	−4.3	−5.0	−5.6

The given example of Ni can be extended to the other $3d$ metal compounds. The most obvious extension is to trivalent Cu compounds which should have spectra similar to divalent Ni. This may be of importance in the study of high-T_c superconductors.

The recent development of a high-resolution monochromator based on the combination of acid phthalate (AP) crystals and multilayers[3,12] has opened the energy region of the $2p \rightarrow 3d$ excitations for the lighter $3d$ metals. This also permits, for these compounds, a detailed theoretical analysis of the near-edge structure. For instance, in the experimental $L_{2,3}$ spectra of Fe compounds we have observed large differences between different spin states.[12] Preliminary calculational results[13] show clearly that the Fe $L_{2,3}$ spectra cannot only be used as a diagnostic tool for the spin but also allow a precise measurement of $10Dq$ in these compounds.

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