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Electronic structure of transition metal fluorides and oxides determined by resonant X-ray absorption and X-ray emission spectroscopies

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Electronic structure of transition metal fluorides and oxides determined by resonant X-ray absorption and X-ray emission spectroscopies

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Experimental data for x-ray absorption at the transition metal $L_{2,3}$ edge for FeF_2 and CoF_2 are presented. They are compared with the results of calculations that include the intra-atomic effects due to the ion atomic multiplet and also of the ligand field splitting of the $3d$ orbitals. Good overall agreement between experiment and theory is found. We also show resonant x-ray emission data for these compounds obtained at selected excitation energies and compare them with the results of the ligand field atomic multiplet calculation. Very good agreement between the experimental and the calculated energy splittings is found. We also found good agreement for the relative intensities of the emission peaks. This indicates that, as in the case of manganese compounds, the low energy loss peaks are due to decay into d-excited states of the ground configuration. A comparison of the emission spectra of $LaMnO_3$, MnF_2, FeF_2, and CoF_2 obtained at excitation energies at the top of the corresponding L_2 absorption peak is presented. This provides data for the projected d-density of states of d^4, d^5, d^6, and d^7 compounds, which are in good agreement with the results of ligand field atomic multiplet calculations.

Keywords: X-ray absorption; X-ray emission; Electronic structure; Transition metal compounds

1. Introduction

Resonant x-ray absorption and emission spectroscopies have become very useful tools to study the electronic structure of highly correlated compounds [1]. This is particularly true for studies at the $L_{2,3}$ edge of the $3d$ transition metal compounds. Their electronic structure is the result of the interplay between intra-atomic effects such as the multiplet structure of the partially filled $3d^n$ subshell and its spin–orbit splitting and the effects due to the interaction

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between the transition metal ion and its ligands, such as the ligand field splitting of the $3d$ orbitals or charge transfer from the ligand into the metal ion. Resonant x-ray absorption at the $L_{2,3}$ edge results in the excitation of a $2p$ electron into an unoccupied $3d$ orbital. This process directly probes the unoccupied states of d symmetry. The $2p$ hole is then filled by resonant x-ray emission, which results in decay into the ground state of the system (elastic emission) or into excited states of the ground configuration (inelastic emission) and thus provides very direct information about the excited states of the $3d^n$ configuration of the transition metal ion [2].

These resonant x-ray absorption and emission spectroscopies have the advantage that in the whole process, the charge state of the transition metal ion does not change. The emission spectra then give direct information about the energy positions and relative intensities of the decay peaks that can be compared directly with a single calculation for the same ion. In this regard, the atomic multiplet ligand field calculations are particularly useful [3]. These calculations start with a Hartree–Fock calculation of the atomic multiplet [4]. Then the effect of the ligand field splitting of the $3d$ orbitals into t_{2g} and e_g orbitals is included [3].

The $3d$ transition metal fluorides are interesting systems in this regard. They are certainly the most ionic compounds, and therefore they should clearly show the effect of the atomic multiplet structure. Experimentally, we have found that the absorption and emission spectra of these compounds have sharp, well-defined features. They are thus good candidates for references of absorption and emission spectra of ionic $3d^n$ compounds. Direct comparison between the spectra of these fluorides and the corresponding oxides also provides information about the effects due to changes in the hybridization with different $2p$ ligand orbitals.

Recently, we published data for x-ray absorption and resonant emission at the manganese $L_{2,3}$ edge in MnF_2 [5]. The results indicate that the x-ray absorption spectrum is the best reference for a Mn^{2+} compound, because the corresponding absorption spectrum of MnO is usually contaminated by the Mn^{3+} spectrum due to surface oxidation [6]. The emission spectra are, however, more bulk sensitive. We therefore found that the resonant emission spectra of both MnF_2 and MnO can be explained within a free ion calculation for Mn^{2+} [7]. We also showed that $LaMnO_3$ is a very good example of a Mn^{3+} (or equivalently a d^4) compound [7].

In this paper, we present experimental results for x-ray absorption and resonant emission for FeF_2 and CoF_2. The data are then compared with atomic multiplet ligand field calculations for Fe^{2+} and Co^{2+}. We show that they constitute very good examples of resonant emission of d^6 (FeF_2) and d^7 (CoF_2) transition metal compounds. We also present a comparison among the emission spectra of $LaMnO_3$, MnF_2, FeF_2, and $LaMnO_3$ recorded with excitation energies at the top of the corresponding L_2 absorption peak. We therefore end up with reference resonant emission spectra for d^4, d^5, d^6, and d^7 transition metal compounds.

2. Experiment

The experiment took place at beamline 8.0 at the Advanced Light Source of Lawrence Berkeley Laboratory. Monochromatized photons from a 5.0 cm undulator (U5.0) are focused onto the sample, and the resulting fluorescence emission spectra are recorded with a high efficiency x-ray spectrometer. This soft x-ray fluorescence spectrometer is a grazing incidence instrument with a fixed entrance slit and a position sensitive area detector. A total electron yield (TEY) spectrum is obtained by recording the total electric current through the sample, as the energy of the exciting photons is scanned. Photon emission spectra are then recorded

at selected values of the incoming photon energy by positioning the spectrometer detector along the Rowland circle to intercept the wavelength region of interest. Details of the beam line and the spectrometer have been published elsewhere [8]. The incoming radiation flux is monitored by the total photocurrent produced in a gold mesh, placed in front of the beam just before the sample chamber. The monochromator energy is calibrated with the absorption spectrum of metallic manganese iron, cobalt, nickel, and copper samples that cover the entire region between 630 and 940 eV. We estimate that this calibration is accurate within 0.3 eV. The emission energy is then determined by the elastic emission peaks present in several of the spectra. The spectrometer detects photons emitted along the polarization direction of the incoming beam, in the so-called unpolarized geometry [9]. The FeF_2 and CoF_2 samples were commercial powders of purity greater than 99%.

The valence emission spectra obtained in the region of the $L_{2,3}$ threshold are affected by self-absorption [10]. We corrected for this effect following the procedure that was described in detail in previous papers [11]. All emission spectra shown in this paper are corrected for self-absorption.

3. Atomic multiplet ligand field calculation

Resonant x-ray absorption and emission is a coherent second-order process that is described by the Kramers–Heisenberg expression:

$$\sigma(\nu_1, \nu_2) \propto \left| \sum \frac{\langle f|\vec{\varepsilon}_2 \cdot \vec{r}|i\rangle \langle i|\vec{\varepsilon}_1 \cdot \vec{r}|g\rangle}{h\nu_1 - (E_i - E_g) - i\Gamma_i/2} \right|^2 \delta[h(\nu_2 - \nu_1) - (E_f - E_g)] \qquad (1)$$

where $|g\rangle$, $|i\rangle$, and $|f\rangle$ are the initial-, intermediate-, and final-state wavefunctions with energies E_g, E_i, and E_f, respectively. The transition operator $\vec{\varepsilon} \cdot \vec{r}$ assumes that all are electric dipole transitions, Γ_i is the $2p$-core-hole width, and the delta function assures overall conservation of energy. In this paper, we make some of the simplest assumptions to evaluate this expression [5]. We calculate the wavefunctions and the transition matrix elements using free-ion single-configuration Hartree–Fock calculations [3]. For the transition metal ions, these calculations start with a $3d^n$ ground configuration ($n = 6$ for Fe^{2+} and 7 for Co^{2+}). The ligand field interaction is calculated for this basis, and the resulting energy matrices are diagonalized. One then calculates the states that result from an electric dipole excitation of a $2p$ electron into the $2p^5 3d^{n+1}$ configuration. We assume that the $10D_q$ splitting parameter is the same in both the ground and excited configurations. In the present calculation, we also neglect the interference terms in equation (1). We also evaluate it at resonance, which makes the Lorentzian denominator equal to the $2p$-core width squared.

In this ligand-field no-interference approximation, an absorption spectrum is obtained by considering all transitions that start in the lowest energy states of the ground configuration, which have significant population at room temperature. Each transition energy is equal to the difference in energy between the ground and excited states, and its intensity is proportional to the square of the electric dipole transition matrix element [3]. For each absorption transition, we obtain an emission spectrum by considering all electric dipole transitions from the excited state into states in the $3d^n$ ground configuration [6]. The intensity of each emission line is then proportional to the product of squares of transition matrix elements $|\langle f|\vec{\varepsilon} \cdot \vec{r}|i\rangle|^2 |\langle i|\vec{\varepsilon} \cdot \vec{r}|g\rangle|^2$.

4. Results and discussion

In figure 1, we present a comparison between the TEY spectrum of FeF_2 and the calculated absorption spectrum of Fe^{2+}. The calculation originally gives [4] the transition matrix elements between the states in the $3d^6$ ground configuration populated at room temperature and the states in the $2p^5 3d^7$ excited configuration, and the corresponding photon energies. These transitions are indicated by vertical lines in the top spectrum. They are then convoluted with Fano profiles [12] with $q = 12.0$ and natural widths of 0.28 up to 719 eV and 0.90 eV between 719 and 735 eV [4]. The sum is then convoluted with a Gaussian instrument profile whose width is 0.6 eV. There is good overall agreement between the experiment and theory for this absorption spectrum. There is a shoulder at 706.4 eV followed by a broad peak centered at 707.8 eV that theory interprets as the result of the superposition of several strong absorption lines. Then there is a second group of peaks whose maximum is at 709.8 eV. The L_3 structure ends with weak peaks centered at $\sim$712 eV. The L_2 absorption feature begins with a shoulder at 719.2 eV, it reaches a broad maximum at 720.3 eV, and ends in a broad weak feature that has a maximum at $\sim$722.6 eV. The main discrepancy between the experiment and theory is the relative intensity of the peak at 709.8 eV. Theory predicts it to be less than half the maximum absorption, whereas the experiment finds it to be larger than 50%.

We found, for MnF_2 and $LaMnO_3$, that emission spectra recorded with an excitation energy at the L_2 edge give the best information about d-excited states in these systems [5, 7]. In figure 2, we present a comparison between the emission spectrum recorded with an excitation energy of 720.3 eV (right at the maximum of the L_2 peak) and the calculated spectrum. Since the ligand field parameter $10D_q$ used in the absorption calculation was small, we decided to
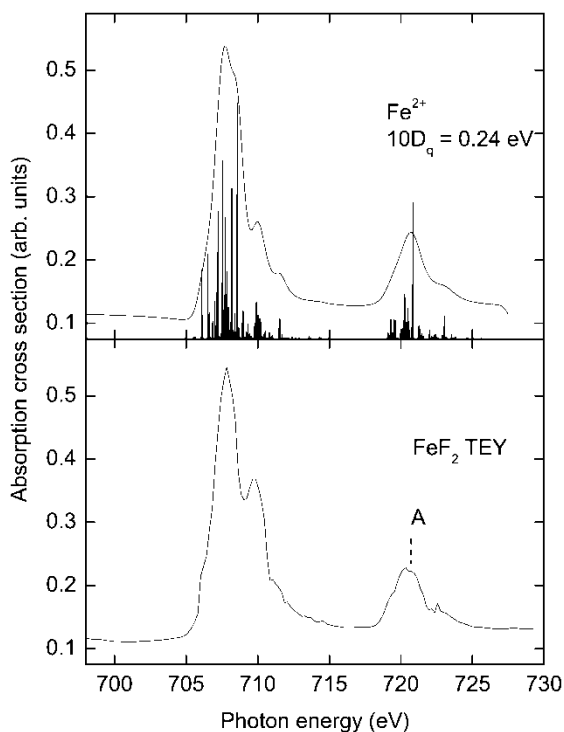

Figure 1. Comparison between the experimental TEY spectrum of FeF_2 (bottom) and the calculated absorption spectrum of a Fe^{2+} ion in an octahedral field (top). For the construction of the theoretical spectrum see the text.
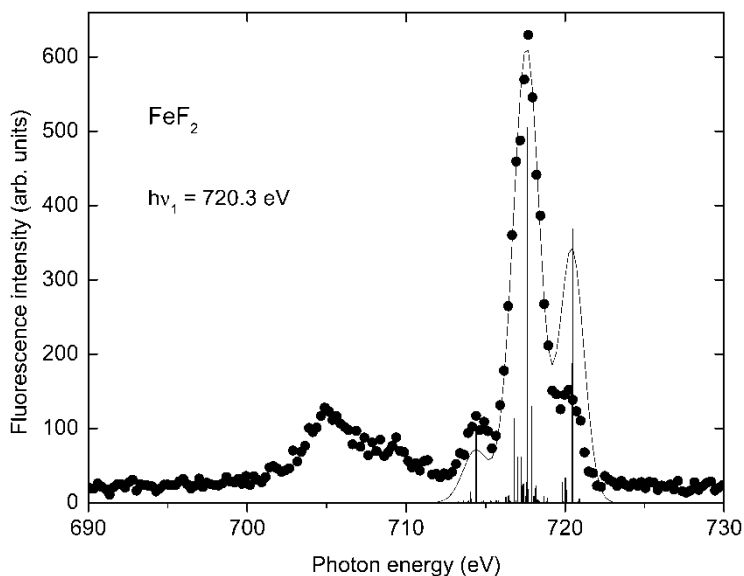
Figure 2. Comparison between the calculated and the experimental emission spectra of FeF$_2$ recorded with an excitation energy of 720.3 eV. The dots give the experimental data, and the solid line is the result of the calculation.
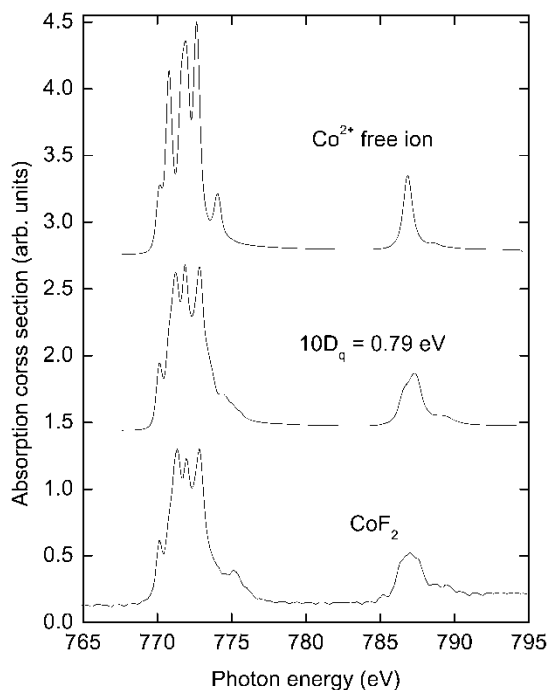

Figure 3. Comparison between the TEY spectrum of CoF$_2$ (bottom) and calculated absorption spectra for Co^{2+} obtained in the free-ion approximation (top) and with a ligand field parameter $10D_q = 0.79$ eV (middle).

perform the emission calculation in the free-ion approximation ($10D_q = 0.$ eV). Even under this assumption, the agreement between the experiment and theory is good. Both predict an elastic emission peak at 720.3 eV followed by a strong peak at 717.7 eV and a small peak at 714.5 eV. The experimental data then continues with several features between 700 and

711 eV that correspond to decay into the $2p_{3/2}$ hole produced *non-resonantly*. This normal L_α emission cannot be included directly into the calculation. The main discrepancy between the data is that the theory predicts a strongest elastic peak. This might be a result of an effect due to our unpolarized detection geometry [9] that is completely neglected in the calculation. In the free-ion approximation, the ground term of Fe^{2+} is a $3d^6$ 5D. The production of a $2p_{1/2}$ hole produces spin-mixed states that then decay into lower spin states of the ground $3d^6$ configuration. The strong inelastic peaks result from decay into triplet states.

In figure 3, we make a comparison between the TEY spectrum of CoF_2 and the results of a free-ion calculation and a ligand-field calculation with $10D_q = 0.79$ eV. Both calculations predict the same overall structure, with the L_3 edge containing a low-energy shoulder followed by three strong lines between 775.5 and 776.6 eV. Then, the free-ion calculation predicts a peak at 774 eV that is smeared in the ligand-field calculations. The L_2 edge in the free-ion calculation has two lines only, while the ligand field gives a low-energy shoulder, then the strongest L_2 peak at 787.3 eV, and a weak and broad feature at higher excitation energies. The agreement between the experiment and the ligand field calculation is rather good for this compound.

Next, we make a comparison between the experimental and the calculated emission spectra of CoF_2. The results are presented in figure 4. On top, we show the TEY spectrum and give two emission spectra, excited at peaks (b) and (e) in the TEY spectrum. A similar comparison was presented before [13] for the free-ion calculation. Here, we use the results of the ligand field with $10D_q = 0.79$ eV. The agreement with the experiment is certainly better for the
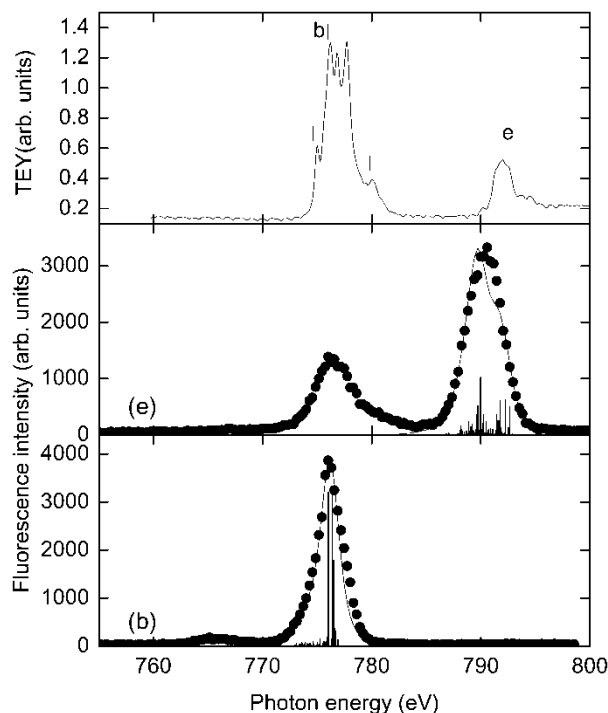

Figure 4. Comparison between calculated and experimental emission spectra of CoF_2. Top: TEY spectrum. Bottom: emission spectrum recorded with an excitation energy of 776.0 eV indicated by (b) in the TEY spectrum. Middle: emission spectrum obtained with an excitation energy of 791.9 eV indicated by (e) in the TEY spectrum. The dots give the experimental data, and the lines are the results of the calculation.
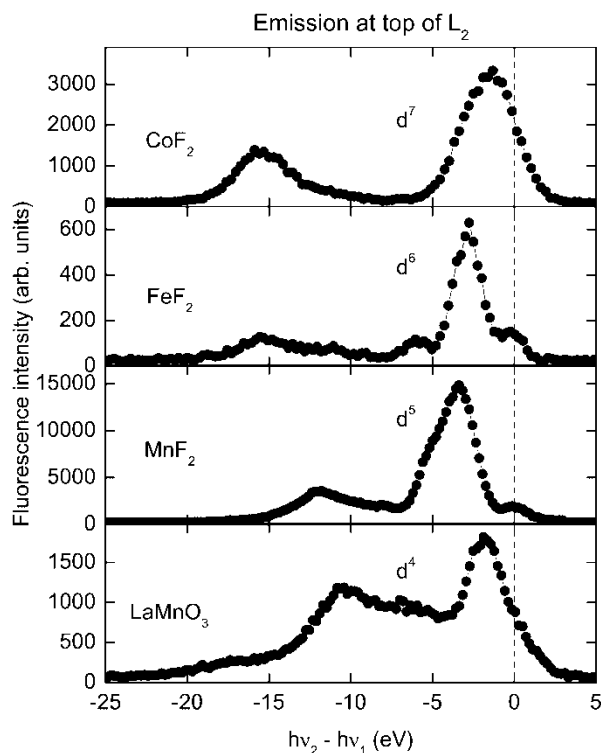
Figure 5. Emission spectra of LaMnO$_3$, MnF$_2$, FeF$_2$ and CoF$_2$ obtained with excitation energies at the top of the transition metal L_2 edge. The spectra are plotted as functions of the negative of the energy loss $h\nu_2 - h\nu_1$.

ligand-field calculation presented here, because in this case, we only need one instrument width to fit the data, whereas in the free-ion calculation, we adjusted it to achieve better agreement with the experiment. Emission at peak (b) is clearly dominated by the elastic peak, but the asymmetry in the line towards lower energies indicates the presence of inelastic peaks that correspond to decay into excited states of the $3d^7$ ground configuration. We also find in (b) a broad emission peak centered at $\sim$765 eV. This emission is due to decay into charge transfer states not considered in the calculation. In (e), decay is dominated into d-excited states with some elastic emission. Theory clearly underestimates the contribution from the elastic peak. At 776.5 eV, the experimental spectrum has the broad L_α normal emission peak that cannot be included in the calculation.

Finally, we present a comparison among the emission spectra recorded for an excitation energy at the top of the transition metal L_2 edge for LaMnO$_3$, MnF$_2$, FeF$_2$, and CoF$_2$ (figure 5). As we saw, these are examples of compounds for which the transition metal appears in the configurations d^4, d^5, d^6, and d^7, respectively. The spectra are plotted as a function of the negative of the energy loss $h\nu_2 - h\nu_1$. Elastic emission therefore appears at zero energy loss. In all these spectra, inelastic is the dominant emission. The position of the maximum of inelastic emission starts at -1.89 eV for LaMnO$_3$, then reaches a minimum value of -3.41 eV for MnF$_2$, and moves towards elastic emission for the other two compounds (-2.86 and -1.45 eV for iron and cobalt, respectively). In all compounds, the ground state corresponds to maximum spin, and the production of d-excited states necessarily means flipping at least one of the electron spins. These energies are therefore representatives of the energies needed to flip a spin in the transition metal compounds. As discussed before, these values are in good agreement with the results of ligand-field calculations.

5. Conclusions

We presented experimental results for x-ray absorption and resonant x-ray emission for the d^6 and d^7 compounds of FeF_2 and CoF_2, respectively. The data are compared with the results of ligand-field calculations. Good agreement between experiment and theory is found. These results complement previous data for d^4 ($LaMnO_3$) and d^5(MnF_2) compounds and allow a direct comparison of the energy needed to flip a spin in the ground configuration of these ionic compounds.

Acknowledgements

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