

Temperature-Dependent 1s2p Resonant Inelastic X-ray Scattering of CoO

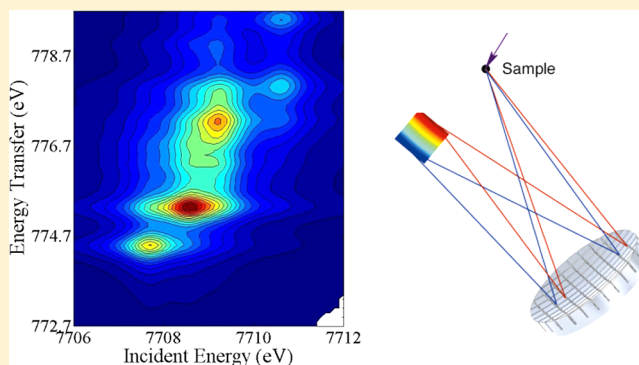
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ABSTRACT: The temperature-dependent 1s2p resonant inelastic X-ray scattering (RIXS) spectra of CoO have been measured with 0.3 eV overall resolution, and the RIXS planes have been analyzed with multiplet calculations. The analysis of the high-resolution 1s2p RIXS plane allows a more detailed determination of the ground-state electronic structure, as compared to 1s X-ray absorption spectroscopy (XAS). The apparent absence of interference effects suggests that the lifetime broadening of the pre-edge states is (significantly) reduced from the edge lifetime broadening. The temperature-dependent RIXS planes are explained as a combination of the ground state and first excited state due to thermal population of the excited state, which are a result of the symmetry distortion, 3d spin–orbit coupling, and magnetic exchange interactions. No features due to charge transfer and nonlocal transitions are observed due to the relatively small cobalt–oxygen overlap as compared to higher valent systems. The successful determination of the spin state and crystal field parameters using hard X-ray experiments promises to make 1s2p RIXS a useful technique for in situ transition metal oxide studies.



I. INTRODUCTION

Transition metal oxides comprise an important range of materials, including magnetic, ferroelectric, and superconducting solids and also battery, fuel cell, and catalyst systems. The X-ray absorption technique has developed into a valuable characterization method for these materials. The enhanced theoretical and experimental investigations on transition metal oxides amplify the understanding of these materials and the possible technological applications. An important facet of transition metal oxides is their electronic structure, which together with their geometry determines their properties and reactivity. Cobalt oxides are important transition metal compounds, and they have applications in, for example, magnetic materials, battery materials, and heterogeneous catalysis.^{1–4} There is a growing interest in cobalt oxides due to their giant thermo-power and ferromagnetism depending on the material details.^{1,5}

Together with NiO, CoO can be considered as a prototype material for electronic structure studies of the late transition metal oxides that are characterized by a charge transfer-induced band gap due to $\text{Co}(3d^7)\text{O}(2p^6) \rightarrow \text{Co}(3d^8)\text{O}(2p^5)$ charge fluctuations.⁶ The related band gap opening is not reproduced in LDA calculations. Modern electronic structure methods, for example, based on dynamical mean-field theory,⁷ reproduce the band gap behavior more appropriately.

X-ray photoemission experiments of CoO have revealed the charge transfer parameters in the early 1990s.⁸ The $3d^7$ ground state implies a complex ground-state configuration with plenty of low energy excitations. The reason is that the $3d^7$ state contains a partially filled T_{2g} shell that is affected by 3d spin–orbit coupling. L edge X-ray absorption experiments revealed that the 3d spin–orbit coupling is not quenched and the 4T_1 ground-state configuration is split into four substates. The E' -symmetry ground state is a Kramers' doublet, and the first excited state is a G symmetry state at excitation energy of approximately 40 meV. Temperature-dependent experiments have confirmed this small excitation energy.⁹ Dispersion due to translation symmetry is not able to remove the 40 meV energy difference. CoO has been studied with 2p3d RIXS, which reveals the charge transfer energies and the dd-excitations.¹⁰ The dd-excitation energies as determined by 2p3d RIXS are in agreement with optical experiments, electron energy loss experiments, and recent nonresonant inelastic scattering experiments.¹¹

In this study, we measure CoO with hard X-ray 1s2p RIXS, using a combination of a high-resolution monochromator and

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The RIXS planes are given as a two-dimensional (2D) contour plot by combining the X-ray absorption and X-ray emission processes.²¹ Cross sections through the contour plot include the constant incident energy (CIE) and constant emission energy (CEE). The CIE is a vertical cross section at fixed excitation energy, and it relates to resonant X-ray emission spectra. The CEE is a diagonal cross section at constant emission energy, and this CEE spectrum identifies with the high-energy resolution fluorescence yield (HERFD) spectrum. The complete pre-edge structures can be integrated yielding the total 1s2p decay intensity of all of the intermediate states to the 2p final state, and this relates to the 1s2p partial fluorescence yield (PFY) in the pre-edge region.

The importance of including thermally excited states to explain the experimental spectrum at temperatures in the range of 200–500 K is well-known.²³ Because of the dependence of temperature on the absorption and emission line shapes, the fractional populations of the excited states have to be taken into account.

IV. RESULTS AND DISCUSSION

Figure 2 shows the overview of the RIXS contour plot measured at 295 K. The diagonal colored stripes indicate the

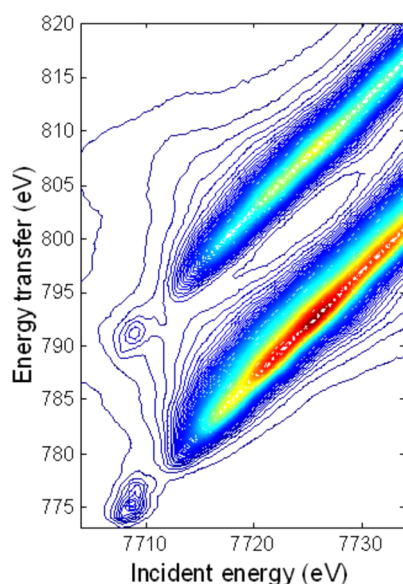


Figure 2. The experimental 1s2p RIXS plane of CoO. Red color indicates high intensity.

1s2p X-ray emission when CoO is excited above the K edge. In addition, the quadrupole pre-edge peak at 7708 eV is visible as two structures on the energy transfer axis, related to, respectively, the $2p_{3/2}$ (L_3) and the $2p_{1/2}$ (L_2) final states. No additional features, for example, due to nonlocal transitions, are observed, in contrast to the higher valent oxides such as TiO_2 ,²⁴ LiCoO_2 ,²⁵ and Fe_2O_3 .²⁶ We will focus on the RIXS spectra as measured in the pre-edge region, visible at the structure at 7708 eV incident energy and 775 eV energy transfer.

In Figure 3, the importance of high-resolution 1s2p_{3/2} RIXS experiments is shown. Figure 3a is measured with the analyzer at 1.0 m yielding a resolution of 1.0 eV and Figure 3b with the analyzer at 2.0 m yielding a resolution of 0.3 eV. It is evident that, as far as energy resolution is concerned, the competition with 2p XAS spectra can only be reached with the 0.3 eV

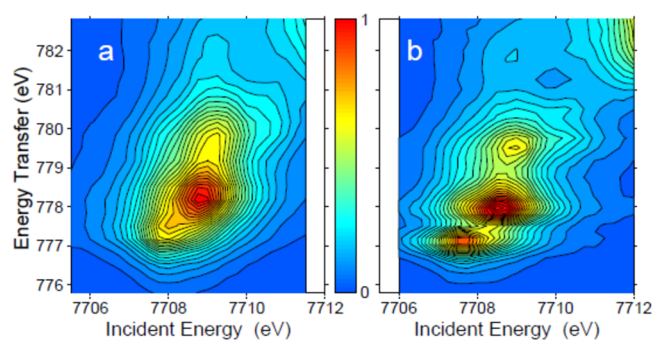


Figure 3. The importance of high-resolution RIXS experiments. The experimental difference between (a) 1.0 eV overall energy resolution and (b) 0.3 eV overall energy resolution is the analyzer position at 1 and 2 m, respectively.

overall resolution data. The data measured with 0.3 eV energy resolution show a number of features in the pre-edge 1s2p RIXS plane, which are only visible as asymmetries in 1 eV energy resolution. Qualitatively, these features can be understood as quadrupole 1s3d excitations from the $3d^7$ ground state to the $1s^13d^8$ intermediate state, followed by the 1s2p X-ray emission decay into the $2p^53d^8$ final states.

Figure 4 shows an analysis of the 1s2p experimental RIXS spectra at 14 and 295 K. The pre-edge has three clearly separated peaks, which are positioned at, respectively, 7707.7 eV with an emission energy of 774.4 eV (referred to as feature A in Figure 4), 7708.6 eV with emission energy of 775.3 eV (feature B), and 7709.1 eV with emission energy of 777.0 eV (marked as feature C). At excitation energies above 7111 eV, the edge absorption is visible above 779 eV energy transfer. On the right side, the CIE cross sections at 7707.7 eV (upper panel) and at 7708.6 eV (lower panel) of both the 14 and the 295 K spectra are given. It is clear from the two-dimensional spectra that for both temperatures, feature B has the highest intensity. The overall spectral shapes at both temperatures are similar, but some features acquire increased intensity at 295 K.

To reproduce the experimental features quantitatively, crystal field multiplet calculations are performed and given in Figure 5. The temperature is included as a Boltzmann weighted sum of the ground states. The experiment is performed with the propagation direction along the x -axis and the E vector along the y -axis. The detection is along the y -axis with the E vector along the x -axis. This is calculated using C_4 symmetry and a combination of incident z -polarized X-rays and excited left plus right polarized X-rays.²⁷

The Kramers–Heisenberg equation adds at each excitation energy Ω the relative weight of the excited states, as calculated from their relative intensity, their energy difference to Ω , and the Lorentzian broadening factor. This implies that states that are closer in energy than their Lorentzian broadening show interference effects. The interference effects can be modulated theoretically by varying the Lorentzian broadening of the intermediate state, from large interference (large Γ_i) to no-interference (zero Γ_i). The results of the calculation with a Lorentzian broadening of 1.0 eV are given in Figure 5a. The three crystal field split peaks A, B, and C, which are seen in the experimental spectrum, are reproduced by the calculation. Figure 5c shows the CIE cross sections through E_A , which should be compared to the experimental cross sections given in Figure 4. From the results, we conclude that feature C is

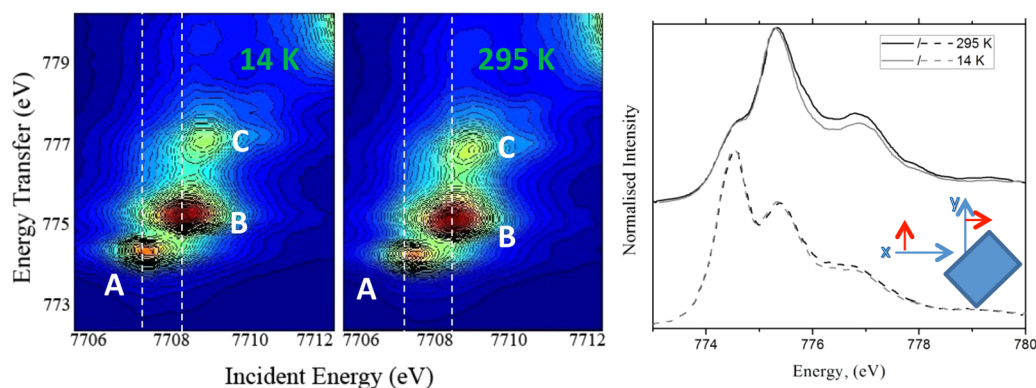


Figure 4. The experimental $1s2p_{3/2}$ RIXS spectra at 14 and 295 K. The CIE cross sections at 7707.7 eV (upper panel) and 7708.6 eV (lower panel) are given for both temperatures. The inset shows the polarization dependence. The electric field vector (E) is indicated with red arrows.

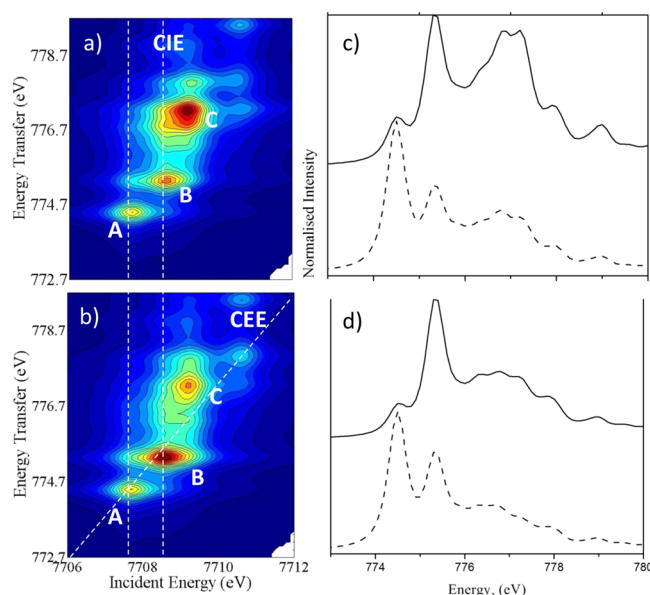


Figure 5. The theoretical $1s2p$ RIXS spectrum is given with (a) and without (b) interference. Panels c and d give the corresponding CIE cross sections at the selected excitation energies E_A (—) and E_B (---).

present with higher intensity in comparison with the experiment.

A calculation with a Lorentzian broadening of 0.0 eV is shown in Figure 5b. Without Lorentzian broadening, the interference effects are omitted by only allowing the excitation and decay via the same intermediate state. Effectively this corresponds to the calculation of the X-ray absorption spectrum times the (excitation state dependent) X-ray emission spectrum. The comparison of Figure 5a and b shows that at the excitation energy through A the effect of interference is negligible. At higher excitation energies (through B), interference effects have a larger effect. The CEE cross section, which is shown as a diagonal cut at constant emission energy in Figure 5b, shows that the two crystal field split peaks A and B have constant emission energy. This suggests that the quadrupole excitation reaches different multiplet states in the K pre-edge, and these states maintain their energy difference in their decay process. From the comparison of the calculations (Figure 5) with experiment (Figure 4), we conclude that the experimental spectrum seems better reproduced with the calculation with zero Lorentzian broadening. This implies that the Lorentzian broadening of 1.0 eV yields too large interference effects. The most likely explanation is that the actual lifetime broadening of the pre-edge peaks is less than 1.0 eV. This implies that the lifetime broadening of the pre-edge

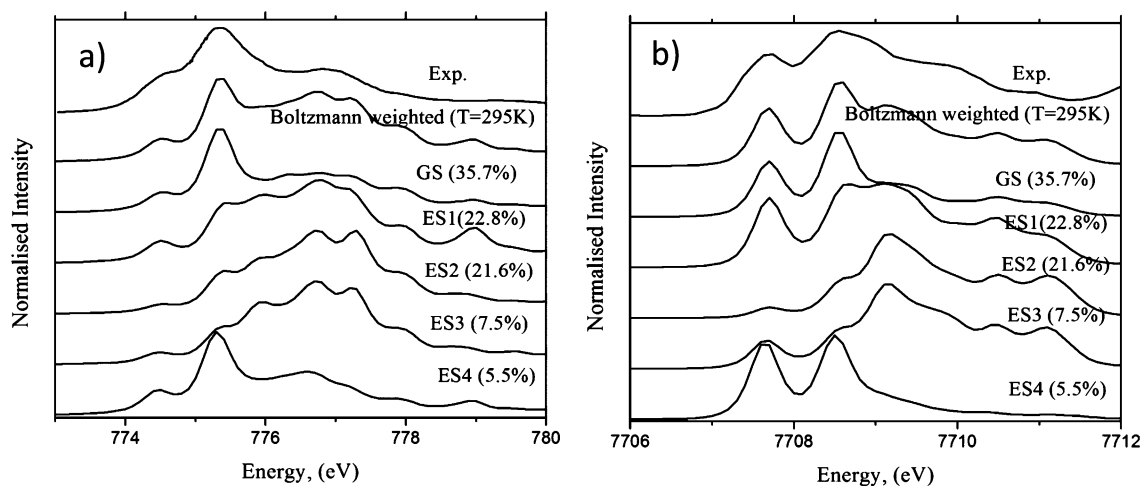


Figure 6. The calculated spectra of the ground state (GS) and the excited states (ES1, ES2, ES3, and ES4). The relative contribution of each state at $T = 295$ K is indicated with the percentage in brackets. (a) CIE at E_B , and (b) CEE through the emission maximum at 6933.2 eV.

peaks seems to be significantly reduced from the lifetime broadening of the main edge.

The temperature dependence on the spectral shapes can be studied by using Boltzmann distribution. The first 12 substates of 4T_1 symmetry Co^{II} ground state are found within an energy range of 126 meV. For the room temperature experiment, there will be a non-negligible contribution from the thermally excited states. At 14 K, 99.9% of the population comes from the ground state. The populations at 295 K are, respectively, 35.7%, 22.8%, 21.6%, 7.5%, and 5.5% for the first five states including the ground state. Out of the 12 states of the Co^{II} ground state, these five states add up to 93% of the total populations. The statistical weights of the populations of these five states (indicated as, respectively, GS and ES1–4) for the CIE cross section at excitation energy E_B and CEE cross section at the maximum fluorescence (6933.2 eV emission energy) are given in Figure 6. In both cases, the calculations are compared to the experimental spectra.

At excitation energy E_B , the inclusion of the thermally excited states adds up the intensity of the features A, B, and C. This intensity gain of the spectral features is in agreement with the experimental observation. The Boltzmann weighted spectra of the partial fluorescence yield (Figure 6b) are in good agreement with the experimental HERFD spectra. The good comparison at finite energy confirms the energy positions of the excited states. In other words, at room temperature, the Co^{II} ground state is a mixture of $^4T-E'$ and ^4T-G symmetry states.

V. CONCLUDING REMARKS

In this work, we have demonstrated the advantage of high-resolution RIXS measurements. The additional features in the K pre-edges are only visible with the experimental resolution of 0.3 eV. By the inclusion of proper crystal field strength, spin orbit coupling, and magnetic exchange on a slightly distorted cubic structure of CoO, adequate agreement with the experimental spectra is achieved. The use of a zero Lorentzian broadening improves the agreement between the intensity patterns of the spectral features with the experimental spectra, suggesting that the lifetime broadening of the pre-edge states is less than 1.0 eV. The temperature dependency on the spectral shape is explained using a Boltzmann distribution of the lowest five states of the 4T_1 multiplet.

The presence of several states within a small energy range of 100 meV implies the existence of thermally populated excited states at higher temperatures. The Boltzmann weighted spectrum of the partial fluorescence yield (at maximum fluorescence) is in good agreement with the HERFD spectrum. Hence, the Co^{II} ground state can be rather considered as a combination of $^4T-E'$ and ^4T-G symmetry states. It can be expected that the occupation of thermally excited states redistributes the charge density as a function of temperature, which could invoke magnetic and/or electronic phase transitions. This change in ground state is an important factor for several applications, for example, in the magneto-optics field where the magnetic ground state determines the magneto-optic effect.

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Notes

The authors declare no competing financial interest.

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