Low energy excitations in CoO studied by temperature dependent x-ray absorption spectroscopy

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We have measured the intricate temperature dependence of the Co L₂,₃ x-ray absorption spectra (2p-3d excitations) of CoO. To allow for accurate total electron yield measurements, the material has been grown in thin film form on a metallic substrate in order to avoid charging problems usually encountered during electron spectroscopic studies on bulk CoO samples. The changes in spectra due to temperature are in good agreement with detailed ligand-field calculations indicating that these changes are mostly due to thermal population of closely lying excited states, originating from degenerate t₂g levels lifted by the spin-orbit coupling. Magnetic coupling in the ordered phase, modeled as a mean-field exchange field, mixes in excited states inducing a tetragonal charge density. The spin-orbit coupling induced splitting of the low energy states results in a non-trivial temperature dependence for the magnetic susceptibility.

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It is an observation that many insulating 3d transition metal compounds do not reveal orbital degrees of freedom in their electronic structure despite the incomplete filling of the 3d shell. This is related to the fact that the symmetry of the crystal often becomes so low that the degeneracy of orbitals is effectively lifted. This could be seen as a consequence of the Jahn-Teller theorem stating that "when the orbital state of an ion is degenerate for symmetry reasons, the ligands will experience forces distorting the nuclear framework until the ion assumes a configuration both of lower symmetry and of lower energy, thereby resolving the degeneracy."

Nevertheless, for some compounds, with CoO and FeO as well known examples, a (nearly) cubic structure exists although these systems have a partially filled t₂g sub-shell. In such cases the orbital degeneracy can be lifted by the spin-orbit coupling (SOC). This in turn leads to quite interesting local physics, not only because of the formation of orbital moments and large magnetocrystalline anisotropies, but also because of a strong temperature dependence in the local magnetic properties as we will address below.

Taking the case of CoO, we will describe its ground state and low-energy local excitations using the theoretical framework laid out by Kanamori and Goodenough. The Co ions in this material are divalent and have 7 electrons in the 3d shell. Due to electron-electron interactions, a Hunds-rule S = 3/2 high-spin ground-state is realized, with an electronic configuration of approximately t₂g⁵e_g². The single hole in the t₂g shell can be in three different orbitals, normally denoted as an xy, xz, or yz orbital. With the SOC being present, one should consider making complex linear combinations of these orbitals like 1/√2(−xz − yz) that carry an orbital momentum of 1 \( \mu_B \) in the z direction. Orbital momentum in the x or y direction can be created by cyclic permutation of the coordinates. One can therefore assign to each t₂g electron a pseudo orbital momentum of \( l = 1 \) (note that it is still a d electron so \( l = 2 \)). For CoO this results in a total pseudo orbital momentum of \( \bar{L} = 1 \). This orbital momentum couples with the spin \( S = 3/2 \) to a state with \( J = 1/2, 3/2, \) and 5/2. The doublet with \( J = 1/2 \) is the ground-state, with the quartet about 40 meV higher and the sextet about 120 meV higher than the ground-state. Furthermore, the sextet is split by the cubic crystal field into a quartet and doublet. In estimating the numbers we have used a SOC constant of \( \zeta = 66 \) meV from atomic Hartree-Fock calculations.

Experimentally one could measure these excitations with the use of inelastic neutron scattering. The interpretation is somewhat complicated as one measures phonons, magnons and spin-orbit excitations all at the same time, but satisfying results have been obtained. Yet, it would be welcome to have an alternative spectroscopic method with perhaps also advantages in terms of element specificity in case one is dealing with a multi-component materials, or higher material sensitivity for, e.g., thin films. In this regard it has been recognized that soft x-ray absorption spectroscopy (XAS) should have the potential to reveal the presence of those excited states: Tanaka and Jo and De Groot have calculated that theoretically one should see a strong temperature dependence in the XAS lineshape. In such an XAS process, the soft-x-ray photon (770-800 eV) is used to promote a 2p Co core electron into the 3d valence shell. This transition is subject to strict dipole selection rules, e.g., \( \Delta J = 0, \pm 1 \) in spherical symmetry, with the result that each particular initial state has its own set of reachable final states. It turned out that the differences between the sets of final states are appreciable when the differences in the initial states can be traced back to differences in the
In Fig. 1 we have plotted the isotropic Co-L$_{2,3}$ XAS spectra calculated for each initial state having a different $J$. Here we used the successful configuration interaction model that includes the full atomic multiplet theory and the hybridization with the O 2p ligands. We have carried out the calculations for the Co$^{2+}$ ion in the CoO$_6$ octahedral cluster using the XTLS8.3 program with parameter values typical for a Co$^{2+}$ system. The spectra are dominated by the Co 2p core-hole spin-orbit coupling which splits them roughly in two parts, namely the $L_3$ ($h\nu \approx 779$ eV) and $L_2$ ($h\nu \approx 794$ eV) white line regions. The curves in Fig. 1 reproduce the main results of Tanaka and Jo$^{13}$ and De Groot$^{14}$. We have not separately shown the two spectra for the doublet and quartet states originating from the $J = 5/2$ but combined them.

The energy splitting between these two set of states is small enough compared to the energy difference between the ground-state and the center of the $J = 5/2$ states so that this splitting is of no real importance if the states are to be populated by temperature. These calculations show that the differences are so large that an experimental resolution of order several 100 meV would be more than sufficient to discriminate the various initial states differing 100 meV or less in energy. Important is only the temperature and the statistics with which the spectra have to be measured.

Nevertheless, it is rather surprising that to the best of our knowledge no experimental data have been reported in the literature so far to confirm the validity of the calculations, i.e. 14-17 years after the appearance of Tanaka and Jo$^{12}$ and De Groot$^{13}$ studies. Indeed, it turned out to be difficult to obtain reliable XAS data of CoO. Standard methods to measure the XAS signal failed so far: the total electron yield (TEY) method cannot be applied since CoO is strongly charging at low temperatures, and the fluorescence yield (FY) method suffers from too strong self-absorption effects, causing severe distortions in the spectral line shapes. We therefore have set out to prepare CoO in thin film form on metallic substrates, thin enough as to avoid charging problems upon measurement using the TEY method and yet thick enough to essentially retain the properties of bulk CoO. The thin film must also be polycrystalline, as to avoid complications caused by the occurrence of (magnetic) linear dichroism effects.$^{17,18,19}$

The XAS measurements were performed at the Dragon beamline of the NSRRC in Taiwan. The spectra were recorded using the total electron yield method in a chamber with a base pressure of $3 \times 10^{-10}$ mbar. The photon energy resolution at the Co L$_{2,3}$ edges ($h\nu \approx 770 - 800$ eV) was set at 0.3 eV. The actual polycrystalline CoO thin film was grown in-situ on a polycrystalline Ag sample by means of molecular beam epitaxy (MBE), i.e. evaporating elemental and Co from alumina crucibles in a pure oxygen atmosphere of $10^{-7}$ to $10^{-6}$ mbar. The base pressure of the MBE system is in the low $10^{-16}$ mbar range. The thickness of the MBE film was about 90 Å as determined using a quartz-balance monitor, which in turn was calibrated using the time period of the oscillation in the intensity of reflection high energy electron diffraction (RHEED) pattern of CoO thin films epitaxially grown on Ag(001)$^{19,20}$ From that single crystal work we also know that a 90 Å CoO film has a Néel temperature of about 290 K, i.e. essentially identical to the 291 K value determined for the bulk material.$^{21}$ The polycrystalline CoO thin film has been measured at normal incidence with a beam-spot size of about 1 mm$^2$. Homogeneity of the thin film has been verified by measuring at several different positions on the thin film resulting in negligible differences of the spectra.

Fig. 2 shows the Co-L$_{2,3}$ XAS spectra of the polycrystalline CoO thin film taken at various temperatures between 77 K and 400 K. The general line shape of the spectra shows the characteristic features very similar to that of bulk CoO$^{22}$, verifying the good quality of our CoO film. The low-temperature spectra have been measured before and after heating to 400 K showing no detectable changes demonstrating the chemical stability of the sample. Important is that high quality spectra can be obtained for all temperatures, and this without the slightest indication for a reduction of the intensity for the lower temperature spectra, demonstrating that our thin film approach is a successful resolution against the
This phase transition is accompanied by a tetragonal distortion and smaller distortions to even lower symmetry. CoO undergoes an anti-ferromagnetic ordering at 291 K. It is well known that CoO at several temperatures. Temperature dependence is due to population of excited states according to Boltzman statistics. Non-cubic distortions and magnetic correlations have been neglected.

A closer look at the experimental spectra in Fig. 2 reveals that there is a small but systematic change in the line shape with temperature. A blow-up of the spectra in the $L_2$ edge range makes this even clearer. To understand this temperature dependence quantitatively, we simulated the spectra by summing up the theoretical distortions (and the exchange field) can mix the low-energy states with different $t_{2g}$ orbital occupation, split by spin-orbit coupling, thereby changing the lineshape of the spectra. As the magnetic correlations and the tetragonal distortion are temperature dependent this could also result in a temperature dependence of the spectra. We will show below that the inclusion of these effects will even improve the already very good agreement between the temperature dependent theoretical and experimental Co $L_{2,3}$ spectra as shown in Fig. 3.

In the top panels of Fig. 4 we show the energy level diagram of the lowest 12 eigen-states of a CoO$_6^{10-}$ cluster as a function of exchange field (left) and tetragonal splitting between the $d_{xy}$ and $d_{xz/yz}$ orbital (right). The inset shows the $t_{2g}$ hole density. For cubic symmetry the ground-state is a Kramer’s-doublet, which has a cubic charge density. For both an exchange field (in the $z$ direction) and a tetragonal contraction of one Co-O bond, the $d_{xy}$ orbital becomes more occupied and the hole resides in a complex linear combination of the $d_{xz}$ and $d_{yz}$ orbital carrying an orbital momentum parallel to the spin of that hole. The bottom panels of Fig. 4 show the changes of spectra (at 0 K) as a function of these non cubic distortions. One can clearly see small changes in the spectra. The line-shape of the changes due to quantum mechanical mixing of the excited states into the ground-state are rather similar to the changes caused by thermal population. This leads to a compensating effect: in going from low to high temperatures, one has a reduction of the exchange field and tetragonal splitting (they eventually disappear above the Néel temperature), and thus changes in a direction opposite as those caused by the thermal population effect. The temperature dependence in the experimental spectrum is thus a result of the thermal population of excited states as shown in Fig. 3, slightly reduced in its magnitude by quantum mechanical mixing of the excited states into the ground-state at low temperatures as shown in Fig. 4. Indeed, a detailed comparison between Figs. 2 and 3 reveal that the theoretical spectra show too much change with temperature, and the inclusion of those quantum mechanical mixing effects from Fig. 4 will improve the agreement even more.

The presence of the SOC has obviously important consequences for the ground state and the magnetic properties of the Co ion. The SOC lifts the orbital degeneracy and the ground-state (without magnetic interactions) becomes a Kramers doublet with an effective $\mu_B = 4.15$, $\mu_B = 4.29$, and $\mu_{eff} = 3.72\mu_B$. The induced Van Vleck moment is $0.015\mu_B$ per Tesla. Exchange fields and crystal distortions mix in excited states, thereby altering the expectation value of the magnetic moment. At the same time
these distortions induce a non-cubic local charge density and create linear dichroism. In order to calculate the low temperature ordered moments we need to make an estimate for the exchange field and tetragonal distortion. CoO has a 1.2% tetragonal contraction at low $T$.\(^\text{21}\) If we interpolate the values for the crystal-field and the exchange field as found for CoO thin films grown on MnO and Ag\(^\text{19}\) we find an exchange field of 12.6 meV and a tetragonal distortion of 25 meV between the $d_{xz}/d_{yz}$ orbital. With these values we find for the ground-state that the total magnetic moments are $S_z = -1.14\hbar$ and $L_z = -1.15\hbar$ ($M_z = 3.44\mu_B$).

The SOC induced splitting of the low lying states has also important consequences for the temperature dependence of the magnetic susceptibility, in an analogous manner as it causes the temperature dependence of the XAS spectra. We have calculated the magnetic susceptibility $\chi = \lim_{H \to 0} \partial M/\partial H$ (which is equal to $M/H$ for $H$ small enough), for a CoO\(_6^{10-}\) cluster. In Fig. 5a we show the susceptibility calculated for the entire cluster including all Van Vleck moments (dotted line) and the susceptibility calculated for the lowest 12 eigenstates (straight line). For the second calculation we have thus neglected the Van Vleck (and Curie) susceptibility induced by the higher lying states, such as found around 1 eV involving a $t_{2g} \rightarrow e_g$ orbital excitation. This roughly corresponds to experimentally subtracting a constant from the measured susceptibility such that the high temperature limit goes to zero. Panel b of Fig. 5 shows $1/\chi$ against the temperature. One can observe that the curve does not follow a linear behavior in a large temperature regime. There are two limiting cases of interest. For $k_B T$ much smaller then the energy of the first excited state one should expect normal Curie-Weiss behaviour. This asymptote is indicated in Fig. 5b by a straight line on the left (blue). The other limit would be when $k_B T$ is much larger then the highest energy of the excited states split by SOC. In this limit one would again expect to retrieve a 're-normalized' Curie-Weiss like behavior. This limit is indicated in Fig. 5b by a straight line on the right hand side (red). One can see that for temperatures starting roughly at 600 K $1/\chi$ shows linear behaviour and the high temperature limit is reasonably achieved. One might naively think that the high temperature region can be used to extract magnetic quantum numbers as it is often done when a Curie-Weiss-like behavior is observed, but then one must also realize that those numbers are not representative for the ground state.

To illustrate this more clearly, we will discuss both limits in more detail. We start with the low temperature limit. In Fig. 5c we plot $\mu_{\text{eff}}^2$ the (apparent) effective magnetic moment squared ($\mu_{\text{eff}}^2$ is defined here as $3k_B$ divided by the temperature derivative of $1/\chi(T)$). In the low temperature limit $\mu_{\text{eff}}^2$ does not become a constant as one should expect for Curie-Weiss behaviour as we did not subtract the Van Vleck moments for the ground-state doublet. (The straight line is calculated for a subtraction of the Van Vleck moments for the lowest 12 states, which still allows the ground-state doublet to have a positive Van Vleck moment and the ex-

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**FIG. 4:** (color online) Top panels energy level diagram of the 12 lowest states of a CoO\(_6^{10-}\) cluster as a function of exchange field (left) and tetragonal crystal field distortion (right). Inset shows the ground-state $t_{2g}$ hole density. Bottom panels: Theoretical Co-$L_{2,3}$ XAS spectra of CoO as a function of exchange fields (left) and tetragonal crystal field distortion (right).
Van Vleck subtracted susceptibility. Panel a: Susceptibility. mark the low (blue) and high (red) temperature limit of the eV and above) excited states neglected. The vertical lines cited states a negative Van Vleck moment such that Θ as defined in the text.

One does not only find a deviation from the ground-state effective moment but the high temperature limit also induces an apparent Weiss temperature. The Weiss temperature Θ is defined here as the intercept of the tangent to the 1/χ(T) curve with the abscissa. This can be calculated by making a series expansion of 1/χ in 1/T. \( \Theta_N = 1/k_B \left( \sum_{i=1}^{N} \nu_i \Delta_i / \sum_{i=1}^{N} \nu_i - \sum_{i=1}^{N} \nu_i \Delta_i / \sum_{i=1}^{N} \nu_i \mu_i^2 / \sum_{i=1}^{N} \nu_i \mu_i^2 \right) \), with \( \Delta_i \) the energy of the i-th set of eigenstates. In panel d of Fig. 5 we plot the apparent Weiss temperature as a function of T. One can see a strong temperature dependence and the Weiss temperature slowly saturates at 242 K. This apparent Weiss temperature has nothing to do with magnetic correlations since they were not included in this single ion calculation. Instead, the strongly varying (apparent) Weiss temperature merely reflects the fact that there are excited states with different magnetic quantum numbers thermally populated.

Interestingly one finds that the high temperature limit for the (apparent) effective moment squared is reached at temperatures much lower then the energy of the highest excited state. We have added vertical bars at the energies of the excited states in Fig. 5 and one can see that \( \mu_{\text{eff}}^2 \) becomes reasonable constant at a temperature that is about half the energy of the highest excited state. Not only does one find that the high temperature regime for \( \mu_{\text{eff}}^2 \) starts at rather low temperatures, one also finds that the low temperature region, where the ground-state Curie-Weiss and Van Vleck moments can be obtained, extends only up to 50K, roughly a tenth of the energy of the first excited state. This is particular disturbing as one naively would expect that excited states would only distort the susceptibility at temperatures comparable to the energy of the excited state.

In the presence of magnetic correlations, such as in the real CoO material, those thermal population effects become very much masked or hidden. One then easily interprets the high temperature Curie-Weiss limit as a region in which one is free from magnetic correlations and yet still can capture the ground state local quantum numbers, and one also easily thinks that the measured Weiss temperature is only due to the magnetic correlations. The application of the Curie-Weiss law obviously leads to errors in case SOC is active.

The effect of SOC excited states on the magnetic susceptibility are well recognized in systems with an open 4f shell. For 3d systems with an open \( t_{2g} \) shell in nearly cubic symmetry these effects should also be important.
In that respect high-spin Fe$^{2+}$, Co$^{3+}$ and Co$^{2+}$ are good candidates to show such effects.

To conclude, we have been able to accurately measure the temperature dependence of the Co $L_{2,3}$ x-ray absorption spectra of CoO. The use of polycrystalline thin films of CoO grown on a Ag substrate allowed us to avoid charging problems usually encountered in electron spectroscopic studies on CoO. The changes in spectra as a function of temperature can be well explained in terms of the thermal population of closely lying excited states, originating from degenerate $t_{2g}$ levels lifted by the spin-orbit coupling. The existence of these excited states also lead to a non-trivial temperature dependence for the magnetic susceptibility, e.g. one cannot apply the Curie-Weiss law to extract the relevant ground state quantum numbers from the high temperature region.

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