Temperature dependence of crystal field excitations in CuO

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Orbital physics in transition metal oxides is a topic that remains in the forefront of modern physics. The complex interplay between orbital and other electron degrees of freedom results in a wide range of phenomena that pose challenges for condensed-matter physics, such as metal-insulator transitions, superconductivity, and colossal magnetoresistance [1]. Cupric oxide CuO (tenorite) is an antiferromagnetic insulator that has recently attracted interest as an induced multiferroic with high T_C [2]. Unlike its periodic-table neighbors NiO or CoO, CuO does not have a cubic structure with an octahedral coordination of the metal ion, but instead has a monoclinic unit cell and a slightly distorted square planar local coordination. These CuO_4 units bear resemblance to the CuO_2 planes in cuprate high-T_C superconductors. An understanding of the electronic structure of CuO is thus an important benchmark for the quest to understand superconductivity. CuO also displays many intriguing properties such as charge-stripe ordering [3] and spin-phonon interaction [4].

The orbital excitations that take place within the 3d shell of a transition metal ion, also called dd or crystal-field excitations, are well-known probes of the local electronic structure. They have traditionally been studied using optical absorption spectroscopies [5], but electron-energy-loss spectroscopies [6] and resonant inelastic x-ray scattering (RIXS) [7–11] have been relatively recent introductions to the dd excitation toolbox. Even more recently, non-resonant inelastic x-ray scattering (NRIXS) has emerged as a complementary, bulk-sensitive and high-resolution tool for dd excitations [12, 13]. Indeed, in many transition metal oxides they have been extensively studied using NRIXS [12], [14–17]. A detailed theoretical framework has been formulated for the interpretation of NRIXS for studies of dd excitations via an effective operator formalism [18].

Only few studies have been reported on the crystal-field and charge-transfer excitations in CuO. Optical-absorption studies cannot probe it since the band gap (∼1.5 eV) [19] is smaller than the dd excitation energies (∼2 eV). Döring *et al* [20] studied CuO using RIXS by resonantly enhancing the charge-transfer excitation at the Cu K absorption edge (E = 8.98 keV). Ghiringhelli *et al* [9, 10] have studied the dd excitations using RIXS at the Cu L_3 absorption edge (E = 930 eV). They reported dd excitation spectra centered at ∼2 eV. Recently, Wu *et al* [21] reported angle-resolved NRIXS data on CuO, assigning three excitations observed at 1.8 eV, 2.1 eV, and 2.2 eV to excitations of the hole occupied by the $x^2 - y^2$ orbital to xy, xz/yz and z^2 orbitals, respectively.

CuO exhibits two successive magnetic transitions at T_{N1} = 213 K and T_{N2} = 230 K [22, 23]. Below T_{N1}, CuO is in an antiferromagnetic commensurate collinear phase, and between the two transition temperatures in an incommensurate spiral phase. The latter phase has recently drawn interest because it has ferroelectric properties with a very high ferroelectric critical temperature $T_C = T_{N2}$ [2]. The band gap has also been shown to have a strong dependence on temperature, due to a relatively

strong electron–phonon coupling [19]. The present study is aimed at the determination of the dd spectra as a function of temperature, especially to see whether the two phase transitions or electron–phonon coupling have detectable influences on the spectral lineshape. While for example the electronic structure of CoO has recently been studied as a function of temperature [24, 25], for CuO temperature-dependent high-energy resolution studies have to our knowledge not been reported.

In this article, we report high-resolution (ΔE = 60 meV) NRIXS spectra of CuO in temperatures between 10–320 K. The observable in NRIXS is the intensity of radiation scattered via an inelastic process where both momentum $\hbar\boldsymbol{q}$ and energy $\hbar\omega$ are transferred to the electron system [26]. In the following we assume atomic units, *i.e.* $\hbar = 1$. The probability for scattering is quantified by the doubly differential cross section, which is related to the electron dynamic structure factor [26] as

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}\omega} = \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{Th}} S(\boldsymbol{q},\,\omega),$$

where $(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{Th}}$ is the Thomson scattering cross section, and $S(\boldsymbol{q},\omega)$, the dynamic structure factor, contains the information on the material properties to be investigated. The same function is measured in electron energy loss spectroscopy (EELS) [6]. Both EELS and NRIXS have their advantages. In general, NRIXS has its strengths in being bulk sensitive, also yielding access to extreme sample environments such as high pressure, and having access to high momentum transfers. The $S(\boldsymbol{q},\omega)$ can be written as

$$S(\boldsymbol{q},\,\omega) = \sum_F \left| \left\langle F \left| \sum_j \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j} \right| I \right\rangle \right|^2 \delta(\Omega_{\mathrm{F}} - \Omega_{\mathrm{I}} - \omega),$$

where $|I\rangle$ (Ω_I) and $|F\rangle$ (Ω_F) are the initial and final states (energies) of the electron system, respectively, with a summation over all electrons j. The dynamic structure factor is also related to the macroscopic dielectric function $\varepsilon(\boldsymbol{q},\omega)$ as

$$S(\boldsymbol{q},\omega) = -\frac{n}{4\pi e^2}\mathrm{Im}[\varepsilon^{-1}(\boldsymbol{q},\omega)]\,.$$

This equivalence is often used to relate optical spectra and dielectric screening to the results of an energy-loss experiment such as EELS or NRIXS [17, 27]. The theoretical framework on how NRIXS can access dipole-forbidden excitations in different systems has been laid down in, e.g., [13], [18], [28–31].

CuO has a monoclinic crystal structure (space group $C2/c$) [32] with eight nonequivalent Cu and O sites in the primitive unit cell [22, 23]. The lattice parameters are a = 4.68 Å, b = 3.42 Å, c = 5.13 Å, $\alpha = \gamma = 90°$ and $\beta = 99.5°$. The structure of CuO can be thought to consist of two different kinds of CuO_4 plaquettes that are at an angle of 77.84° with respect to each other. The orientation of the $\boldsymbol{q}$-vector with respect to the planes is thus in general an average over the two nonequivalent planes.

In the following discussion we assume Cu^{2+} ions in a CuO_4 plaquette with a D_{4h} point group symmetry. Within the crystal field model [33], the local field splits the 3d energy levels into a_{1g} (d_{z^2}), b_{1g} ($\mathrm{d}_{x^2-y^2}$), b_{2g}(d_{xy}) and (nearly) doubly degenerate e_g(d_{xz} and d_{yz}). In the ground state, the hole occupies the $\mathrm{d}_{x^2-y^2}$ orbital. More refined calculations [16, 34–42] can be done in order to include Cu–O hybridization and band structure but the crystal field model is sufficient to capture the overall energy-level picture. The CuO_4 plaquettes in CuO are not square, but rather almost rectangular parallelograms with side lengths of 2.62 and 2.90 Å, and exhibit two different Cu–O distances (1.95 and 1.96 Å). This lifts the degeneracy of the d_{xz} and d_{yz} orbitals, with an energy splitting that is expected to be ∼60 meV [35]. In this work we study the dd excitations in CuO, i.e. excitations where the hole state is lifted from the ground state $\mathrm{d}_{x^2-y^2}$ orbital to other Cu^{2+} d orbitals. We denote hole excitations to the d_{xy}, d_{z^2}, d_{xz} and d_{yz} orbitals as the xy, z^2, xz and yz excitations, respectively.

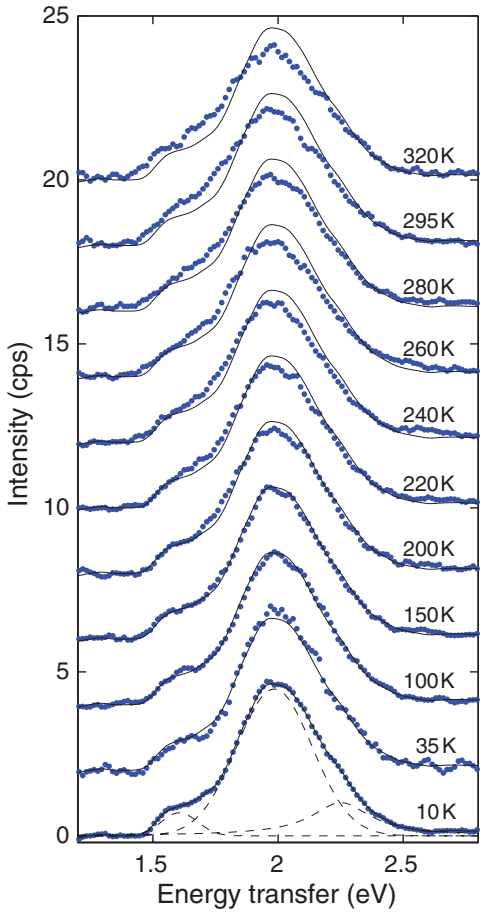

Figure 1. CuO dd excitation spectra (dots) measured as a function of temperature. A smoothed version of the curve measured at T = 10 K (solid line) is shown for reference throughout. The dashed lines drawn together with the spectrum at T = 10 K are the result of fitting three Pearson VII functions to that spectrum.

The experiment was performed at the beamline ID16 of the European Synchrotron Radiation Facility[1]. The incident photon beam was monochromatized using a combination of Si(111) premonochromator and a Si(444) channel cut to a bandwidth of 40 meV. The beam was focused using a toroidal mirror to a spot size of 30 × 100 μm^2 ($V \times H$) on the sample. We used a spectrometer designed for high-energy resolution NRIXS experiments [43]. It was equipped with six diced Si(444) analysers at a Bragg angle of 88.5°, observing

[1] In 2013, The IXS beamline ID16 was replaced by a new upgraded beamline ID20 of the European Synchrotron Radiation Laboratory.

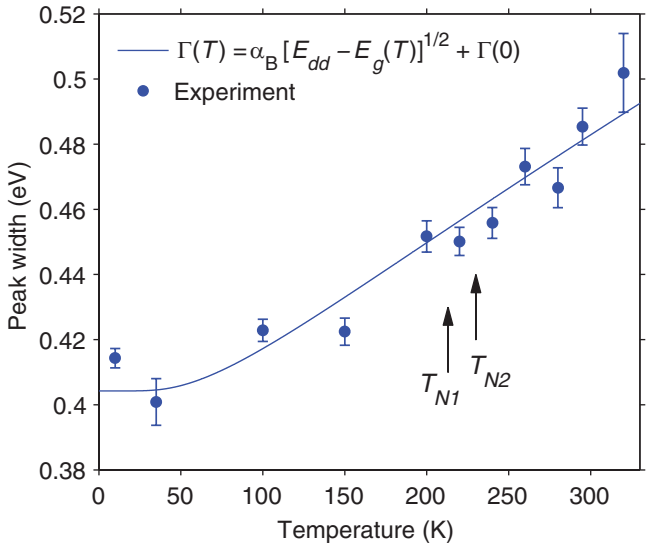

Figure 2. The dd peak width (points) compared to a fit based on the band gap width E_g as a function of temperature (line).

the intensity of scattered photons with a constant energy of ∼7.9 keV. The total energy resolution was 60 meV. The sample temperature was controlled using a miniature He-flow cryostat. The sample was a single crystal of CuO (the same as that used in [20]). The spectra were measured at a fixed momentum transfer value $q = |\boldsymbol{q}| = (7.5 \pm 0.1)$ Å with the average $\boldsymbol{q}$ in the direction $\boldsymbol{q} \| [23\bar{4}]$. Based on the expected angular dependence of dd excitations [18], in this geometry the *xz*/*yz* and z^2 peaks are expected to be excited most strongly, with the *xy* peak being weak. The spectra were measured at several temperatures between 10 and 320 K.

All the spectra collected as a function of temperature, after subtracting a sloping background due to the quasielastic line tail, are shown in figure 1. The spectra have been normalized to have the same area between 1–3 eV. The spectra can be broken into a few components: a main peak at 2 eV and a weaker peak manifesting itself as a shoulder at 1.6 eV, and an even weaker shoulder (mainly visible at the lowest temperatures) at 2.2 eV. A recent *ab initio* calculation [35] predicts the excitations to be assigned as, from lowest to highest energy, *xy*, *xz*/*yz*, and z^2. The peak assignment can be confirmed by studying either their angular dependence [8] or their dependence on *q* [18]. Indeed, this assignment has recently been supported by an angle-resolved study of Wu *et al* [21]. In this work, we concentrate on the overall temperature dependence of the spectra.

The main effect of increasing the temperature from $T = 10$ K is a clear broadening of the overall spectral shape. Due to the broadening, the low-energy shoulder seems to merge into the main peak and is nearly undetectable at room temperature. To emphasize the behaviour, a smoothed version of the spectrum recorded at $T = 10$ K is shown as a reference throughout. Thus, an important result is the bandwidth of the excitations: with a 60 meV energy resolution the main peak has a width of the order of 400 meV even at $T = 10$ K. This is partly due to the overlap of the *xz*/*yz* and z^2 excitations, but even then the individual components have a width of about ∼300–400 eV. While in the orbital ionic picture the 3d states are expected to have a very narrow line shape, when switching on the band structure the 3d states gain non-negligible bandwidth due to the electron–ion interaction and hybridization [36, 44–46]. The observed width extrapolated to $T = 0$ K may thus reflect the width of the density of states of the occupied and unoccupied 3d bands [16]. Time-dependent density functional theory that takes into account band structure, realistic transition matrix elements and local field effects could possibly explain the spectral linewidth and shape in a more detailed way [47–49]. Also, the spin–orbit interaction (∼100 meV) should be taken into account for a full description of the spectra. Simultaneously with dd excitations, excitations of lattice vibrations, modeled by a Franck–Condon treatment, have been used to explain finite-width lineshapes of dd excitation spectra in $Ca_2Y_2Cu_5O_{10}$ [50]. Alternatively, one can consider the coupling between the crystal field excitations and the continuum of states above the band gap, and relate the temperature dependence of dd excitations to the thermal behavior of the band gap itself. It should be noted that the dd excitations in NiO also have non-negligible bandwidth of the order of 200 meV, [51] even though the band gap is larger in NiO (∼4 eV in comparison to E_g ∼1.35 eV of CuO at room temperature).

In order to quantify the change in shape as a function of temperature, we fitted the spectra using Pearson VII functions [52]. An example of such a fit in the case of $T = 10$ K is shown in figure 1. Since the lowest and highest energy peaks are weak in this geometry, neither their position nor their width could be fitted very reliably, especially in the data recorded at high temperatures. However, the determination of the width of the main peak at 2.0 eV can be done with a high accuracy. The resulting fitted values for the width (full-width at half maximum, FWHM) of the 2.0 eV peak are shown in figure 2 as a function of temperature. One important result is that the peak width across different temperatures does not have a significant relation to the magnetic transitions as it does not exhibit significant changes across either transition temperature. Instead, the thermal behavior of the peak width seems to be rather smooth across the studied temperature range.

The width of the band gap of CuO has been reported to vary from $E_g = 1.55$ eV at $T = 0$ K to 1.35 eV at $T = 300$ K [19]. If the relatively large width of the dd excitations (∼400 meV) is due to interaction with continuum states owing to the presence of the band gap, the decreasing gap width with increasing temperature could explain the observed behavior. In this scenario, an increase of the density of states at, or near to, the energy of the dd excitations could increase the width of the dd peaks. The temperature dependence of the optical gap has been explained to be due to the large electron–phonon coupling [19]. Electron–phonon coupling thus seems to be a natural reason for the temperature dependence of the dd excitations as well. Also, magnetic correlations that are responsible for the magnetic transitions at T_{N1} and T_{N2} may contribute to the temperature dependence of the band gap. Their effect, though, is expected to be marginal and will be neglected here.

Using a Bose–Einstein statistical factor for phonons with average energy of $k_B\theta$, the gap energy as a function of temperature [19] can be fitted to a form [53]

$$E_g(T) = E_B - a_B\left[1 + \frac{2}{e^{\theta/T} - 1}\right],$$

where $E_B = 1.66$ eV, $a_B = 0.1$ eV and $\theta = 196$ K. We assume a density of states above the gap of the free-electron form $\rho(E) \propto \sqrt{E - E_g}$, when $E \geqslant E_g$, and $\rho(E) = 0$ when $E < E_g$. Assuming a linear dependence of the *dd* spectral linewidth Γ on the density of states at the *dd* excitation energy,

$$\Gamma(T) = \alpha_B\sqrt{E_{dd} - E_g(T)} + \Gamma(0),$$

we get a good agreement with the experiment with $\Gamma(0) = 0.0569$ eV and $\alpha_B = 0.526$ eV$^{1/2}$. The resulting fit is shown in figure 2. Even if the neighboring dd excitations may give a non-negligible contribution to $\Gamma(0)$, the temperature dependence is the most interesting result here. The fit agreement is good, yielding insight that the interaction with the continuum states could be the underlying reason for the dd excitation lineshape. The dependence of the band gap as a function of temperature has in turn been interpreted to be due to electron–phonon coupling [19].

There are also other approaches which can be used to investigate the temperature dependence of crystal field excitations. The *ab initio* optical absorption spectrum in the range of dd excitations in NiO has been calculated based on molecular dynamics simulations in finite temperature [54], but to our knowledge, such calculations do not exist for CuO. A finite distribution of Cu–O bond lengths in finite temperatures, due to thermal disorder, is expected to have an effect similar to the one observed here. This is because the dd excitation energy is proportional to a_{Cu-O}^{-5}, where a_{Cu-O} is the Cu–O bond distance. Furthermore, in principle, the coupling to the lattice could possibly be quantified from phonon parameters [55, 56]. Wray *et al* [25] found that the temperature dependence of crystal-field excitations in CoO could be explained as anti-Stokes scattering and interatomic many-body dynamics. Providing a complete description of the coupling of vibrational and electronic excitations is a problem of high-level complexity. Approximations such as the Franck–Condon principle can be used to simplify the task. Recently, some of us have used a classical approach to explain the temperature dependence of core-electron excitations of gas-phase CO_2 [57]. Lee *et al* [50] provided a detailed analysis of the linewidth of the dd excitations in $Ca_2Y_2Cu_5O_{10}$, based on a Franck–Condon treatment. Here, our experimental data on CuO, and the good agreement obtained by considering the evolution of the density of states at the dd excitation energy, give an important benchmark for studies of the coupling of the dd excitations and lattice vibrations.

In conclusion, we have measured the dd excitation spectra of bulk CuO with non-resonant IXS with high-energy resolution as a function of temperature. Most importantly, the study reveals the coupling of orbital excitations to other electron states via the temperature dependence of their spectral shape. We discuss different approaches that can explain this behavior. Empirically, we show that the results are compatible with a relation of the band gap and the bandwidth of dd excitations, thus highlighting the crystal field level coupling to the continuum of states above the band gap. The presented data on the temperature dependence of the dd excitations are an important benchmark for understanding the coupling of orbital and other degrees of freedom in CuO.

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