ESRF	**Experiment title:** Crystal-field excitations of CuO studied by nonresonant inelastic x-ray scattering	**Experiment number:** HE-3036
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Report:

At beamline ID16 we investigated the crystal-field excitation spectra of CuO as a function of temperature. CuO exhibits two successive magnetic transitions at T_{N1} = 213 K and T_{N2} = 230 K [1,2]. Below T_{N1} CuO is in an antiferromagnetic commensurate collinear phase, and between the two transitions in an incommensurate spiral phase. The latter has recently drawn interest because it has ferroelectric properties with a very high ferroelectric critical temperature $T_C = T_{N2}$.

The experiment aimed at the determination of the energy diagram of the Cu 3*d* bands as a function of temperature, especially across the two phase transitions. The measured quantity was the crystal-field, (a.k.a. *dd*) excitation spectrum often studied by optical spectroscopies, electron-energy-loss spectroscopy (EELS) or soft-x-ray resonant inelastic x-ray scattering. However, high-resolution studies have been not reported, especially never as a function of temperature. Since it is the 3*d* manifold that is responsible for the magnetism of CuO, we found it important to study the *dd* excitation spectra as a function of temperature.

The experiment was done using the non-resonant inelastic x-ray scattering technique at beamline ID16. The incident beam was monochromatised using a combination of a Si(111) premonochromator and a Si(444) backscattering channel-cut, and focused using a toroidal mirror. The bandwidth of incident photons was 40 meV and the focus 50×130 μm^2 at the sample. The sample was a single crystal CuO in a helium-flow cryostat environment. The spectra were measured using the recently developed high-resolution large-solid-angle spectrometer [3].

A total of six diced analyzer crystals employing the Si(444) reflection in backscattering were employed to analyze the scattered spectrum. The total energy resolution of the experiment was 50 meV.

The spectra were measured at a fixed momentum transfer value $q = 8$ Å^{-1} in a fixed direction, determined experimentally in the beginning to yield best signal/noise ratio. The spectra were measured at several temperatures between 10 and 320 K. Two representative examples are shown in Fig. 1. The spectra can be broken into two components: a main peak at 2 eV and a weaker but sharper peak manifesting itself as a shoulder at 1.6 eV. The main effects of temperature are a clear broadening and a slight redshift when temperature is increased. A fit of two Pearson VII functions to the spectra reveals the behaviour of the two effects as a function of temperature, also shown in Fig. 1. A surprising result is that neither behaviour has a significant relation to the magnetic transitions. However, the effects are clear and easily detectable. We can approximately relate the effects at the moment to the lattice vibrations via the Debye-Waller factor (broadening) and lattice expansion with an increasing temperature [4] (redshift). The coupling to lattice can be further quantified from phonon parameters [5]. The results have an important impact on the exact determination of the CuO crystal-field splitting as a function of lattice parameters, and thus also profound influence on the crystal field theory. A manuscript of the results is under preparation.

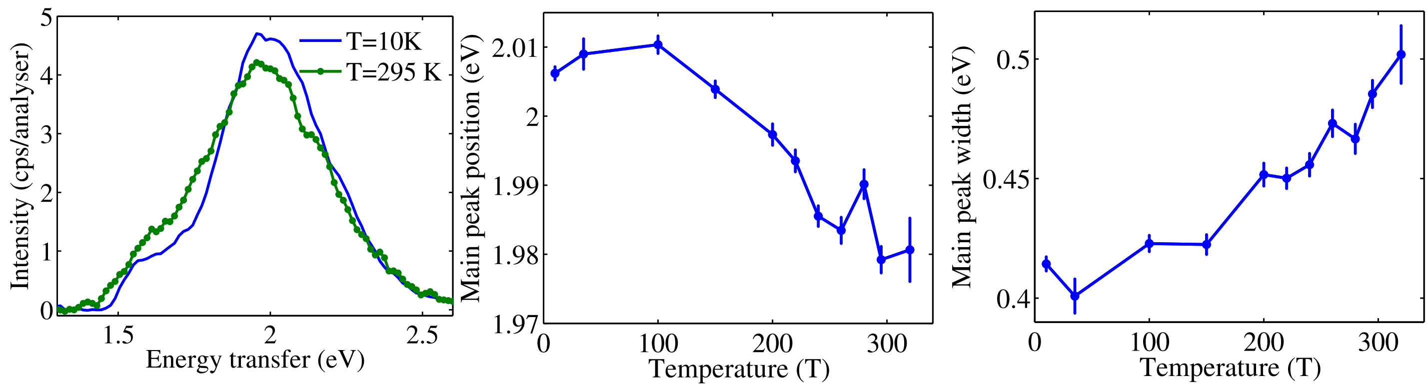

Figure 1. Left: representative measured *dd*-excitation spectra at two different temperatures. Middle: fit result for the main peak energy. Right: fit result for the main peak full width at half maximum.

[1] J. B. Forsynth, P. J. Brown and B. M. Wanklyn, *Magnetism in cupric oxide*, J. Phys. C: Solid State Phys. 21, 2917 (1988)

[2] B. X. Yang et al. *Magnetic neutron scattering study of single crystal cupric oxide*, Phys. Rev. B 39, 4343 (1989)

[3] R. Verbeni et al. *Multiple-element spectrometer for non-resonant inelastic X-ray spectroscopy of electronic excitations*, J. Synchrotron Rad. 16, 469 (2009)

[4] H. Yamada et al. *Lattice distortion and magnetolattice coupling in CuO*, Phys. Rev. B 69, 104104 (2004)

[5] A. B. Kuz'menko et al. *Infrared spectroscopic study of CuO: Signatures of strong spin-phonon interaction and structural distortion*, Phys. Rev. B 63, 094303 (2001)