EXECUTIVE SUMMARY OF THE THESIS

Ligand field and magnetic excitations in High Entropy Oxides studied by RIXS

LAUREA MAGISTRALE IN ENGINEERING PHYSICS - INGEGNERIA FISICA

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Academic year: 2022-2023

1. Introduction

The search of new materials with innovative and unique properties has become the key of technological progress. In this respect, High Entropy Oxides (HEOs) are an emergent class of compositionally disordered materials which has attracted a strong interest within the science community for their peculiar properties, including low thermal conductivity, colossal dielectric constant and superionic conductivity [1]. HEOs are compounds where the high level of entropy, related to the random and homogeneous distribution of at least five elemental species over the cationic lattice sites, favours the stabilization of a single-crystalline phase. A complete understanding of their stabilization process requires the introduction of some thermodynamic arguments: a single phase stabilizes when the variation of the Gibbs free energy ΔG associated to the synthesis process is negative, i.e.

$$\Delta G = \Delta H_f - T\Delta S_{config} < 0 \qquad (1)$$

where T is temperature, ΔH_f is the enthalpy of formation and ΔS_{config} is the configurational entropy i.e. the variation of entropy attributed to the random arrangement of cations over the cationic sub-lattice sites. It can be evaluated as

$$\Delta S_{config} = -R\sum_{i=1}^{N} \chi_i \ln \chi_i, \qquad (2)$$

where $R = 8.314$ Jmol^{-1}K^{-1} is the universal gas constant, N is the number of cations and χ_i is the molar fraction of species i. One can notice that ΔS_{config} is maximum in an equimolar system, where $\chi_i = 1/N$. Equation 1 clarifies that a HEO is stabilized when the entropic contribution dominates the free energy landscape over ΔH_f, so that entropy, together with temperature, acts as a driving force to the single-phase stabilization. In 2015, Rost et al. [2] synthesized the first ever HEO from an equimolar mixture of the parent oxides MgO, CuO, NiO, CoO and ZnO. This prototypical compound, named Mg-CNCZ, exhibits a rock-salt structure and is stabilized at approximately 850°C. It has been proposed, both experimentally and theoretically, that CuO_6 octahedra might suffer from tetragonal distortion, even though an estimate of the associated bond-length variation and energy gain is missing in the literature. Moreover, despite the fact that non-magnetic and magnetic ions with different moments are distributed randomly in the lattice, Mg-CNCZ is long-range ordered, with ferromagnetic (111) planes that

are antiferromagnetically coupled. The Néel temperature is estimated to approximately 120 K. We here introduce also the equimolar four-component oxide named CNCZ, mostly equivalent to Mg-CNCZ, except for missing the non-magnetic Mg ions. Having less species than Mg-CNCZ, CNCZ has a smaller configurational entropy and, according to equation 1, is expected to require higher temperatures to stabilize. The structural, electronic and magnetic properties of Mg-CNCZ and CNCZ are the object of study of this work, which aims at giving an original contribution to the HEOs world.

2. Resonant Inelastic X-ray Scattering from Cu^{2+}

Resonant Inelastic X-ray Scattering (RIXS) is a photon in-photon out spectroscopic technique able to probe elementary excitations, including ligand-field and magnetic excitations, in a variety of solid samples. We performed RIXS at the copper L_3 edge. In Mg-CNCZ and CNCZ the formal valence of Cu is 2+: for a $3d^9$ electronic configuration only one hole occupies the 3d states, such that no electronic correlation is present. This way, at a single ion level, the description of the electronic structure of Cu^{2+} ions is fairly simple. According to Crystal Field (CF) theory, the octahedral symmetry splits d orbitals in two set of degenerate levels: 4-fold degenerate e_g states and 6-fold degenerate t_{2g} states. On top of this, the system may also suffer from Jahn-Teller (JT) distortion, that is a spontaneous symmetry-breaking local distortion of octahedral complexes: the cubic symmetry is reduced to a tetragonal symmetry upon elongation (or compression) of the octahedron along one of its axes, say z. The degeneracy of e_g and t_{2g} states is therefore lifted: the $d_{3z^2-r^2}$ undergoes a strong energy stabilization with respect to $d_{x^2-y^2}$, as well as d_{xz} and d_{yz} with respect to d_{xy}. The energy difference between $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ is, consequently, a measure of the degree of JT distortion, and $d_{x^2-y^2}$ represents the hole ground state. The CF picture is refined by the Ligand Field (LF) model, which takes into account possible hybridization between Cu 3d and O 2p orbitals, but introduces additional parameters, such as the charge-tranfer energy and the Slater-Koster overlap integrals. According to the LF model, dd and charge-transfer exci-

tations arise from transitions between bonding and anti-bonding states. We either use the CF or the LF model to interpret the high-energy excitations in the RIXS spectra. In order to assign RIXS experimental features to the excitations predicted by CF or LF models, scattering cross sections have been calculated adapting the work by Moretti Sala on a single Cu^{2+} ion [3] to account for all the possible orientations of octahedral complexes in a powder, assuming that these are randomly and homogeneously oriented in space.

3. Experimental results and discussion

RIXS experiments have been carried out at the European Synchrotron Radiation Facility (ESRF), in Grenoble (France), specifically at the ID32 RIXS beamline. Four scattering geometries ($2\theta = 70°, 90°, 110°, 145°$) have been tested on both samples, with in-going π photon polarization. For $2\theta = 90°$, we have also tested σ polarization, collecting a total of 10 spectra. Preliminary x-ray absorption spectroscopy (XAS) measurements have also been performed with the aim to check the valence of the constituent species. We probed the $L_{2,3}$ absorption edges of transition metal species with partially filled shells i.e. Cu, Ni and Co, and the K edge of O. All XAS spectra reveal that probed ions exhibit a valence of 2+, as expected.

3.1. dd excitations

Regarding RIXS spectra, we first addressed the analysis of dd excitations with the CF model. They consist in two distinct features: a broad and less intense peak centered at approximately 1 eV and a more intense feature centered at 1.4 eV. Little variations in the shape and intensity of the peaks are observed as a function of the scattering angle, even though a mild depression of the more intense peak collected at $2\theta=145°$ is observed. The effect of varying the incident polarization is, instead, more pronounced. These observations, combined with calculated RIXS cross sections, have been exploited to assign the peaks to specific dd excitations. In particular, the peak at 0.1 eV has been assigned to transitions from the $d_{x^2-y^2}$ to the $d_{3z^2-r^2}$ state, while the intense peak includes excitations to d_{xy}, d_{xz} and d_{yz} states. Interestingly, when comparing the RIXS

spectra of Mg-CNCZ and CNCZ at equivalent experimental conditions, a systematic blue-shift of all the features is observed for CNCZ (Fig. 1). To quantify the shift, all spectra have been fitted with four Gaussian functions, assuming a spin-orbit coupling of 50 meV, which lifts the degeneracy of d_{xz} and d_{yz} states. The relative intensity of the Gaussians have been forced to calculated RIXS cross sections, so that a very limited number of free parameters has been used to fit the spectra. Excitation energies for the $d_{3z^2-r^2}$ are estimated to be 0.96 eV and 1.08 eV for Mg-CNCZ and CNCZ, respectively, implying that the JT distortion is sizeable in both compounds and favours their stabilization in a single phase; more precisely, Mg-CNCZ benefits from a 0.12 eV higher energy gain than CNCZ.
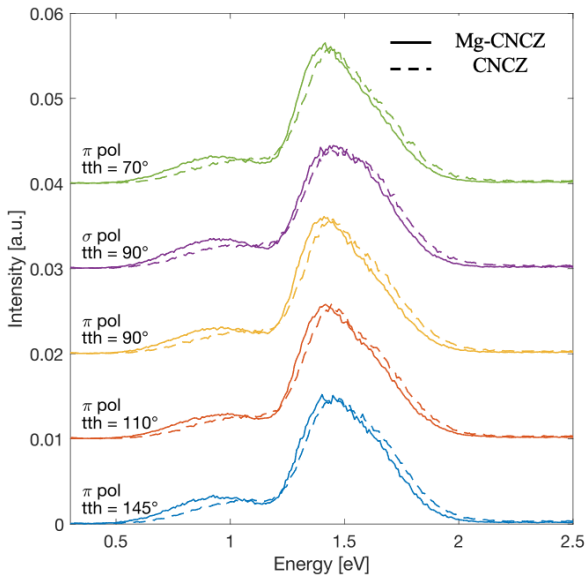

Figure 1: Crystal field excitations at all scattering geometries for Mg-CNCZ and CNCZ samples.

3.2. Charge-transfer excitations

A closer look to the high-energy spectral region reveals very weak features spanning from 2.5 eV to 8 eV, attributable to charge-transfer excitations (Fig. 2). Our main observation is that these have a slightly different spectral shape in Mg-CNCZ and CNCZ; in particular, the spectral weight around 2.5 (6) eV is less (more) intense for Mg-CNCZ than CNCZ. Together, changes in dd and charge-transfer excitations can be rationalized within LF theory by a variation of

the energy difference between bonding and anti-bonding states involving apical oxygens, which is possibly smaller in Mg-CNCZ than in CNCZ.
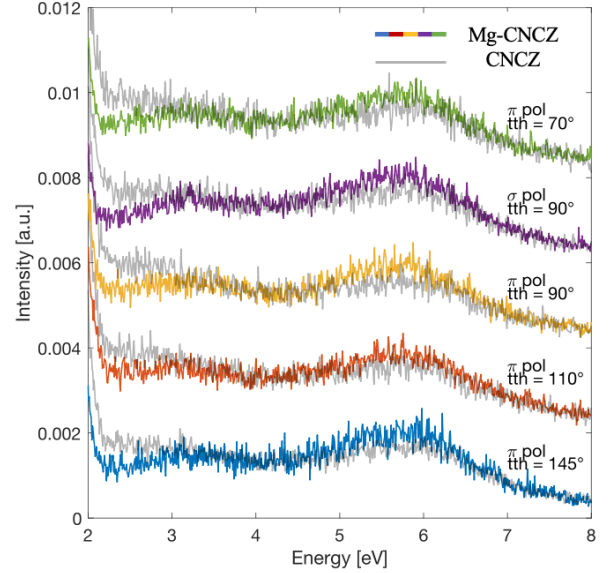

Figure 2: High-energy region of RIXS spectra highlighting charge-transfer features in Mg-CNCZ and CNCZ, at all experimental conditions.

3.3. Magnetic excitations

Even though the low-energy spectral region is dominated by the elastic transition, a clear peak is found in all spectra at energies slightly smaller than 100 meV, which can likely be assigned to magnetic excitations, given the anti-ferromagnetic nature of probed HEOs. The most relevant observation is the relative position of the magnetic features in Mg-CNCZ and CNCZ. In the five-component compound, the energy of the magnetic peak is systematically smaller than in CNCZ, regardless of the scattering geometry. To learn more about this, we fitted the elastic and the magnetic peak with two Gaussian functions; unlike for dd excitations, peaks from spectra at distinct scattering angles have been fitted independently to check possible magnetic dispersion. Interestingly, the ratio of the spin-flip excitation energies in the two systems comes close to $\frac{4}{5}$. This result can be explained noting that Mg-CNCZ contains an extra non-magnetic ion, which contributes to weaken the exchange interaction strength on average. Thus, in Mg-CNCZ the energy required

to flip one spin is smaller. This interpretation is supported by quantitative arguments: the average spin of constituent elemental species in Mg-CNCZ and CNCZ is $\frac{3}{5}$ and $\frac{3}{4}$, respectively, and their ratio is $\frac{4}{5}$. A more rigorous derivation of the magnetic energy ratio has been developed starting from the Heisenberg hamiltonian and within the assumption that spin waves are coherently excited at resonant sites only, i.e. Cu^{2+} sites. To account for the random distribution of ions, the spin-flip excitation energy E_{sf} is evaluated as the average of the energies required to flip the spin of a Cu^{2+} ion interacting with each of the available N species:

$$E^{sf} = 6 \left[2S_{Cu} \sum_i^N p_i J_{Cu,i} S_i \right] \qquad (3)$$

The average is weighted over the probability p_i that the first-neighbour site is occupied by the species i. The multiplication by 6 accounts for the number of first neighbours. Developing equation 3 for Mg-CNCZ ($N = 5$, $p_i = 0.2 \ \forall \ i$) and for CNCZ ($N = 4$, $p_i = 0.25 \ \forall \ i$), and taking their ratio, we again obtain $\frac{4}{5}$.

Finally, we have addressed the momentum dependence of magnetic excitations, since a systematic trend was clearly visible from fitted magnetic energies as a function of the scattering angle. To reproduce the dispersion of magnetic excitations we adapted the work from Hutching and Samuelsen for the calculation of the magnetic structure factor to include the RIXS cross section and within the assumption that all interactions between Cu and magnetic ions have the same energy $JS_{Cu}\bar{S}$, where $\bar{S}$ is the average spin of metal ions. As depicted in Fig. 3, the trend is correctly reproduced both in Mg-CNCZ and CNCZ, and J has been estimated to be approximately 22 meV.

4.   Conclusions and perspectives

RIXS has been demonstrated, for the very first time, to be a powerful tool for probing structural, electronic and magnetic properties of HEOs. All experimental results appear consistent with the state-of-the-art literature and provide novel information about prototypical HEOs. By analyzing dd and charge-transfer excitations, we have established with certainty
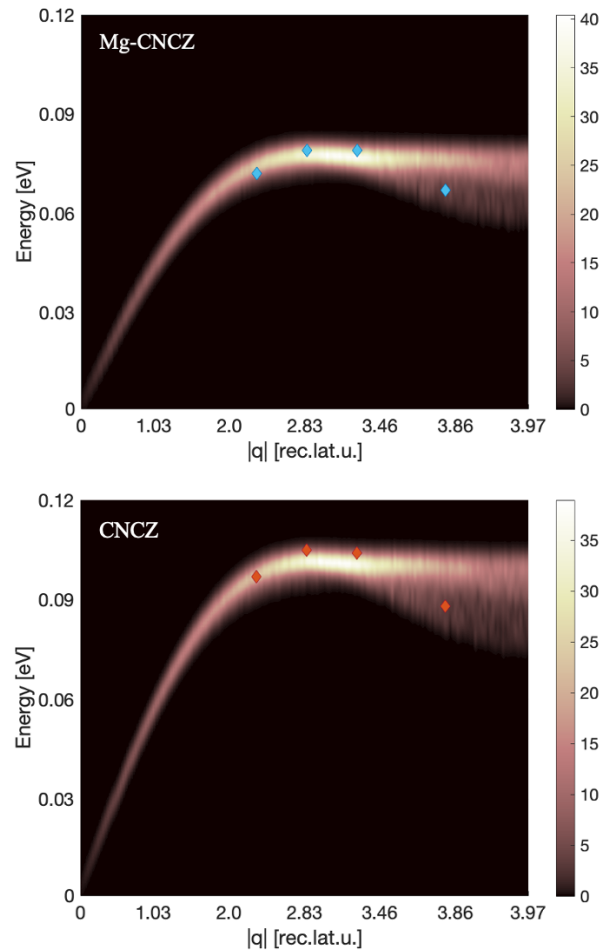
Figure 3: Simulation of the magnetic dispersion in Mg-CNCZ (upper panel) and in CNCZ (lower panel). Shaded colours represent the intensity of the magnetic excitation, while diamond markers depict experimental measurements.

that CuO_6 octahedral units in Mg-CNCZ and CNCZ suffer from sizeable Jahn-Teller distortions. The possibility of a distortion that lowers the local symmetry of Cu^{2+} sites from cubic to tetragonal was already observed from the refinement of the crystal structure in both samples, but a precise estimate of the energy associated to it could not be made. Here, we provide a direct measurement of the energy associated to the JT instability for both Mg-CNCZ (0.96) and CNCZ (1.08 eV). Moreover, the investigation of the low-energy spectral region has revealed that the relative energies of the magnetic peaks in the two systems is $\frac{4}{5}$, coinciding to the ratio between the average spin values of available elemental species in Mg-CNCZ and CNCZ: indeed, the extra non-magnetic ion found in the five-component HEO reduces the effective

magnetic interaction, thus decreasing the spin-flip excitation energy. Within the framework of the Heisenberg model, and assuming that RIXS coherently excites spin waves at resonant sites only, we have developed a more formal derivation of the factor $\frac{4}{5}$, reproducing the experimental evidence. Finally, we have explained the momentum dependence of the magnetic excitations by including the magnetic structure factor $S_m(\mathbf{q}, E)$ in the calculations for the magnetic excitation intensity, together with a proper expression for the energy dispersion relation $\hbar\omega(\mathbf{q})$. By doing so, we have quantified the effective anti-ferromagnetic coupling J to approximately 22 meV. A more solid interpretation of the magnetic behaviour of HEOs, however, calls for further investigations. To test the validity of our interpretation of the RIXS process on these magnetically disordered materials it could be interesting to perform RIXS at the absorption edges of other elemental species. In addition, temperature-dependent measurements could be relevant to improve our understanding of their magnetic properties. In conclusion, we have demonstrated that RIXS is capable of providing a plenitude of novel information about prototypical Mg-CNCZ and CNCZ compounds, and we believe that it can be a relevant technique also for studying other related compounds, with the aim to fully explore the emergent realm of HEOs.

5.   Acknowledgements

References

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