Experimental report

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Proposal: **5-23-705** **Council:** 4/2017

Title: Magnetism and superconductivity inthe FeRESr2Cu2Oy system

Research area: Materials

This proposal is a new proposal

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Samples:
FeSr2RECu2Oy (RE: Y, Ho, Pr)
FeSr2YCu2Oy

Instrument	Requested days	Allocated days	From	To
D20	2	1	15/06/2018	16/06/2018
D2B	2	2	16/04/2018	18/04/2018

Abstract:

The so-called MT-1212 phases resulting from copper substitution in the YBCO model compound by other transition metals allows to study the effect of the charge reservoir block structure in the superconducting properties. We have recently observed an unexpected functionality in the Mo-1212 system: a dependence of the Cu(2)/MT(2)-O(3) distance (CuOap) with the Tc contrary to the usual trend and a mutual red-ox process between the transition metal cations (Cu and Mo). Here we address this problem in the analogue Fe-1212 system.

This FeSr2RECu2Oy system undergoes a structural evolution between Ima2 and P4/mmm space groups after subsequent reducing/oxidizating treatments, which are accompanied by a progressive change in the magnetic/superconducting properties. The aim of this proposal is a detailed structural description of the iron environment evolution, in connection with the associated magnetic structure, throughout the phase transformation. The neutron diffraction study is to be complemented with an electronic description by means of X-Ray absorption spectroscopy and electron energy loss spectroscopy -EELS- (in progress).

Magnetism and superconductivity in the $FeYSr_2Cu_2O_y$ system

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Introduction and aims

The so-called M-1212 phases, resulting from total or partial substitution of copper in the YSCO parent compound by other transition metals, are suitable candidates in studying the subtle dependence of the superconducting properties with the crystal structure. In particular, there are crucial structural parameters for the appearance of superconductivity, in close relation with the charge transfer process: the apical distance and the inter-intra bilayer spaces [1-3]. Our recent studies in the $Mo_xCu_{1-x}RESr_2Cu_2O_y$ (Mo-1212) system have in fact shown two unusual features. First, NPD data reflects a dependence of the apical Cu-O1 distance with the critical temperature (Tc) that is opposite to the general families' trend [4]. And, moreover, a mutual red-ox process between the transition metal cations (Cu and Mo) has been observed by means of XPS [5]. To continue the study of this unusual behavior, we have addressed these structure-property relations in the analogue Fe-1212 system, with special interest in the evolution of the mentioned structural parameters, the TM oxidation states and the resulting superconducting properties.

Total iron by copper substitution in the charge reservoir layer can be realized at ambient pressure, resulting in $FeSr_2RECu_2O_{7+\delta}$ phases. The oxygen content (δ) can be widely modified depending on the annealing conditions, resulting in different iron coordination environments.
Subsequent oxygenation induces a progressive structural transformation, accompanied by the appearance of superconductivity, with different values of the critical temperature depending on the oxidation degree. In addition, signs of the presence of magnetic interactions coexisting with superconductivity have been pointed out from magnetization measurements. We aim to describe the structural/electronic evolution by means of neutron powder diffraction, joined to XAS and Mossbauer spectroscopies, in order to connect the evolution of the iron environment through the oxygenation process with the resulting magnetic/superconducting properties.

Description of the experiment

For a detailed structural characterization, high resolution powder diffraction measurements have been performed at room temperature at the D2B instrument, with a wavelength of λ= 1.5940 Å. Two oxidized samples with $FeSr_2RECu_2O_{7+\delta}$ (RE= Ho, Nd) composition have been measured (labeled as Ho-OA and Nd-OA respectively) so as to test the effect of the rare earth size and magnetic moment in the superconducting properties. In order to study the structural evolution with the oxidation degree, four samples with composition $FeSr_2YCu_2O_{7+\delta}$ have also been measured, corresponding to the different annealing processes: the as prepared sample, the N2 annealed sample (Y-R) and two ozonized samples (Y-OA1 and Y-OA2).
To address the possible presence of long-range magnetic ordering, the two end members of this $FeSr_2YCu_2O_{7+\delta}$ system have been measured: the reduced non-superconducting Y-R sample, and the mostly oxidized Y-OA2 sample, which presents the highest Tc. Thermal scans using a longer wavelength (λ= 2.394 Å) have been acquired for that aim in the high flux D20 instrument, over the 4.1-300 K temperature range.

Results

First, we addressed the structural evolution with the oxidation degree in the $FeSr_2YCu_2O_{7+\delta}$ compounds. The RT NPD data for the reduced Y-R sample (**Figure 1a**) has been fitted within the Ima2 space group, reflecting the formation of an orthorhombic $\sqrt{2}$ ap x $\sqrt{2}$ ap x 6ap unit cell (a= 22.910(0) Å; b = 5.456(4) Å; c= 5.404(4) Å) due to ordering of the $[FeO_4]$ tetrahedral units. The determined oxygen content of $\delta=0.08$ reflects an almost complete reduction to Fe^{3+}, confirmed by the BVS calculation which gives an iron valence of $V_{Fe}= 3.26$, and a low copper valence of $V_{Cu}= 2.16$.

After the ozone treatment, the Y-OA1 and Y-OA2 samples do have tetragonal symmetry. The refinement of the RT NPD data within the P4/mmm space group (**Figure 1b-c**) results in acceptable agreement factors, giving high oxygen contents of $\delta(OA1) = 0.57$ and $\delta(OA2) = 0.83$. This increase in the oxygen content is accompanied by the oxidation of both copper and iron cations: $V_{Fe}(OA1) =3.56$ /$V_{Cu}(OA1)=2.34$ and $V_{Fe}(OA2)=4.27$ /$V_{Cu}(OA2)=2.37$. It is, indeed, remarkable that the charge increase is mostly localized around the iron cations, resulting in an unusually high iron valence.

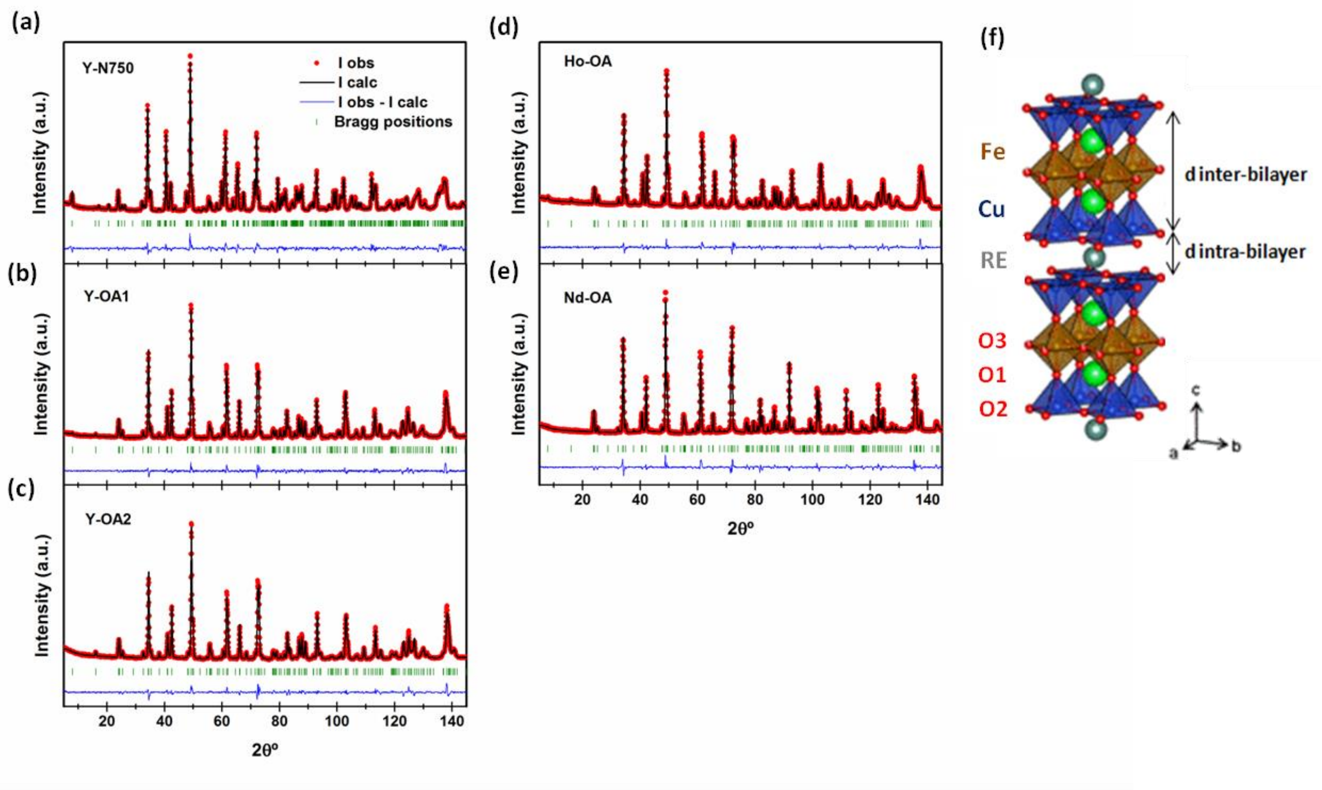

Figure1. Rietveld refinement of the RT NPD data for the (a) Y-R (b) Y-OA1 and (c) Y-OA2 samples with $FeSr_2YCu_2O_{7+\delta}$ composition; and ozonized (d) Ho-OA and (e) Nd-OA samples with $FeSr_2RECu_2O_{7+\delta}$ composition with RE= Ho and Nd respectively. (f) YBCO-type structure derived for all the compounds, with different occupation at the O3 site depending on the oxygen content.

For the yttrium containing compounds, the evolution of the above mentioned structural parameters have shown a clear correlation with the critical temperature. With the oxidation, the anisotropic contraction of the unit cell results in a decrease of the inter bilayer distance at the expense of a greater intra bilayer space, accompanying the increase in the critical temperature. The Cu-O1 apical distance shows a mayor contraction, while the in-plane Cu-O2 distance remains almost constant. Furthermore, a clear displacement of Sr atoms away from the superconducting planes has been observed, presumably following the addition of holes from the charge reservoir layer to the CuO_2 superconducting planes. These structural trends correlate with the increase in the Tc from 30 K in the OA1 sample to 70 K in the more oxidized OA2 sample.

We next addressed the effect of the RE size on the superconducting properties. The samples containing either Ho or Nd are not superconducting after the ozone treatment. In the case of the $FeSr_2NdCu_2O_y$ sample (**Figure 1e**), the refinement of the RT NPD data suggests a structural explanation for the absence of superconductivity, based on the presence of atomic disorder. An almost 50% of anti-site disorder between Nd and Sr is derived, giving a $Fe(Sr_{1.5}Nd_{0.5})(Nd_{0.5}Sr_{0.5})Cu_2O_y$ composition. This disorder seems to be the main reason for the suppression of superconductivity, since the oxygen content is very similar to that of the Y-OA1 sample. Moreover, from the above discussed crystal parameters, a higher Tc would be expected for this compound containing a higher RE. In the Ho case (**Figure 1d**), however, no anti-site disorder is observed due to the smaller RE size. The reason behind the absence of superconductivity in the Ho-OA sample remains unclear from this experiment.

Finally, we focused on the evaluation of the possible presence of magnetic long-range ordering in the Y-OA2 sample. The thermal scans performed at the D20 instrument allowed the identification of magnetic reflections for this superconducting sample, echoing the presence of iron long-range AFM ordering at T_N=100 K > Tc= 70 K. Interestingly, the reduced non-superconducting Y-R sample also presents long range AFM ordering, in this case associated to the copper sublattice.

This experiment has hence demonstrated the complex interplay between the crystal structure and the charge distribution in this Fe-1212 system, and its role in the resulting magnetic and superconducting properties.

References

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