Spin Density Distribution in a Mixed Valence Iron(II)-Iron(III) Formate Framework presenting electric and magnetic order

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1. Introduction

One of the main features of molecular compounds is the possibility of combining different properties in a synergic way giving a multifunctional material. The ability to combine rigid and flexible ligands within the same material is one of the advantages of these compounds, and the correct selection of these ligands could allow the mobility of a specific part of the system either in the main framework itself or as guest molecules. Here we will discuss an example where the order-disorder of a component plays a key role in one of the properties that provide multifunctionality to the material: the disorder-order of the dimethylamine molecule in the Iron(II)-Iron(III) system $[NH_2(CH_3)_2]_n[Fe^{III}Fe^{II}(HCOO)_6]_n$ is in the origin of the observed electric transition from paraelectric to antiferroelectric. In combination with the mentioned electric properties, this compound shows also magnetic order in the form of Nel N-Type ferrimagnetism, thus opening a new strategy for combining electric and magnetic orders in the design of multiferroic materials [1].

2. Neutron diffraction

The structure of $NH_2(CH_3)_2]_n[Fe^{III}Fe^{II}(HCOO)_6]_n$ has been characterized by means of neutron diffraction at VIVALDI and D19 instruments, where a crystallographic phase transition was observed from the high temperature structure [P-31c; $a = b$=8.2550(12) and c=13.891(3) at room temperature] to a lower symmetry one [R-3c; $a = b$=14.2600(17) and c=41.443(8) at low temperature] (see Figure 1). On the other hand, the magnetic behaviour of this compound can be described as the addition of two anti-ferromagnetically coupled sublattices containing different spin carriers Fe^{III} and Fe^{II}, respectively, with an ordering temperature of 37 K, and which are responsible of the different magnetic behaviours at low temperature.[2] The different spins of the neighbouring ions [S=5/2 and S=2] result in a ferrimagnetic state.

Polarized neutron diffraction measurements aimed at clarifying the spin density map in order to understand the influence of the counter ion in the magnetic properties were carried out at D3 instrument. Measurements of the flipping ratios were performed with magnetic field of 9 Tesla at 45K, over the magnetic ordering temperature. The results point to an unusual weak spin density located around the counterions which suggests a non-negligible role in the magnetic behavior for the amine group (Figure 2).

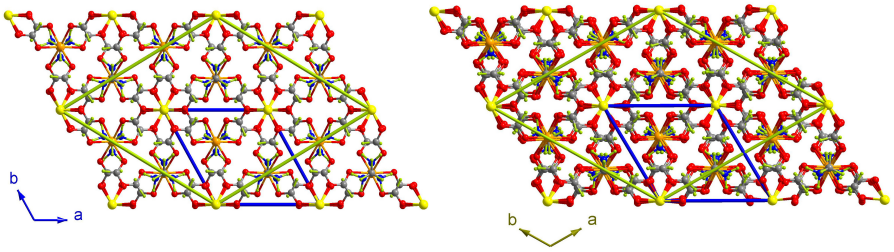

Figure 1. View of the relation between the high temperature (blue) and low temperature (green) unit cells at 200K (left) and at 45K (right)

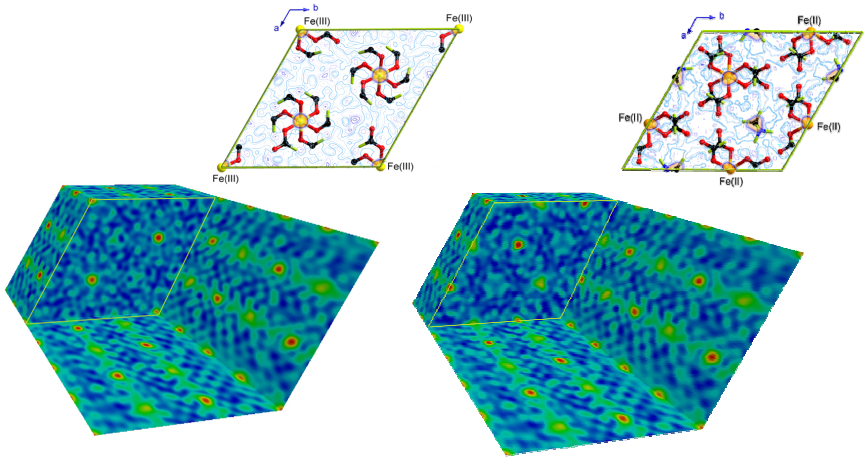

Figure 2. Spin density maps resulting from flipping ratio measurements at 45K, where it can be appreciated the high spin density around the counterions. Views of the unit cell as well as a detail of a slice at z=0.32 (left) and at z=0.25 (right)

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References

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