ESRF	**Experiment title:** In-situ diffractometric study of the melting of cooperative Jahn-Teller distortion in $KMg_xCu_{1-x}F_3$	**Experiment number**: HE-2800
Beamline: ID31	**Date of experiment**: from: 24.04.2008 to: 28.04.2008	**Date of report**: 17.09.09
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Report:

In strongly correlated electron systems several degrees of freedom (lattice, charge, spin and orbital) are intimately connected. This is the case for the relation between the orbital ordering (OO) and the cooperative Jahn-Teller distortion (cJTD).

In a seminal work, Kugel and Khomskii [1] pointed out that in presence of strong electron correlation, orbitals are subject to exchange interaction and a pre-existing OO tends to amplify any lattice instability (i.e. the cJTd follows the OO). In this scenario, the pseudo-cubic perovskite $KCuF_3$ has always been considered as a model system for testing the Kugel-Khomskii model. However, very recent LDA + DMFT calculations by Pavarini et al. [2] showed that the superexchange mechanisms in $KCuF_3$ is not strong enough to stabilise the OO up to T=800 K, a temperature at which the OO is experimentally believed to still survive [3].

The stabilisation energy of cJTD may be determining, in theory, by inducing the tetragonal to cubic phase transition (which correspond to the melting of cJTD) throughout a suitable heating cicle.

Since temperatures high enough to induce melting of cJTD are not reahable for $KCuF_3$ due to sample decposition, in the present experiment we have used a different strategy to disentangle the effect of the different active interactions in $KCuF_3$, i.e. "orbital dilution". This has been obtained by partially substituting copper with magnesium forming $KCu_{1-x}Mg_xF_3$ solid solutions. At room temperature $KCu_{1-x}Mg_xF_3$ is isostructural with $KCuF_3$ (space group *I4/mcm*) for x<0.26, while it is isostructural with $KMgF_3$ (space group *Pm-3m*) for x>0.42 [4].

In this experiment we have performed XRPD measurements on samples of (x=0.10, 0.13, 0.15, 0.20, 0.25) composition. The patterns were collected at beam-line ID31 (λ=0.295130 Å). Samples were heated up to about 900 °C using a hot-air blower. The data were collected whilst warming at 2 $Kmin^{-1}$ ($2 \leq 2\theta \leq 20°$), and cooling at the same rate down to room temperature. Structural parameters and mass fractions were obtained by Rietveld refinement using the GSAS software suite [5] and its graphical user interface EXPGUI [6].

Figure 1 shows the XRPD patterns at different temperatures for the x = 0.25 sample, in a characteristic 2θ region. Below 200 °C, only the peaks of the (2 2 0) and (0 0 4) reflections of the tetragonal structure are

present. Upon increasing the temperature the (2 0 0) reflection of the cubic structure appears. As it is evident from the relative peak intensities, the amount of cubic phase increases with temperature while the amount of tetragonal phase decreases correspondingly. For $T \geq 673$ K the phase transition is almost complete.

All the investigated samples showed a similar behaviour at increasing tempertature. It should be noted that: i) the same behaviour is obtained for all the compositions [7]; ii) the phase transition is reversible; iii) the temperature of appearing of the cubic phase and of disappearing of the tetragonal phase increased at decreasing magnesium concentration (see figure 2).

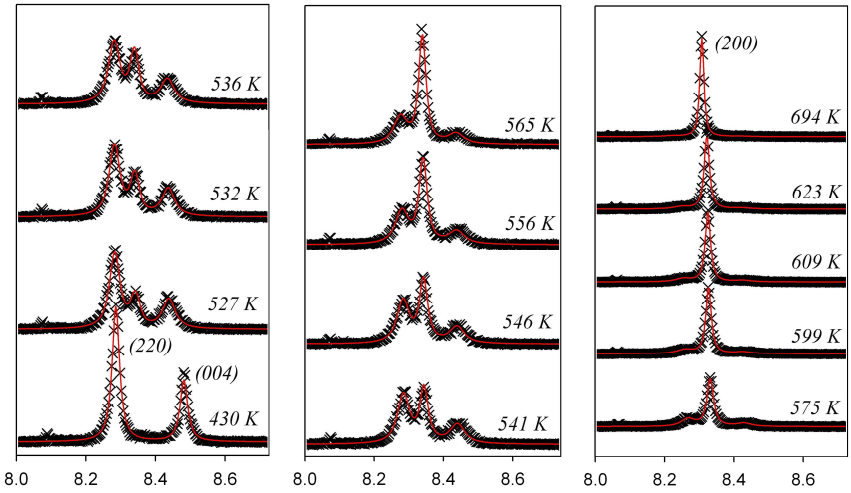

Figure 1– Details of selected XRPD patterns, as collected for different temperatures, referring to the x=0.25 sample. The crosses are the experimental points while the full lines are the results from the Rietveld refinement. The numbers in brackets are the Miller indexes of the diffraction peaks**.**

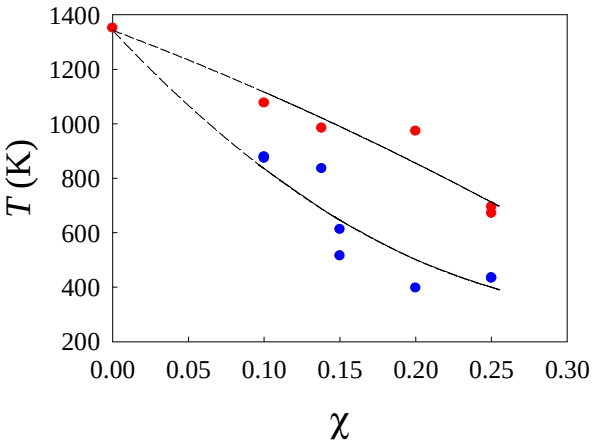

Figure 2. – $KCu_{1-x}Mg_xF_3$ structural phase diagram in the Cu-rich zone. The existence fields of the cubic and tetragonal solid solution (S.S.) are drawn. The dots are the experimental points derived from the analysis of the diffraction patterns for the different compositions: blue points refer to the appearance of the cubic phase, red point to the disappearing of the tetragonal phase. The lines are guide to the eye, drawn according to the topology of the phase diagrams. The extrapolation to x=0 is sketched by the dotted lines [8].

References

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