ESRF	**Experiment title:** Study of the cooperative Jahn-Teller distortion in the $KMg_{1-x}Cu_xF_3$ (0<x<1) solid solution	**Experiment number**: CH-2026
Beamline: ID31	**Date of experiment**: from: 21/07/2005 to: 27/07/2005	**Date of report**: 07/09/07
Shifts: 18	**Local contact(s)**: Dr. Michela Brunelli	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Marco Scavini*, Serena Cappelli*, Giovanni Cornara

Department of Physical Chemistry and Electrochemistry, University of Milan, Italy.

Paolo Ghigna*

Department of Physical Chemistry "X Rolla", University of Pavia, Italy.

Claudio Ferrero*, Claudio Mazzoli*

ESRF, Grenoble, France.

Report:

Polycrystalline samples of $KMg_xCu_{1-x}F_3$ with (x = 0, 0.20, 0.40, 0.60, 1) were studied as a function of magnesium concentration x and temperature in order to detect short range and long range structural changes as a function of the above parameters.

The most part of the XRPD diffraction patterns were collected at low temperature (5 < T < 300 K), using a Liquid-helium-cooled cryostat (λ = 0.35030(1) Å). Conversely, some patterns were collected from room temperature up to about 800 K using an hot-air blower on $KMg_{0.2}Cu_{0.8}F_3$ samples (λ = 0.34855(4) Å).

All data have been refined in the reciprocal space, using GSAS programs package. Selected diffraction patterns, collected in a large Q interval (Q_{max} ~ 20 $Å^{-1}$.) have been refined also in real space (PDF method) using the PDFgetX-PDFFIT package.

For x=0 and 0.2 samples at room temperature, their crystallographic structure can be described as a tetragonally distorted perovskite (c/a ~ 0.9, space group *I4/mcm*): elongated CuF_6 octahedra (along either a or b axes) are rearranged in an antiferrodistorsive type-G pattern. For x=0.4, 0.6 and 1, the structure distortion completely disappears (space group *Pm-3m*).

Patterns collected on the cubic sample of composition closest to the tetragonal phase (x=0.6) did not evidenced structural transitions even for temperatures as low as 5 K.

Conversely patterns collected on the tetragonal sample of composition closest to the cubic phase (x=0.8) showed a structural transition. Fig. 1 shows the XRPD patterns relative to the $KMg_{0.2}Cu_{0.8}F_3$ sample at different temperatures in a characteristic 2θ region. At room temperature, only the peaks belonging to the tetragonal structure are present.. Upon increasing the temperature the peaks of the cubic structure appear. As it is evident from the relative peak intensities, the amount of the cubic structure increases with temperature while the amount of the tetragonal structure decreases correspondingly; for $T \geq 784$ K the phase transition is almost complete.

Thus, by increasing the temperature the compound is brought from a monophasic state, through a biphasic region, in a different monophasic state. This behavior is characteristic of a 1st order phase transition in a bicomponent phase diagram without miscibility gap. The topology of the structural phase diagrams requires two monophasic regions to be separated by a biphasic one.

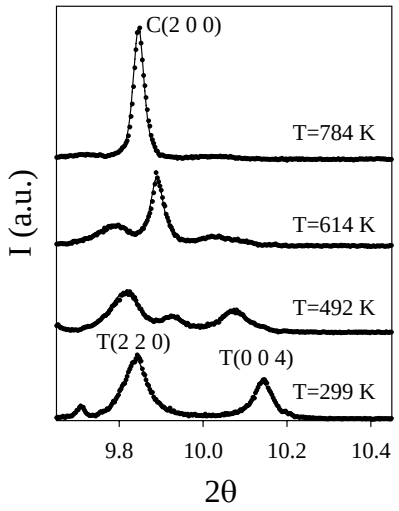

Fig. 1. – Details of selected XRPD patterns collected at different temperatures. Full circles: experimental data; full lines: Rietveld refinements. The numbers in brackets are the Miller indexes of the diffraction peaks. T and C refer to tetragonal and cubic phases, respectively.

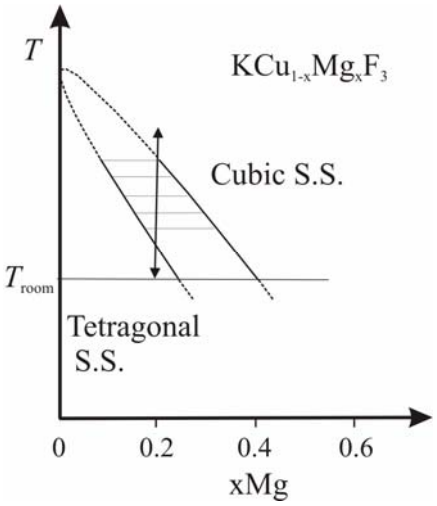

Fig. 2. – $KCu_{1-x}Mg_xF_3$ tentative structural phase diagram in the Cu rich zone. The existence fields of the cubic solid solution (S.S.) and of the tetragonal S.S., separated by a biphasic region are evidenced. The double arrow is a graphical representation of the heating and cooling treatments (isoplet).

Finally, patterns collected on $KCuF_3$ samples did not shown evidences of structural transition from RT to 5 K, despite the several magnetic transition which $KCuF_3$ undergoes in this temperature interval.

Fig. 2 shows a tentative $KCu_{1-x}Mg_xF_3$ phase diagram obtained from the experimental data shown in Fig. 2 and the existence of a biphasic zone at room temperature in the range $0.26 \leq x \leq 0.42$ [1]. In Fig. 2 the abscissa is the Mg content and the ordinate is the temperature, the dotted lines at low Mg content delimitate the most important region for understanding the physics of $KCuF_3$ and the energy scales of its relevant degrees of freedom.

Long measurements in a large Q range, performed on all the samples at 40K, share light on the local structure of the samples.

Althought the site symmetry (-432) of the Cu site in cubic $KMg_{1-x}Cu_xF_3$ samples should bring to a unique Cu-F distance (octahedral Cu environment) as in pure $KMgF_3$, x = 0.6 e 0.4 samples show at least two different Cu-F distances (see Fig.3). This means that non-cooperative Jahn-Teller distortion of Cu environment is present even for samples with Mg concentration as large as x=0.6.

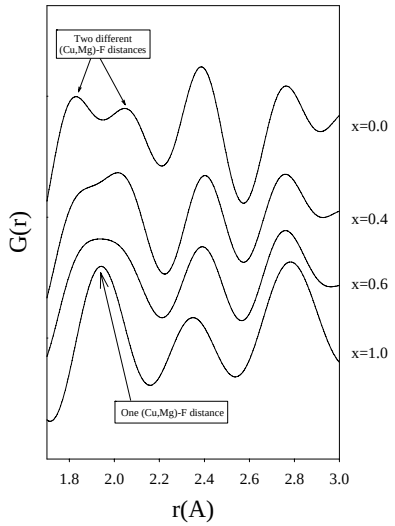

Fig. 3. – Details of G(r) curves at 40K for $KCu_{1-x}Mg_xF_3$ samples.

References

[1] C. Oliva, M. Scavini, S. Cappelli, C. Bottalo, C. Mazzoli, P. Ghigna, *J.Phys.Chem.* **B111** (2007) 5976