



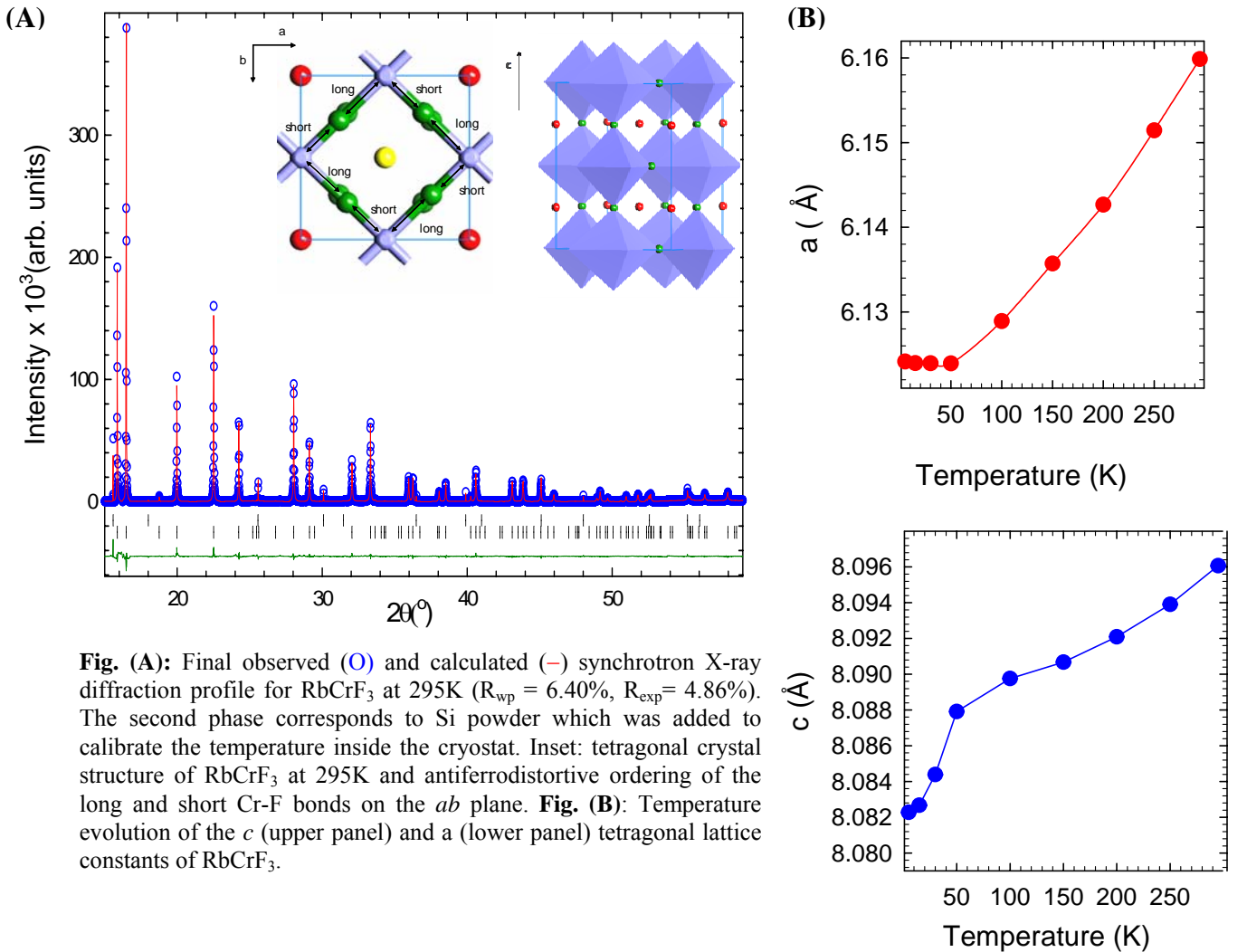
	<b>Experiment title:</b> Structural characterisation of ternary $\text{Cr}^{2+}$ perovskite-type fluorides	<b>Experiment number:</b> CH2385
<b>Beamline:</b> ID24	<b>Date of experiment:</b> from: 5/12/2007 to: 11/12/2007	<b>Date of report:</b> 27/2/2008
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## Report:

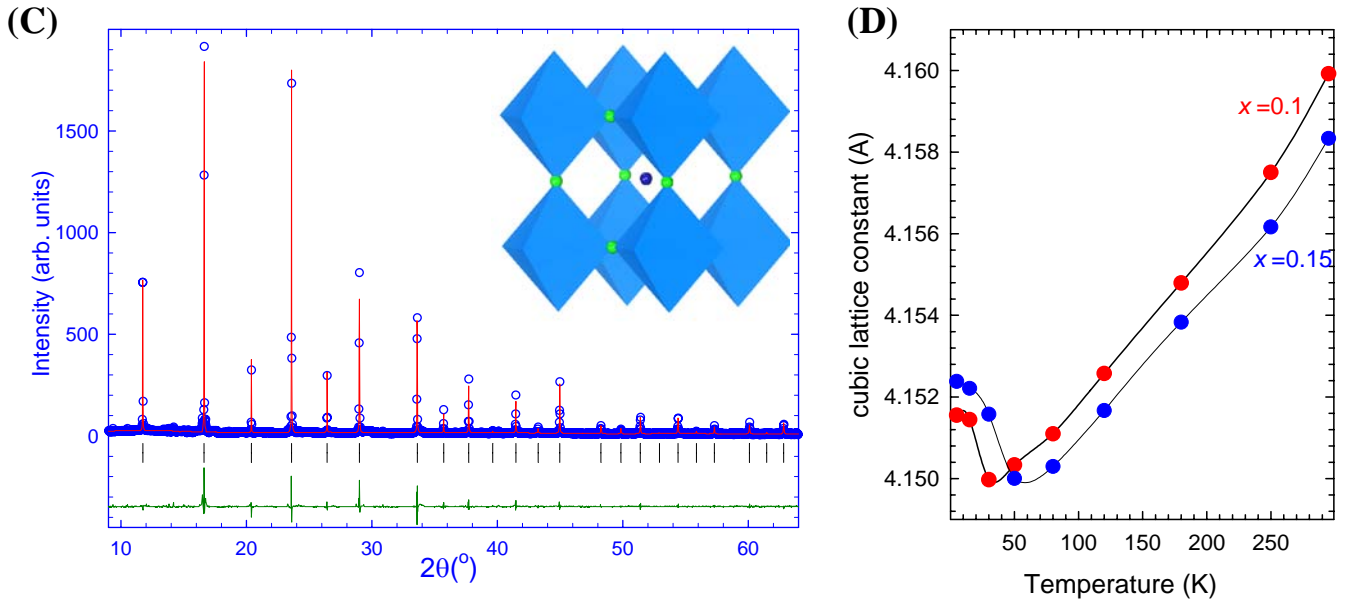
The chemistry of ternary  $\text{Cr}^{2+}$  fluorides,  $\text{ACrF}_3$  has not been explored in a systematic way due to the difficulties in devising reliable protocols for the preparation of single-phase materials. Nonetheless the presence of the Jahn-Teller  $\text{Cr}^{2+}$  ( $d^4$ ) cation with its active orbital degrees of freedom implies that these systems will have properties intrinsically unattainable in comparable fluorides with non-JT-active transition metal ions and entirely novel phenomena can be expected. Establishing a route for the synthesis of single phase, highly crystalline materials has indeed proven to be a challenging task due to the high reactivity of the fluoride ions and the presence of the air sensitive  $\text{Cr}^{2+}$  cation. However, we were successful in achieving a reliable synthetic procedure to afford phase-pure polycrystalline powders of the parent  $\text{KCrF}_3$  and  $\text{RbCrF}_3$  fluorides. Despite the deceptive simplicity of  $\text{KCrF}_3$ , probing its structural and magnetic properties as a function of temperature ( $5 < T < 1000$  K) has revealed a very rich phase diagram. At ambient temperature,  $\text{KCrF}_3$  is tetragonal and isostructural with  $\text{KCuF}_3$ , exhibiting large cooperative Jahn-Teller distortions which are driven by orbital ordering (ID31). However, unlike  $\text{KCuF}_3$  whose structure remains robust to the lowest temperatures studied,  $\text{KCrF}_3$  exhibits a phase transition to a monoclinic structure on cooling below 250 K. The monoclinic phase is characterised by increased distortion and pronounced tilting of the  $\text{CrF}_6$  octahedra and survives down to *ca.* 30 K. On further cooling, a re-entrant transition, accompanied by negative thermal expansion, occurs – this behaviour is reminiscent of the analogous response of some members of the CMR  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  family of materials. Very importantly, the orbitally ordered phase of  $\text{KCrF}_3$  is also a weak ferromagnet (canted antiferromagnet) with  $T_N$  of 46 K [1]. In analogy with  $\text{LaMnO}_3$ , our neutron powder diffraction measurements have shown that the superexchange interactions within the orbitally ordered (OO) planes give rise to ferromagnetic (FM) coupling between neighbouring  $\text{Cr}^{2+}$  spins. The AFM coupling between the OO FM planes is responsible for the appearance of long range AFM order, while the origin of the accompanying weak ferromagnetism arises from the presence of a small spin canting. We extended our studies of the structural properties of the  $\text{KCrF}_3$  system to examine its response to heating above ambient temperature. Using high-temperature synchrotron X-ray powder diffraction measurements (ID31), we found that the static cooperative distortion of the structure which provides the signature of orbital ordering at the  $\text{Cr}^{2+}$  sites disappears at  $T_{JT} = 973$  K. The melting of the orbital order of the quarter-filled  $e_g$  orbitals on heating occurs abruptly and is accompanied by a transition to a cubic structure with a reduced volume [2]. Theoretical calculations have also demonstrated that the ground state of  $\text{KCrF}_3$  is a Mott insulating state with a substantial conduction bandwidth leading to the possibility for the kinetic energy of charge carriers in electron- or hole doped derivatives of  $\text{KCrF}_3$  to overcome the polaron localisation at low temperatures, in analogy with the situation encountered in the CMR manganates. [3]

These preliminary results provided strong evidence for the need to investigate systematically the properties of the family of  $A_{1-x}\text{CrF}_3$  ternary fluorides ( $A = \text{K, Rb}$ ;  $0 \leq x \leq 0.3$ ). Therefore, the aim of the ID31 experiment CH2385 was to initiate the characterization of the crystal structures of these systems as a function of composition, doping level and temperature. The most significant results are summarized below.

- 1) The high-resolution synchrotron X-ray powder diffraction profile of  $\text{RbCrF}_3$  at 295K revealed that its structure is body centered tetragonal ( $a = 6.15987(1) \text{ \AA}$ ,  $c = 8.09607(1) \text{ \AA}$ ,  $a=b > c/\sqrt{2}$ , space group  $I4/mcm$ ) in analogy with  $\text{KCrF}_3$ . The final Rietveld refinement shows that the  $\text{CrF}_6$  octahedra are strongly axially distorted, comprising short Cr-F bonds ( $2.02302(1) \text{ \AA}$ ) along the  $c$ -axis and alternating long ( $2.373(1) \text{ \AA}$ ) and short ( $1.938(1) \text{ \AA}$ ) Cr-F bonds in the  $ab$  plane providing compelling evidence for the presence of a cooperative Jahn-Teller distortion which leads to an antiferrodistortive ordering of the  $3d_{3x^2-r^2}$  and  $3d_{3y^2-r^2}$  orbitals (OO) in the  $ab$  plane (Fig. (A)). Along the  $c$  axis, the orbital ordering pattern is rotated by  $90^\circ$  in consecutive layers ( $a$ -type). The orbitally ordered tetragonal phase is extremely robust upon cooling and no changes in the crystal structure are observed down to 5 K ( $a = 6.12413(1) \text{ \AA}$ ,  $c = 8.08227(1) \text{ \AA}$ ,  $a=b > c/\sqrt{2}$ , space group  $I4/mcm$ ). This is drastically different from the behaviour of  $\text{KCrF}_3$  and is associated with the increased tolerance factor ( $\tau = 1.05$ ). The larger cation size of  $\text{Rb}^+$  as compared to  $\text{K}^+$  increases the magnitude of the CJTD ( $\Delta d = 67.6 \times 10^{-4}$  at 295K). However, in contrast with  $\text{KCrF}_3$  the octahedral distortion parameter decreases on cooling reaching a minum at 5 K ( $\Delta d = 60.0 \times 10^{-4}$ ). Magnetic and neutron powder diffraction measurements have shown that  $\text{RbCrF}_3$  behaves as a weak ferromagnet (canted antiferromagnet) with  $T_N$  of 55 K with a similar magnetic structure and smaller degree of spin canting as compared to  $\text{KCrF}_3$ . On ID31 we observed that the magnetic transition is accompanied by an anomalous lattice response showing the strongly correlated nature of the system.



2) Our synthetic program has also focused in obtaining single phase polycrystalline materials containing  $\text{Cr}^{2+}/\text{Cr}^{3+}$  mixed valence. Following a synthetic route analogous to that for the parent material and including in the reaction mixture variable amounts of  $\text{CrF}_3$ , we were able to isolate systems with stoichiometry  $\text{K}_{1-x}\text{CrF}_3$  ( $x = 0.1, 0.15, 0.2$ ). Very surprisingly, high-resolution powder diffraction measurements at room temperature have revealed that samples with composition  $\text{K}_{1-x}\text{CrF}_3$   $x = 0.1, 0.15$  adopt a cubic perovskite structure with lattice constants  $a_p = 4.159919(7) \text{ \AA}$  for  $x = 0.1$  and  $a_p = 4.158333(7) \text{ \AA}$  for  $x = 0.15$  (space-group  $Pm-3m$ ). These results revealed that 10% dilution of the JT active sites is sufficient for the suppression of the CJTD and the disappearance of the orbital ordering. The molar magnetic susceptibility,  $\chi_M$  measured in an applied field of 1 T for compositions with  $x = 0.1$  and  $x = 0.15$  clearly shows in both cases the onset of long range AF ordering with a Néel temperature  $T_N \sim 50 \text{ K}$ . The measured  $\chi_{MT}$  at 300 K gives values for the effective magnetic moment which is consistent with the presence of mixed valence  $\text{Cr}^{2+}/\text{Cr}^{3+}$  ions. The dependence of the magnetization at various fields in the temperature range between 80 and 2 K show that both compositions should be described as weak ferromagnets. The structural properties were followed for both compounds as a function of temperature between 5 and 300 K. The cubic perovskite structure is robust upon cooling and no structural phase transitions are observed. However, the evolution of the volume as a function of temperature clearly shows the onset of negative thermal expansion (NTE) at  $\sim 30 \text{ K}$  for both compositions. Inspection of the diffraction profiles revealed that the occurrence of NTE is accompanied by a significant loss of intensity and peak broadening suggesting the formation of spatial inhomogeneities. Very interestingly, this phenomenon does not seem to be related to the magnetic transition which instead occurs at the higher temperature of 50 K. We further investigate this effect performing ESR measurements on  $\text{K}_{0.9}\text{CrF}_3$  which revealed the existence of a second magnetic transition at  $\sim 35 \text{ K}$  [4]. The evolution of the line-width ( $\Delta H_{\text{Lor}}$ ) and the effective  $g$  value ( $g_{\text{eff}}$ ) as a function of temperature show abrupt changes below 35 K. Further measurements are needed to shed a light on the nature of this second magnetic transition which is not observed in the bulk magnetic measurements. However, we could preliminarily explain this results considering the coexistence of ferromagnetic inhomogeneities/islands ( $\text{Cr}^{+3}$  doping) embedded in an antiferromagnetic matrix in analogy with the well established behaviour of the CMR manganates



**Fig. (C):** Final observed (O) and calculated (—) synchrotron X-ray diffraction profile for  $\text{K}_{0.9}\text{CrF}_3$  at 295K ( $R_{\text{wp}} = 5.83\%$ ,  $R_{\text{exp}} = 4.42\%$ ). Inset: the cubic perovskite structure of  $\text{K}_{0.9}\text{CrF}_3$  at 295K **Fig. (D):** Evolution of the unit cell volume of  $\text{K}_{1-x}\text{CrF}_3$  ( $x = 0.1, 0.15$ ).

## References

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- [4] Margadonna S., unpublished results
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