Symmetry-mode analysis of the superstructure of $KMnCrF_6$

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The structure of the tetragonal tungsten bronze (TTB) fluoride $KMnCrF_6$ was reinvestigated. The high-temperature tetragonal cell ($P4_2/mbc$) distorts to orthorhombic $Ccc2$, with $a \approx b \approx \sqrt{2}a_{TTB}$, $c \approx 2c_{TTB}$ below 400 K.[1,2] However, a small number of additional reflections could only be indexed using a monoclinic supercell, with $a \approx 2\sqrt{2}a_{TTB}$, $b \approx \sqrt{2}a_{TTB}$ and $c \approx 2c_{TTB}$, containing ~100 independent sites. To handle the high number of parameters, we use the symmetry mode description in a combined neutron- and X-ray refinement. Although subtle, these structural distortions may suggest the presence of ferroelectric/ ferroelastic states well above the onset of ferrimagnetic order (T_C = 23 K) [1,2].

1. Background

Multiferroic materials show coupling of ferroelastic, ferroelectric and/ or ferromagnetic order parameters. The coexistence of the latter two is considered rare, in particular in perovskite oxides, where empty *d*-shells favor the off-centring of ions but counteract magnetism. Clearly, non-oxide, non-perovskite multiferroic systems are not affected by this intrinsic limitation. Examples include the tetragonal tungsten bronze (TTB) fluorides $K_xM^{2+}{}_xM^{3+}{}_{1-x}F_3$ (x = 0.4 - 0.6) that show electric and magnetic ordering [3]. The here presented $KMnCrF_6$ is related to K_xFeF_3, in which the multiferroic properties are observed in its orthorhombic phase [4].

2. Generating a starting model

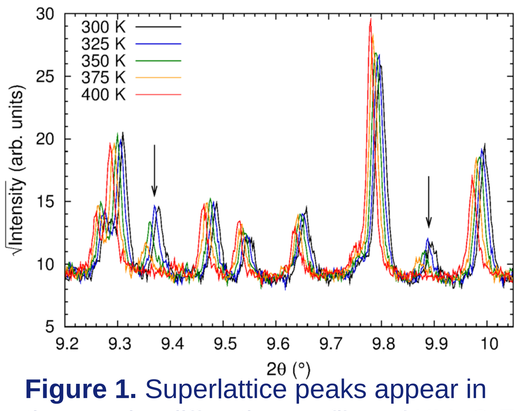

Figure 1. Superlattice peaks appear in the powder diffraction profiles of $KMnCrF_6$ below T = 400 K. The most prominent reflections are marked with the arrows can be indexed as (3 5 1) and (3 7 1) with a primitive orthorhombic supercell ($a \approx 2c_{TTB}$, $b \approx 2\sqrt{2}a_{TTB}$ and $c \approx \sqrt{2}a_{TTB}$.

Data collected on beamline ID22 (ESRF), λ = 0.40091 Å.

S.G.	$P222$	$P222_1$	$P222_1$	$P2_12_12$
basis	(0,0,1) (2,2,0) (-1,1,0)	(0,0,1) (-1,1,0) (-2,-2,0)	(0,0,1) (2,2,0) (-1,1,0)	(-1,1,0) (-2,-2,0) (0,0,1)
origin	(0, ½, ¼)	(-½,0, ¼)	(½, ½, ¼)	(0,0, ¼)
#sites	114	106	106	98
#displ.	270	278	278	286
#occ.	46	42	42	38

Table 1. Possible subgroups obtained with ISODISTORT[5] from the parent phase $P4_2/mbc$, assuming a primitive cell with basis ($2\sqrt{2}$ x $\sqrt{2}$ x 1) and point group 222 $D2$.

The number of positional parameters in these supercells is ~15x higher as compared to $P4_2/mbc$, which has 12 independent sites with 19 fractional coordinates.

3. Refinement strategy

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'{{{mode definitions
  prm !a1 0   min -4.00 max 4.00 'P4_2/mbc[0,0,0]GM1-(a)[Mn1:c:dsp] Au(a)
  prm !a2 0   min -4.00 max 4.00 'P4_2/mbc[0,0,0]GM4-(a)[Mn1:c:dsp] Au(a)
  prm !a3 0   min -2.83 max 2.83 'P4_2/mbc[1/4,1/4,0]SM1(0,a,0,0)[Mn1:c:dsp] Bu_1(a)
  prm !a4 0   min -2.83 max 2.83 'P4_2/mbc[1/4,1/4,0]SM1(0,a,0,0)[Mn1:c:dsp] Bu_2(a)
  prm !a5 0   min -2.83 max 2.83 'P4_2/mbc[1/4,1/4,0]SM1(0,a,0,0)[Mn1:c:dsp] Bu_3(a)
  ... }}}'
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Figure 2. Extract from the input file generated by ISODISTORT[5] for $P222_1$. Initially, all symmetry-adapted modes (displacive and occupational) are zero, corresponding to the high-symmetry parent structure.

1) Consecutive refinement of the parameters against the combined X-ray and neutron data using batch processing and TOPAS in "launch" mode
   → starting parameters

2) Combined refinement with all parameters; after convergence reset parameters to zero and fix in consecutive cycles, if |prm| < esd (and later if |prm| < 3esd)
   → "active" modes

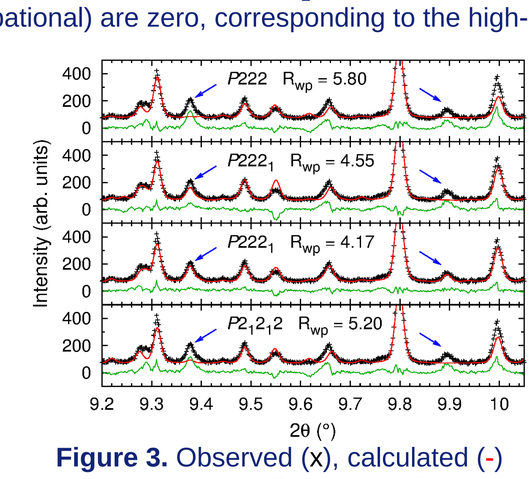

Figure 3. Observed (x), calculated (-) and difference (-) Rietveld profiles for the four cells listed in Table 1.

The best fit is obtained for space group $P222_1$ with the origin choice (½ , ½, ¼).

4. Symmetry mode refinement of supercell

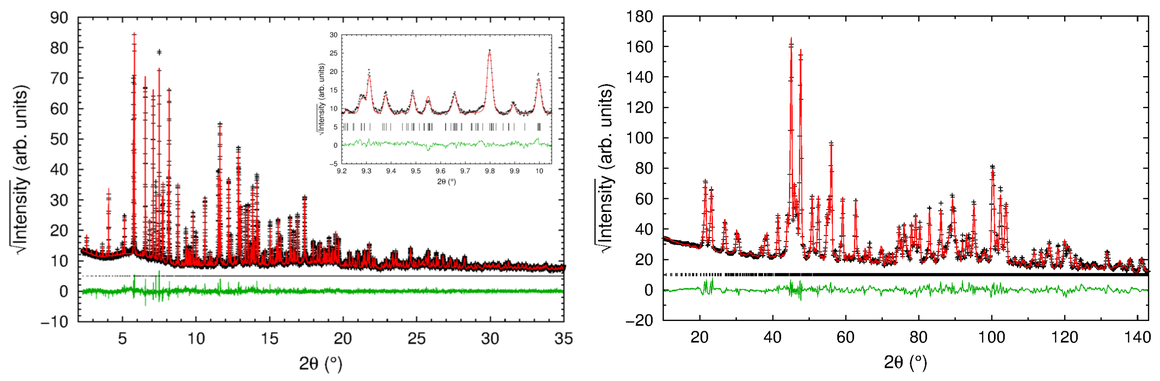

Figure 4. Observed (+), calculated (-) and difference (-) powder diffraction Rietveld profiles of $KMnCrF_6$, refined in space group $P2_12_12$ using symmetry-adapted mode analysis. The combined refinement gave lattice parameters of a = 7.91467(4) Å, b = 35.726(3) Å and c = 17.8766(14) Å using 47 displacive and 7 occupational modes; R_{wp} = 4.11 %. The X-ray (left) and neutron (right) data were collected on beamlines ID22, ESRF (λ = 0.400912 Å) and D20, ILL (λ = 1.87 Å), respectively.

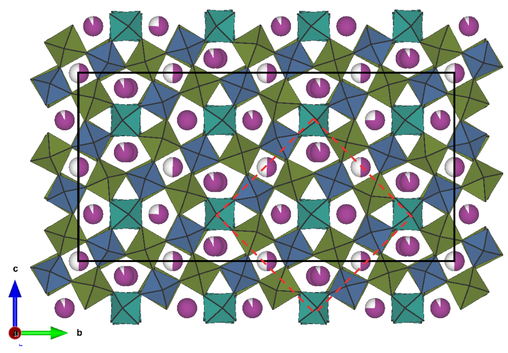

Figure 5. The b-c-plane of the TTB structure with the $P2_12_12$ cell marked with a black line. The red dashed square outlines the high-temperature $P4_2/mbc$ cell. Octahedra of MnF_6 (■) and CrF_6 (■) alternate around the perovskite cage, while the extra-perovskite is mixed $(Mn,Cr)F_6$ (■).

k-point/ mode	A_s	A_p
[0,0,0] Γ_1^+	0.49437	0.24718
[0,0,0] Γ_4^+	0.56739	0.28369
[0,0,0] Γ_1^-	0	0
[0,0,0] Γ_4^-	0	0
[¼, ¼,0] Σ_1	0.81784	0.40892
[¼, ¼,0] Σ_4	3.53962	1.76981
[½, ½,0] M_5^+	0.85371	0.42686
[½, ½,0] M_5^-	0	0
overall	3.80696	1.90348

Table 2. The mode amplitudes A_s (supercell-normalized) and A_p (parent-cell-normalized) obtained from mode-decomposition of the refined superstructure in ISODISTORT[5].

5. Conclusions

Structural modulations related to octahedra tilting are known for numerous TTB materials, including prototypic $Ba_2NaNb_5O_{15}$ (BNN)[6]. Correctly described, the resulting super-structures may resolve split atomic positions and sheared octahedra present in average structural models. However, the large increase in parameters poses a challenge for stable and reliable refinements.

The symmetry-adapted mode analysis used here, allows us to explore systematically all possible superstructures for a given cell and point group symmetry. Further, the overall number of positional parameters could be reduced by a factor of ~6 without reducing the quality of the fit. Further work studying the temperature-dependence of the modes and magnetic ordering is ongoing.

References.

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