edge-sharing MO_6 (M = octahedrally coordinated cations) octahedra forming parallel MO_4 chains. The crystal structures of all compounds in this family are derived from an aristotype structure in space group $P4/mbm$ following a hierarchical scheme of subgroup relationships. Meanwhile, several compounds are added to this family, also extending the Bärnighausen tree representing all branches and cross-relationships of the symmetry derivations. Mullite itself is an aluminosilicate with an incommensurately modulated structure [3] reinvestigated here by single-crystal neutron-diffraction analysis of a high-quality 2:1 mullite. Its average crystal structure can be derived from the sillimanite structure by a disordered arrangement of $(Al,Si)O_4$ tetrahedra linking the octahedral chains according to the substitution scheme $2Si^{4+} + O^{2-} \rightarrow 2Al^{3+} +$ vacancy. The reaction involves removal of oxygen atoms from the structure and the formation of oxygen vacancies. Replacing Si by Al yields the oxygen vacancies and causes a migration of undersaturated Al to the so-called T* sites (red tetrahedra linking to bridging oxygen forming the T_3O clusters.

We have performed statistical calculations in a $2\times2\times2$ and a $3\times3\times2$ supercell to find the maximum number of symmetrically independent oxygen-vacancy configurations assuming one to four vacancies in the $2\times2\times2$ case and up to seven vacancies in the $3\times3\times2$ supercell. The total number of combinations is given just by the binomial coefficient

$$\binom{n}{k} = \frac{n!}{k!(n-k)!}$$

with k representing the number of vacancies and n being the site multiplicity of the vacancy positions. As an example, the number of combinations for k = 2 vacancies distributed over n = 8 sites in the $2\times2\times2$ supercell (corresponding to mullite with $x = 0.25$) is 28 as calculated from the binomial coefficient. Out of this number, only 20 combinations are crystal-chemically possible, and among these combinations, there are only 6 which are symmetrically independent. We are representing here the full ordering scheme of possible and independent oxygen vacancy distributions as a basis for the interpretation of the incommensurate modulation scheme of mullite.

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Keywords: mullite-type compounds, oxygen vacancies, incommensurate structure

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Polymorphism in the quasi-1D quantum magnet, [Ni(HF₂)(pyz)₂]PF₆

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While there are many examples of polymorphism in molecules, polymorphism in 3D coordination networks relatively rare. In this work, we will present one instance of this type of polymorphism and the related magnetic behavior of the different polymorphs.

The crystal structures of two polymorphs of $Ni(HF_2)(pyrazine)_2PF_6$ were determined by synchrotron X-ray powder diffraction. The two polymorphs are a monoclinic ($C2/c$; a=9.9481(3) Å, b=9.9421(3) Å, c=12.5953(4) Å, β=81.610(3)˚) and tetragonal phase ($P4/nmm$; a=9.9187(3) Å, c=6.3497(2) Å). Both consist of one-dimensional Ni-FHF-Ni chains which are connected by pyrazines to create a three-dimensional framework, with a PF_6^- counter ion occupying the voids in this network. The main difference between these two polymorphs is that in the monoclinic phase the Ni-FHF-chains are buckled, while in the tetragonal phase the chains are linear. The influence of these structural differences on the magnetic properties will be discussed.

Keywords: polymorphism, coordination polymers, magnetism

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Predicting switchable multi-ferroic ruddlesden-popper phases & phase transitions

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The n=2 Ruddlesden-Popper compound $Ca_3Mn_2O_7$ forms a structure in polar space group $Ccm2_1$ at room temperature [1], [2], and is therefore potentially ferroelectric. The structure can be considered derived from a higher symmetry parent, in I4/mmm, through the combined 'tilting' and 'rotation' of the Mn-centred octahedra. It is known to order magnetically below about 110 K, the ordering being predominantly antiferromagnetic but with a small ferromagnetic component [3]. It can therefore be classified as multiferroic. It has recently been pointed out [4] that the coupling of the polarisation to magnetisation in $Ca_3Mn_2O_7$ might allow switching of the magnetisation by reversing the polarisation, or vice versa. This has motivated a group theoretical analysis of the potential for this coupling and the phase transitions expected as temperature is increased.

The octahedral 'tilt' is associated with irreducible representation (irrep) X3- of the parent space group I4/mmm, whereas the 'rotation' is associated with irrep X2+. Polarisation is carried by the mode associated with GM5-, which is a secondary distortion produced when X2+ and X3- act together. The antiferromagnetic structure below 110 K, as reported [3], appears to be associated with irrep mX1-. This distortion acting along with the tilting (X3-) leads to a ferromagnetic component mGM5+. The Brigham Young software [5] shows that we have a fourth degree invariant of the form X2+*GM5-*mX1-*mGM5+, and it is this term that indicates the possibility of reversing the magnetisation (mGM5+) by reversing the polarisation (GM5-) and *vice versa*.

In the related phase $Ca_3Ti_2O_7$, mode amplitudes calculated from the room temperature structure [1], are found to be 0.84 and 1.04 for X2+ and X3- respectively. This suggests that X2+ would vanish first upon heating giving a path to I4/mmm via an intermediate in Cmcm. Mode amplitudes for $Ca_3Mn_2O_7$ however, are 0.73 and 0.67 for X2+ and X3-, so there must be some possibility that X2+ will disappear first giving a path via a structure in Cmca as intermediate. Comparison with structures calculated *ab initio* [4], [6] show that the polarisation determined from the room temperature structure of $Ca_3Mn_2O_7$ [2] is in reasonable agreement with that from *ab initio* calculations [4], but for $Ca_3Ti_2O_7$ the polarisation from the analysis above is less than from *ab initio* by a factor five.

These analyses will be developed more fully to demonstrate the utility of the analysis for predicting potentially useful material characteristics.

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