Complex A-site magnetism in quadruple perovskite materials

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The A-site ordered quadruple perovskites AAʻ³B₄O₁₂ can accommodate transition metal cations at the square-planar Aʻ site (Fig. 1(a)). When the B site is occupied by non-magnetic cations, the complex magnetic interactions between the spins at the orthogonally-oriented Aʻ-sites can result in a wide variety of non-trivial magnetic orders.[3] For example, Aʻ-site Cu²⁺ (S = 1/2) spins can align either ferromagnetically (FM) in CaCu₃Sn₄O₁₂ or CaCu₃Ge₄O₁₂ (T_C = 10 and 13 K respectively), or antiferromagnetically (AFM) in CaCu₃Ti₄O₁₂ (T_N = 25 K) as a result of competition between direct exchange and superexchange interactions (Fig. 1(b)).[3] Aʻ-site Mn³⁺ (S = 2) in YMn₃Al₄O₁₂ yields a G-type AFM structure (T_N = 37 K) and Mn²⁺ (S = 5/2) spins in LaMn₃V₄O₁₂ break the symmetry to form a helix-type AFM structure (T_N = 44 K, Fig. 1(c)).[4,2]

![Figure 1](https://example.com/figure1.png)

Figure 1. (a) The quadruple perovskite structure AAʻ³B₄O₁₂ with square-coordinated Aʻ-site cations (blue spheres). (b) FM and AFM spin structures of CaCu₃B₄O₁₂ for B = Ge⁴⁺, Sn⁴⁺ and Ti⁴⁺ (respectively). (c) The helix-type AFM structure of LaMn₃V₄O₁₂. (d) The triple-k AFM spin structure found for CaFe₃Ti₄O₁₂.

We recently revisited the material CaFe₃Ti₄O₁₂ with S = 2 (Fe²⁺) centres at the Aʻ-sites for which initial studies did not find any long range magnetic order down to 4.2 K.[1] This absence of magnetic ordering was notably unconventional. We discovered that the Fe²⁺ (S = 2) spins in CaFe₃Ti₄O₁₂ order in a complex triple-k AFM ground state at T_N = 2.8 K (Fig. 1(d)). In contrast to most magnetic insulating oxides, the Heisenberg superexchange between first- and second-neighbour spins are minimised by strong easy-axis anisotropy. Further-neighbour interactions yield the resulting spin ground state. On application of magnetic field, a canted FM spin structure is induced. This magnetic ordering is contrastingly different from those previously reported for Aʻ-site magnetic quadruple perovskite materials. Furthermore, our results show that exotic long-range magnetically ordered ground states can emerge in large-spin systems when the symmetric exchange is quenched.


Keywords: quadruple perovskite materials; A-site magnetism; spin structures; neutron powder diffraction; high pressure

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