

Complex A-site magnetism in quadruple perovskite materials

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The A-site ordered quadruple perovskites $AA'_3B_4O_{12}$ can accommodate transition metal cations at the square-planar A' 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 A'-sites can result in a wide variety of non-trivial magnetic orders.[3] For example, A'-site Cu^{2+} ($S = 1/2$) spins can align either ferromagnetically (FM) in $\text{CaCu}_3\text{Sn}_4\text{O}_{12}$ or $\text{CaCu}_3\text{Ge}_4\text{O}_{12}$ ($T_C = 10$ and 13 K respectively), or antiferromagnetically (AFM) in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ($T_N = 25$ K) as a result of competition between direct exchange and superexchange interactions (Fig. 1(b)).[3] A'-site Mn^{3+} ($S = 2$) in $\text{YMn}_3\text{Al}_4\text{O}_{12}$ yields a G-type AFM structure ($T_N = 37$ K) and Mn^{2+} ($S = 5/2$) spins in $\text{LaMn}_3\text{V}_4\text{O}_{12}$ break the symmetry to form a helix-type AFM structure ($T_N = 44$ K, Fig. 1(c)).[4,2]

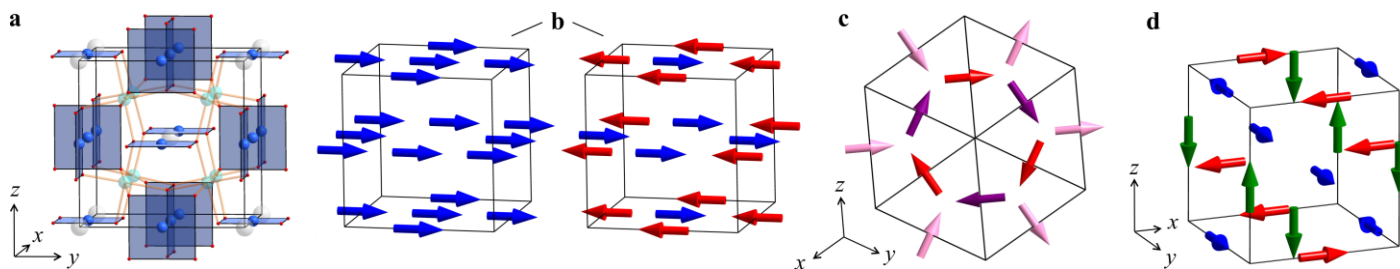


Figure 1. (a) The quadruple perovskite structure $AA'_3B_4O_{12}$ with square-coordinated A'-site cations (blue spheres). (b) FM and AFM spin structures of $\text{CaCu}_3B_4O_{12}$ for $B = \text{Ge}^{4+}$, Sn^{4+} and Ti^{4+} (respectively). (c) The helix-type AFM structure of $\text{LaMn}_3\text{V}_4\text{O}_{12}$. (d) The triple- k AFM spin structure found for $\text{CaFe}_3\text{Ti}_4\text{O}_{12}$.

We recently revisited the material $\text{CaFe}_3\text{Ti}_4\text{O}_{12}$ with $S = 2$ (Fe^{2+}) centres at the A'-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 Fe^{2+} ($S = 2$) spins in $\text{CaFe}_3\text{Ti}_4\text{O}_{12}$ 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 A'-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.

[1] Reiff, W. M., Leinenweber, K. & Parise, J. (1997a). *MRS Proc.* 453, 387.

[2] Saito, T., Toyoda, M., Ritter, C., Zhang, S., Oguchi, T., Attfield, J. P. & Shimakawa, Y. (2014b). *Phys. Rev. B.* 90, 214405.

[3] Shimakawa, Y. & Mizumaki, M. (2014c). *J. Phys. Condens. Matter.* 26, 473203.

[4] Toyoda, M., Saito, T., Yamauchi, K., Shimakawa, Y. & Oguchi, T. (2015d). *Phys. Rev. B.* 92, 014420.

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