Giant magnetoelasticity at a spin gap transition in the 5d oxide $Ba_3BiIr_2O_9$

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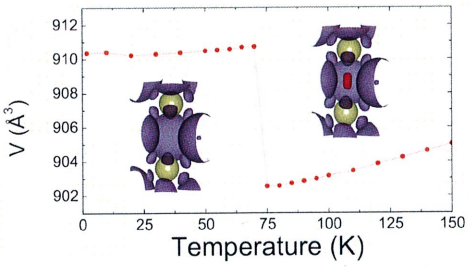
The 4*d* and 5*d* transition metals have much more diffuse valence orbitals than their 3d (first-row) transition metals. Quantum cooperative phenomena that arise due to changes in the way these orbitals overlap and interact, such as magnetoelasticity, are therefore relatively rare in 4*d* and 5*d* compounds. However, we recently discovered a 6H-perovskite $Ba_3BiIr_2O_9$, containing 5*d* Ir^{4+} (S = 1/2) dimerised into isolated face-sharing Ir2O9 bi-octahedra, which exhibits a giant magnetoelastic effect – the largest of any known 5*d* compound – upon the opening a spin-gap at T* = 74 K. [1] The first-order transition observed by neutron powder diffraction is characterised by a remarkable 4% increase in Ir–Ir distance and 1% negative thermal volume expansion. The transition is driven by a dramatic change in the interactions among Ir 5*d* orbitals, and represents a crossover between two very different, competing, ground states: one that optimises direct Ir–Ir bonding (at high temperature); and one that optimises Ir–O–Ir magnetic superexchange (at low temperature).



[1] W. Miiller et al., J. Am. Chem. Soc. 134, 3265 (2012).