Spin-state crossover in lower-mantle minerals and lanthanum cobaltite ($LaCoO_3$)

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Abstract

The electronic spin state of a transition metal ion is determined by the number of unpaired electrons in its 3*d* shell. For a transition metal ion in a crystal, its spin state varies with temperature and/or pressure. This phenomenon is called spin-state crossover. It is known that spin-state crossover in iron-bearing minerals can cause anomalous changes in the mineral's elastic and thermodynamic properties. However, the spin-state crossover in $(Mg,Fe)SiO_3$ perovskite, the most abundant mineral in the Earth's lower mantle, still remains unclear. With the guidance of first-principles phonon calculation, we have found several metastable equilibrium positions for iron in different spin states. By comparing the computed electric field gradient (EFG) of iron in these states with the Mössbauer spectroscopy measurements, we have clarified some of the major controversial points in this complicated system. Similar approach was used to study the spin-state crossover in $LaCoO_3$, a phenomenon that has been puzzling for decades. We have demonstrated that the spin state of cobalt can be unambiguously identified my measuring its EFG. We have also demonstrated that the crossover from low-spin to intermediate-spin state in the temperature range of 0-90 K is very unlikely.