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Elastic and anelastic anomalies due to spin-state transitions in orthorhombic perovskite from isoelectronic behavior of Co^{3+} and Fe^{2+}

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Abstract

Elastic and anelastic anomalies associated with spin-state transitions of Co^{3+} in $NdCoO_3$ and $GdCoO_3$ perovskites with the *Pnma* structure have been investigated using resonant ultrasound spectroscopy (RUS) at high frequencies (0.1–1.5 MHz) and dynamic mechanical analysis (DMA) at low frequencies (0.1–50 Hz). Analysis of spontaneous strains related to octahedral tilting transitions and calculated using lattice parameter data from the literature show that the sequence of changing spin states with increasing temperature, low spin → low spin + high-spin → intermediate spin, is accompanied by significant variations in shear strain due to changes in ionic radius of the Co^{3+} ions. This implies significant spin state/strain coupling, which, in turn, leads to renormalization of the shear modulus. In $NdCoO_3$ the shear strains are small, so the coupling is weak and the shear modulus increases with falling temperature in a manner that scales semi-quantitatively with an empirical spin order parameter. In $GdCoO_3$ the shear strains are much greater and softening of the shear modulus by up to ~35% in the low-spin + high-spin field arises through the influence of both the spin state/strain coupling and the order parameter susceptibility. Enhanced acoustic dissipation is also observed in the low-spin + high-spin field and is tentatively attributed to mobility of transformation twin walls, which are likely to have structures modified by changes in local Co^{3+} spin-state populations. Co^{3+} is isoelectronic with Fe^{2+} and, although the spin-state transitions observed in cobaltate and silicate perovskites are not the same, the large shear strains associated with octahedral tilting in $(Mg,Fe)SiO_3$ at high pressures suggest that the effects of a high-spin → intermediate-spin transition of Fe^{2+} would be closely analogous to those shown by $GdCoO_3$. A spin-state transition of Fe^{3+} in silicate perovskite would have a similar influence, due to the change in radius and its influence on octahedral tilting via the Goldschmidt tolerance factor.

Keywords: Phase transition, spin state, resonant ultrasound spectroscopy, dynamic mechanical analysis