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Vibrational and elastic properties of ferromagnesite across the electronic spin-pairing transition of iron

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ABSTRACT

Ferromagnesite [$(Mg,Fe)CO_3$] has been proposed as a candidate host mineral for carbon in the Earth's mantle. Studying its physical and chemical properties at relevant pressures and temperatures helps our understanding of deep-carbon storage in the planet's interior and on its surface. Here we have studied high-pressure vibrational and elastic properties of magnesian siderite [$(Mg_{0.35}Fe_{0.65})CO_3$] across the electronic spin transition by Raman and X-ray diffraction spectroscopies in a diamond-anvil cell. Our results show an increase in Raman shift of the observed lattice modes of magnesian siderite across the spin transition at 45 GPa as a result of an ~8% unit-cell volume collapse and a 10% stiffer lattice (higher bulk modulus). C-O bond lengthening in the strong, rigid $(CO_3)^{2-}$ unit across the spin transition contributes to a competitive decrease in Raman shift, most evident in the Raman shift decrease of the symmetric stretching mode. Combined vibrational and elastic results are used to derive the mode Grüneisen parameter of each mode, which drops significantly across the transition. These results suggest that the low-spin state has distinctive vibrational and elastic properties compared to the high-spin state. Analyses of all recent experimental results on the $(Mg,Fe)CO_3$ system show no appreciable compositional effect on the transition pressure, indicating weak iron-iron exchange interactions. Our results provide new insight into understanding the effects of the spin transition on the vibrational, elastic, and thermodynamic properties of $(Mg,Fe)CO_3$ as a candidate carbon-host in the deep mantle.

Keywords: Ferromagnesite, spin transition, X-ray diffraction, Raman spectroscopy, diamond-anvil cell