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High-pressure spectroscopic study of siderite ($FeCO_3$) with a focus on spin crossover

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Abstract

Fe-bearing carbonates have been proposed as possible candidate host minerals for carbon inside the Earth's interior and hence their spectroscopic properties can provide constraints on the deep carbon cycle. Here we investigate high-pressure spin crossover in synthetic $FeCO_3$ (siderite) using a combination of Mössbauer, Raman, and X-ray absorption near edge structure spectroscopy in diamond-anvil cells. These techniques sensitive to the short-range atomic environment show that at room temperature and under quasi-hydrostatic conditions, spin crossover in siderite takes place over a broad pressure range, between 40 and 47 GPa, in contrast to previous X-ray diffraction data that described the transition as a sharp volume collapse at approximately 43 GPa. Based on these observations we consider electron spin pairing in siderite to be a dynamic process, where Fe atoms can be either high spin or low spin in the crossover region. Mode Grüneisen parameters extracted from Raman spectra collected at pressures below and above spin crossover show a drastic change in stiffness of the Fe-O octahedra after the transition, where they become more compact and hence less compressible. Mössbauer experiments performed on siderite single crystals as well as powder samples demonstrate the effect of differential stress on the local structure of siderite Fe atoms in a diamond-anvil cell. Differences in quadrupole splitting values between powder and single crystals show that local distortions of the Fe site in powder samples cause spin crossover to start at higher pressure and broaden the spin crossover pressure range.

Keywords: Siderite, carbonate, deep carbon cycle, spin transition, diamond-anvil cell, Mössbauer spectroscopy, Raman spectroscopy, XANES, differential stress