Spin crossover and hyperfine interactions of iron in ferromagnesite $(Mg,Fe)CO_3$

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Iron-bearing magnesium carbonates [$(Mg,Fe)CO_3$] have attracted significant attention in recent years, as they are potential carbon carriers in the Earth's deep lower mantle. Thorough knowledge of $(Mg,Fe)CO_3$ polymorphs under high pressure and temperature, including the effects of iron and spin crossover in these minerals, is thus crucial for understanding the Earth's deep carbon cycle. In this work, we use the density functional theory + self-consistent Hubbard U (DFT+U_{sc}) method to study the spin crossover in ferromagnesite, the stable $(Mg,Fe)CO_3$ phase up to 80-100 GPa. Our calculation shows that iron in this mineral undergoes a crossover from the high-spin (HS, $S = 2$) state to the low-spin (LS, $S = 0$) state at around 45-50 GPa. The intermediate-spin (IS, $S = 1$) state is energetically unfavorable and plays no role in the spin crossover. The anomalous changes in volume, density, and bulk modulus accompanying with the HS-LS crossover obtained in our calculation are in great agreement with experiments. Also consistent with experiments, our calculation shows that the HS-LS transition pressure in ferromagnesite barely depends on iron concentration (12.5-100%), in contrast with ferropericlase [(Mg,Fe)O], where the HS-LS transition pressure significantly increases with iron concentration. To unambiguously identify the iron spin state in ferromagnesite, predictive calculations for the iron nuclear quadrupole splitting (QS) are performed for future comparisons with Mössbauer spectra. Given the highly accurate results shown in this work, we believe DFT+U_{sc} method can make reliable predictions on the high-pressure $(Mg,Fe)CO_3$ phases (>100 GPa), whose structural, physical, and chemical properties are still open questions.