

## Structure and compressibility of Fe-bearing Al-phase D

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### ABSTRACT

Due to its large thermal stability, Al-phase D, the  $(\text{Al},\text{Fe}^{3+})_2\text{SiO}_6\text{H}_2$  member of the dense hydrous magnesium silicate (DHMS) phase D, may survive along hot subduction geotherms or even at ambient mantle temperatures in the Earth's transition zone and lower mantle, therefore potentially playing a major role as a water reservoir and carrier in the Earth's interior. We have investigated the crystal structure and high-pressure behavior of Fe-bearing Al-phase D with a composition of  $\text{Al}_{1.53(2)}\text{Fe}_{0.22(1)}\text{Si}_{0.86(1)}\text{O}_6\text{H}_{3.33(9)}$  by means of single-crystal X-ray diffraction. While the structure of pure Al-phase D ( $\text{Al}_2\text{SiO}_6\text{H}_2$ ) has space group  $P6_3/mcm$  and consists of equally populated and half-occupied  $(\text{Al},\text{Si})\text{O}_6$  octahedra, Fe-incorporation in Al-phase D seems to induce partial ordering of the cations over the octahedral sites, resulting in a change of the space group from  $P6_3/mcm$  to  $P6_322$  and in well-resolved diffuse scattering streaks observed in X-ray images. The evolution of the unit-cell volume of Fe-bearing Al-phase D between room pressure and 38 GPa, determined by means of synchrotron X-ray diffraction in a diamond anvil cell, is well described by a third-order Birch-Murnaghan equation of state having an isothermal bulk modulus  $K_{T0} = 166.3(15)$  GPa and first pressure derivative  $K'_{T0} = 4.46(12)$ . Above 38 GPa, a change in the compression behavior is observed, likely related to the high-to-low spin crossover of octahedrally coordinated  $\text{Fe}^{3+}$ . The evolution of the unit-cell volume across the spin crossover was modeled using a recently proposed formalism based on crystal-field theory, which shows that the spin crossover region extends from approximately 30 to 65 GPa. Given the absence of abrupt changes in the compression mechanism of Fe-bearing Al-phase D before the spin crossover, we show that the strength of H-bonds and likely their symmetrization do not greatly affect the elastic properties of phase D solid solutions, independently of their compositions.

**Keywords:** DHMS, phase D, X-ray diffraction, equation of state, spin crossover