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# Compressional behavior and spin state of δ-(Al,Fe)OOH at high pressures

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## Abstract

Hydrogen transport from the surface to the deep interior and distribution in the mantle are important in the evolution and dynamics of the Earth. An aluminum oxy-hydroxide, δ-AlOOH, might influence hydrogen transport in the deep mantle because of its high stability extending to lower mantle conditions. The compressional behavior and spin states of δ-(Al,$Fe^{3+}$)OOH phases were investigated with synchrotron X-ray diffraction and Mössbauer spectroscopy under high pressure and room temperature. Pressure-volume (*P*-*V*) profiles of the δ-($Al_{0.908(9)}{}^{57}Fe_{0.045(1)}$)$OOH_{1.14(3)}$ [Fe/(Al+Fe) = 0.047(10), δ-Fe5] and the δ-($Al_{0.832(5)}{}^{57}Fe_{0.117(1)}$)$OOH_{1.15(3)}$ [Fe/(Al+Fe) = 0.123(2), δ-Fe12] show that these hydrous phases undergo two distinct structural transitions involving changes in hydrogen bonding environments and a high- to low-spin crossover in $Fe^{3+}$. A change of axial compressibility accompanied by a transition from an ordered ($P2_1nm$) to disordered hydrogen bond (*Pnnm*) occurs near 10 GPa for both δ-Fe5 and δ-Fe12 samples. Through this transition, the crystallographic *a* and *b* axes become stiffer, whereas the *c* axis does not show such a change, as observed in pure δ-AlOOH. A volume collapse due to a transition from high- to low-spin states in the $Fe^{3+}$ ions is complete below 32–40 GPa in δ-Fe5 and δ-Fe12, which is ~10 GPa lower than that reported for pure ε-FeOOH. Evaluation of the Mössbauer spectra of δ-($Al_{0.824(10)}{}^{57}Fe_{0.126(4)}$)$OOH_{1.15(4)}$ [Fe/(Al+Fe) = 0.133(3), δ-Fe13] also indicate a spin transition between 32–45 GPa. Phases in the δ-(Al,Fe)OOH solid solution with similar iron concentrations as those studied here could cause an anomalously high $\rho/v_\Phi$ ratio (bulk sound velocity, defined as $\sqrt{K/\rho}$) at depths corresponding to the spin crossover region (~900 to ~1000 km depth), whereas outside the spin crossover region a low $\rho/v_\Phi$ anomaly would be expected. These results suggest that the δ-(Al,Fe)OOH solid solution may play an important role in understanding the heterogeneous structure of the deep Earth.

**Keywords:** δ-AlOOH, δ-(Al,Fe)OOH, hydrous minerals, high-pressure, X-ray diffraction, Mössbauer spectroscopy, diamond-anvil cell, synchrotron, water transport in the deep mantle