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Re-examination of the hydrogarnet structure at high pressure using neutron powder diffraction and infrared spectroscopy

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ABSTRACT

Time-of-flight neutron powder data and synchrotron infrared absorption spectra were collected for katoite hydrogarnet [$Ca_3Al_2(O_4D_4)_3$] at pressures to 9.4 and 9.8 GPa, respectively. The phase transition from space group $Ia3d$ to $I\bar{4}3d$ was observed in the neutron spectrum at ~7.5 GPa, as indicated by the presence of two weak reflections (730 and 530) that violate the hkl conditions ($hk0$, $h \neq 2n$) imposed by the a-glide operation. However, attempts to refine the high-pressure structure in space group $I\bar{4}3d$ did not significantly improve the fit and produced a chemically unreasonable O-D bond length at the second D position. Structure refinements in $Ia3d$ indicate that (1) the O-D bond length, corrected for the effects of thermal motion, remains essentially constant (~0.95 Å) with increasing pressure; (2) hydrogen bond lengths shorten with increasing pressure; however, the variation in O-D···O angles indicates a preferential strengthening of H bonds; and (3) the compression mechanism is characterized by bond shortening rather than bond bending. The new results are in excellent agreement with both high-pressure X-ray diffraction experiments and ab initio calculations, and illustrate the need to eliminate peak broadening in high-pressure neutron powder experiments. IR spectra collected for the same sample showed discontinuities in both O-H and O-D vibrational frequencies at ~5 GPa, suggesting that deuteration does not significantly affect the pressure of the transition. The higher pressure observed for the transition in the neutron data is probably due to lower signal-to-noise levels, which mask the weaker, symmetry-forbidden reflections at lower pressure.