

High-pressure phase transitions in rubidium and caesium hydroxides. Electronic supplementary information

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1 Phase relations in rubidium and caesium hydroxides

In Figure 1, the known phases of both RbOH(D) and CsOH(D) are shown schematically, as function of temperature and pressure. The nomenclature follows the Paderborn group.[Krobok and Holzapfel(1994), Otto and Holzapfel(1995)]

- Phase I is a cubic "free rotator" phase, with quasi-spherical OH⁻ units. This phase occurs in all alkali hydroxides except LiOH(D).
- Phase II, space group $P2_1/m$, occurs in all of NaOH(D), KOH(D), and RbOH(D), and is layered and proton-disordered. Phase III, space group $Cmcm$, is found in CsOH(D) and the equivalent to phase II. In RbOH(D) and CsOH(D), these phases are stable at (or just above) room temperature.
- Upon further cooling, phases II and III transform into phase IVb (for RbOH(D), space group $Cmc2_1$), and phase IVc (for CsOH(D), space group $P2_12_12_1$), respectively. Both are layered and proton-ordered. An alternative view (promoted in Figure 1) is that of zig-zag OH chains through cation channels. Both low-temperature phases can be produced at room temperature under moderate compression (less than 10 kbar).
- Upon further compression, RbOH is found in the current work to transform to phase VI, which is the same as KOH(D)-VI and probably proton-disordered at room temperature. Lastly, CsOH is found here to transform to phase VII, a slightly more compact stacking of the cation channels and hydrogen-bonded chains.

2 Phonon dispersion data

In Figure 2 and 3, the phonon dispersion curves and density of states (DOS) are shown for the phases RbOH-IVb, RbOH-VI, CsOH-IVc, and CsOH-VII, all at $P = 10$ GPa. All are obtained using the PHON program in appropriate supercells, and using the calculation parameters given in the main manuscript.

References

- [Krobok and Holzapfel(1994)] M. P. Krobok and W. B. Holzapfel, *J. Phys. Condens. Matter*, 1994, **6**, 9789–9806.
- [Otto and Holzapfel(1995)] J. W. Otto and W. B. Holzapfel, *J. Phys. Condens. Matter*, 1995, **7**, 5461–5476.

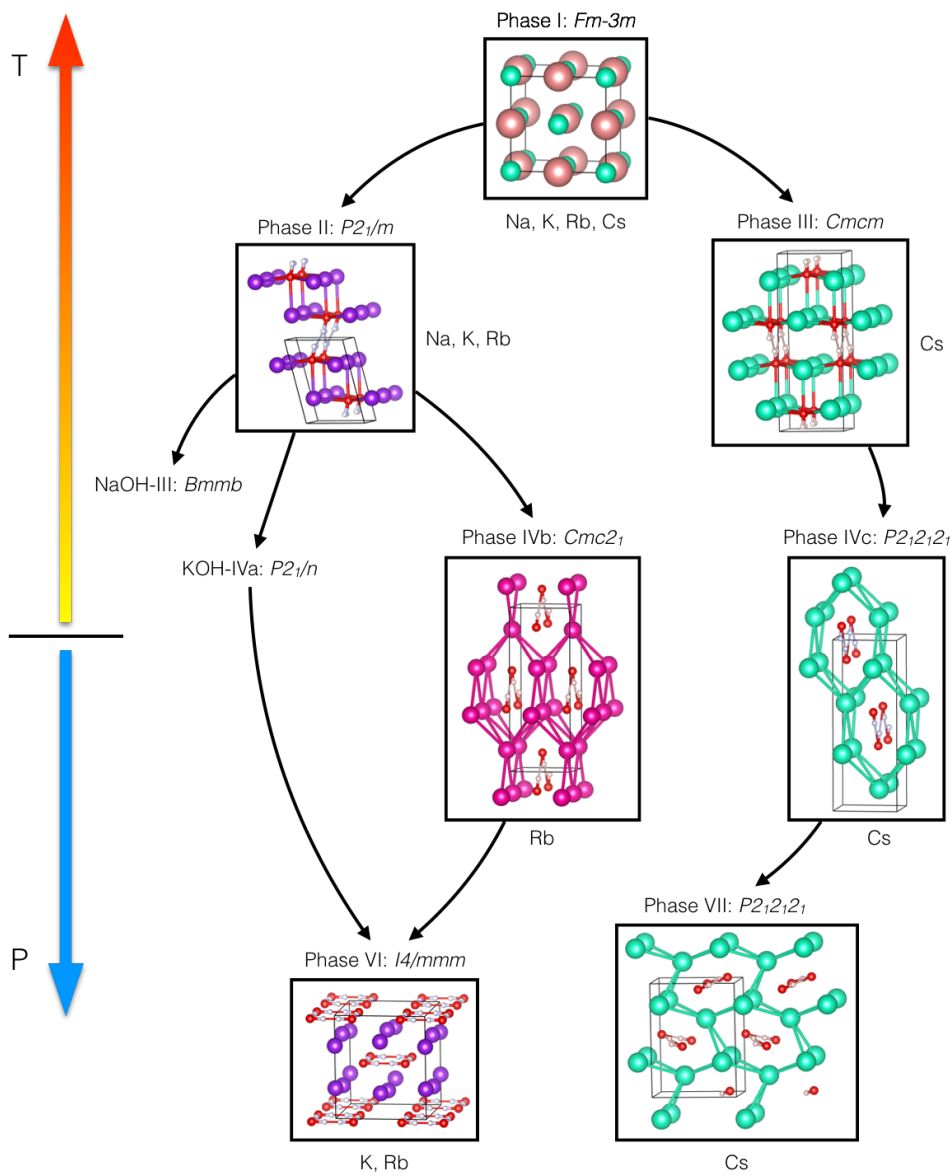


Figure 1: Phase sequence in RbOH and CsOH as function of temperature and pressure, with commonly used labels and respective space group symbols given for each structure.

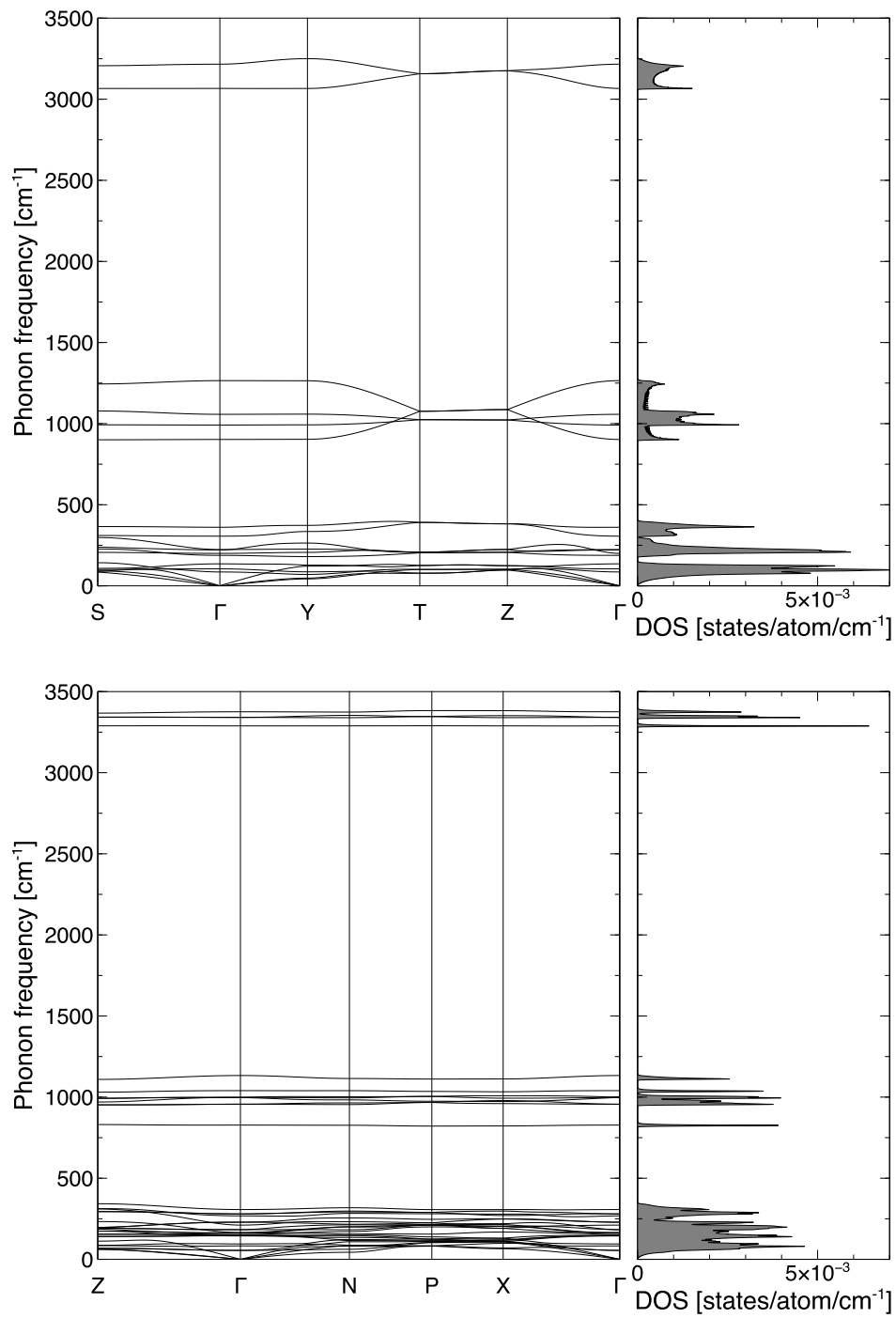


Figure 2: Phonon dispersions of RbOH-IVb ($Cmc2_1$, top) and RbOH-VI ($I4/m$, bottom), both at $P = 10$ GPa.

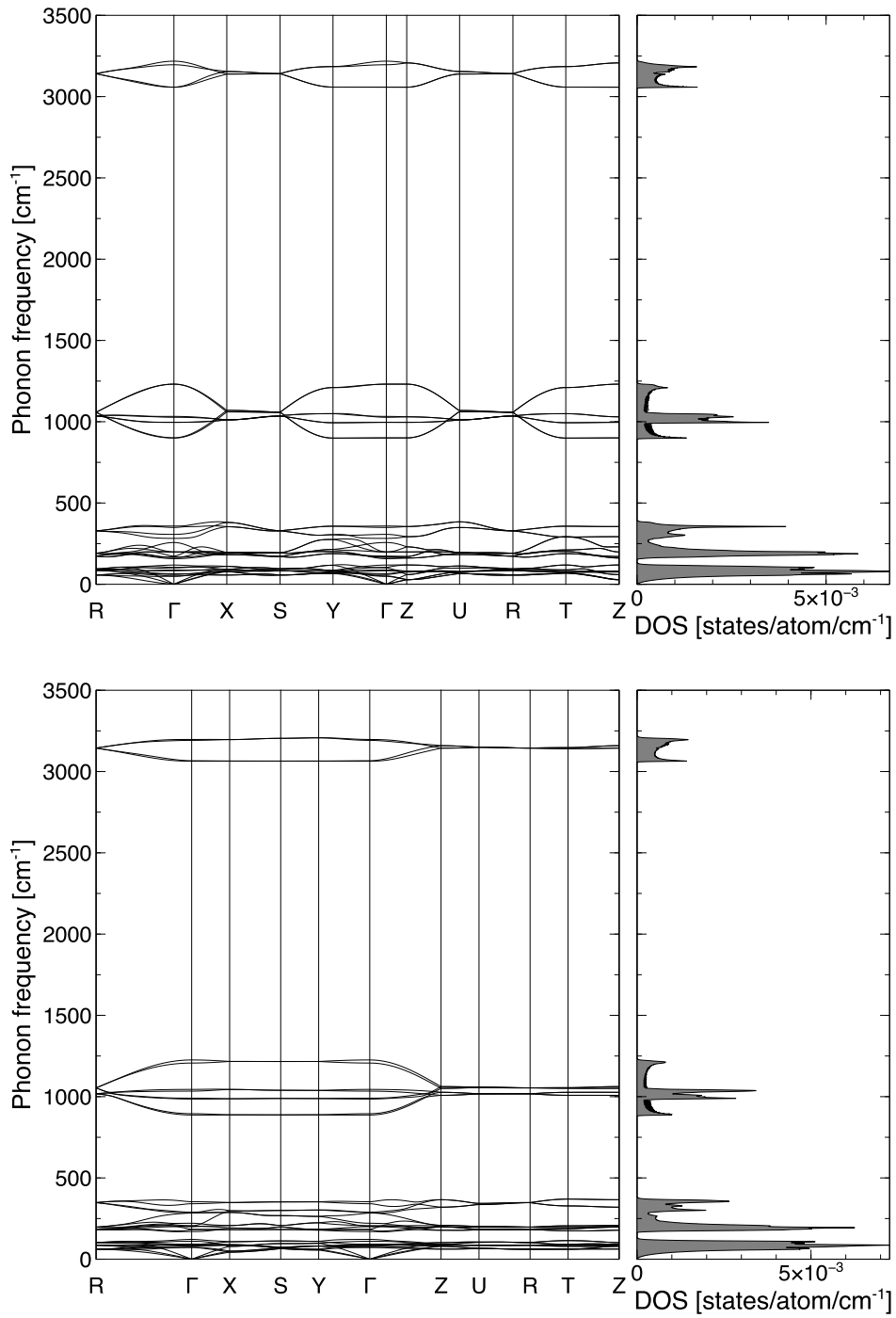


Figure 3: Phonon dispersions of CsOH-IVc (*Pnma*, top) and CbOH-VII (*P2₁2₁2₁*, bottom), both at $P = 10$ GPa.