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Thermal equations of state for B1 and B2 KCl

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ABSTRACT

Compressibility of solids generally drops as compression proceeds. Bonds shorten and stiffen with density increase in the same structure. However for the B1-B2 phase transition in many measured alkali halides, bond lengths increase in going to the denser phase. And IR mode frequencies decrease (Hofmeister 1997), leading to the counter-intuitive expectation that compressibility should *increase* in going to the denser B2 phase. Past volume measurements have been equivocal at best in recognizing any such compressibility increase. New thermal equations of state for B1 and B2 KCl from in-situ X-ray diffraction measurements of phase volumes on Station 16.4 of the CLRC Daresbury Laboratory are no less equivocal about the issue of whether compressibility increases or decreases across the transition. In contrast, the new volume measurements show an easily resolved thermal expansion increase in going from B1 to B2 KCl. The product $\alpha \cdot \boldsymbol{K}$, which is better known than either α or $\boldsymbol{K}$, increases from 0.0195 ± 0.0005 kbar/°C in B1 to 0.0275 ± 0.0009 kbar/°C in B2 KCl. Yagi (1978) demonstrated a similar increase for KF, also supported mainly by increases in α. This increase can also be seen in RbCl (Walker et al. 2001). Bond weakening indicated by the thermal expansion increase is consistent with the elusive compressibility increase that is expected across the B1-B2 transition but which is not resolved from volume measurements. The thermal effects are more visible than the compressional effects on $\alpha \cdot \boldsymbol{K}$ across the transition. Bond tightening upon decompression reduces α, increases solid viscosity, and hence decreases the Rayleigh number. An upwelling of material undergoing a decompression phase change with decrease of coordination number may have its convective friskiness damped at such a transition.