**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 \( \alpha \cdot K \), which is better known than either \( \alpha \) or \( K \), 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 \( \alpha \). 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 \( \alpha \cdot K \) across the transition. Bond tightening upon decompression reduces \( \alpha \), 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.

**INTRODUCTION**

Compression of alkali halides has been a useful guide to the behavior of structurally simple condensed matter, such as deep mantle oxides. Studies of simultaneous compression and heating are necessary to understand the properties of a planetary interior that is hot as well as compressed. Of the alkali halides, KCl is conspicuous in not having a thermal equation of state (EOS) unless one assumes \( \alpha = \alpha_0 \cdot K_0 \) is a constant where \( \alpha \) = thermal expansion, \( \alpha_0 \) = ambient \( P\cdot T \) thermal expansion, \( K = \) bulk modulus, and \( K_0 \) = the ambient \( P\cdot T \) bulk modulus. We undertook an in-situ X-ray diffraction (XRD) pressure-temperature study of both the B1 and B2 phases of KCl to fill this gap. We report here a confirmatory restudy of our preliminary KCl effort (Johnson et al. 2001) with a new detector (Barnes et al. 1998) and improved X-ray illumination and calibration procedures (Walker et al. 2001, 2000).

There is controversy about whether the bulk modulus increases or decreases across the B1-B2 transition in KCl. This may be appreciated by comparing the contradictory reports of Vaidya and Kennedy (1971, it decreases), Yagi (1978, it increases), Boehler and Zha (1987, it decreases), Campbell and Heinz (1991, it increases), Hofmeister (1997, it decreases), and Johnson et al. (2001, it increases). The new thermal EOS for both phases of KCl allows insight to be achieved from examination of \( \alpha \cdot K \) rather than just \( K \) across the transition.

**EXPERIMENTAL METHOD**

Dehydrated powders of reagent KCl and NaCl were ground with admixed BN to prepare samples for loading into 12 mm truncated edge length cubic/octahedral multi-anvil assemblies. Experimental observation of phase volume by in-situ energy dispersive X-ray diffraction (EDXRD) at high pressure and temperature was performed on the Station 16.4 multi-anvil device at CLRC Daresbury Lab (Clark 1996). Press and X-ray beam characteristics, assembly details, and operating proce-