

ISIS Experimental Report

Rutherford Appleton Laboratory

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Title of Experiment: Thermal expansion and incompressibility of epsomite

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Introduction. The presence of salts such as MgSO_4 in chondritic meteorites led to the suggestion that the water-rich icy moons of the Gas Giant planets would have ice mantles dominated by multiply-hydrated salts such as epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ (Kargel 1991). This suggestion has been supported by observational evidence from the Near Infrared Mapping Spectrometer (NIMS) instrument aboard the Galileo space-craft, which orbited Jupiter from 1995 to 2003; multispectral images of the surfaces of Jupiter's icy moons, Europa, Ganymede, and Callisto have been interpreted as showing deposits of hydrated alkali salts. When constructing geophysical models of these icy moons, it is therefore important to know the phase behaviour and physical properties of the constituent materials under the appropriate pressure and temperature conditions (0 - 2 GPa, 100 - 300 K).

Previous high-pressure studies of epsomite (Bridgman 1948a,b; Livshits *et al.*, 1963; Hogenboom *et al.*, 1995; Grasset *et al.*, 2001a,b; Nakamura, 2003) have included a number of observations of phase transformations, but these are frequently contradictory, and the nature of the high-pressure phases has never been determined by in-situ diffraction experiments.

Aims. Our aims were to measure the coefficient of volume thermal expansion at atmospheric temperature, and at one or more pressures up to ~ 5 kbar; to measure the incompressibility up to 5.5 kbar at room temperature; and to observe any phase transformation that may - or may not - take place in the pressure range 0 - 5.5 kbar.

Experimental. Deuterated epsomite was prepared by crystallisation from a solution of magnesium sulfate in D_2O . Crystals were dried, ground and sieved (to a grain size of $100\mu\text{m}$) in a helium-filled glove bag. The ambient-pressure run was carried out in an Al slab can; the room-temperature run to 5.5 kbar in a TiZr pressure cell; and the high-pressure thermal expansion runs in an Al pressure cell. In the TiZr cell we employed Ar-gas as a pressure transmitting fluid (since we were already using argon in a concurrent study of ice II), and in the Al cell we employed He-gas.

In the slab can, diffraction data were collected at 2 K for 14 hours ($480\mu\text{Ahr}$) for detailed structure refinement. Data were then collected in the backscattering detectors from 5 - 300 K in 5 K increments (Fig. 1). In the TiZr cell, diffraction data were collected in the 90° detector bank from 1.1 - 5.5 kbar in 1100 bar increments upon compression, and from

5.0 - 0.6 kbar in 1100 bar increments upon decompression. In the aluminium pressure cell, diffraction data were collected on the 1.4, 3.0, and 4.5 kbar isobars from 290 - 50 K, in 10 K increments. Data were also collected upon decompression from 4.5 kbar at 50 K, in 500 bar increments.

Results. The three experiments have allowed us to fit a full thermal equation of state to the measured P-V-T surface of epsomite. The shape of the P-V-T surface is not particularly remarkable, but the details of the axial expansivities and incompressibilities are very interesting. The *a*-axis exhibits negative linear thermal expansion from 30-250 K at room pressure. With increasing pressure, the axial expansivity turns positive again below ~90K. The effect of this is a significant drop in the *a*-axis incompressibility below 90K. Conversely, the *b*-axis expansivity turns negative below 90K at high-pressure, leading to a large stiffening of the *b*-axis incompressibility.

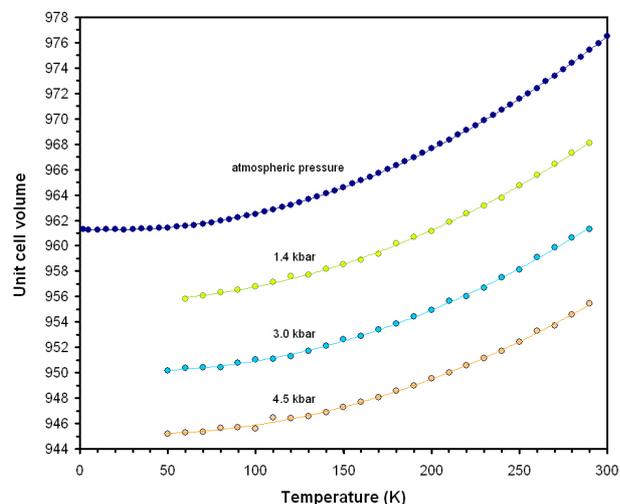


Fig. 1. The unit cell volume (\AA^3) as a function of temperature at four pressures. Solid lines are second-order polynomial fits to the data.

References

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