

THERMOELASTIC PROPERTIES OF MIRABILITE AND MERIDIANIITE DETERMINED USING EXPERIMENTAL AND COMPUTATIONAL TECHNIQUES.

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Introduction: The presence of soluble salts such as MgSO_4 and Na_2SO_4 in chondritic meteorites has led to the suggestion that hydrated salts such as mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and meridianiite ($\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$) may be major rock-forming minerals in the mantles of large icy moons [1], in addition to pure water ice. Evidence for hydrated alkali salts on the jovian satellites has been observed by the Near Infrared Mapping Spectrometer (NIMS) instrument aboard the Galileo space-craft [2][3]. To interpret the observed surface morphologies of the icy moons and to understand their thermal evolution, geophysical models of their interiors must be constructed. To do this we need to know the phase behaviour, thermoelastic, and transport properties of the constituent materials under the appropriate pressure and temperature conditions, i.e. up to ~ 5 GPa, and from 100 – 300 K. We are therefore engaged in a program of cross-disciplinary research to determine these properties of planetary ices and hydrates using both computational and experimental methods (see contributions by Fortes *et al.*, Middleton *et al.*, and Grindrod *et al.*, this volume).

Both mirabilite and meridianiite pose experimental and computational challenges by virtue of their crystallography: mirabilite is monoclinic, has a large and complex unit-cell, and exhibits hydrogen-bond disorder; meridianiite is a triclinic crystal (the only symmetry is an inversion centre), and its structural and thermoelastic properties are dominated by weak hydrogen-bonding. Difficulties with the formation and handling of phase-pure specimens means that application of computational mineral physics is the only way to reliably obtain certain material properties. Here we describe combined time-of-flight neutron powder diffraction studies and quantum mechanical calculations of the thermoelastic properties of mirabilite and meridianiite.

Experimental method: Deuterated crystals of mirabilite and meridianiite were grown from supersaturated aqueous solutions of D_2O and ground to a powder. Neutron diffraction data from these powders were collected on the HRPD instrument at the ISIS neutron spallation source, Rutherford Appleton laboratory. Highly accurate lattice parameters obtained from these data as a function of temperature allow determination of the molar volume and full thermal expansion tensor, as well as yielding crystal structures which are used to

provide insight into the origin of the behaviour of the bulk elastic properties of the crystal.

Computational method: Quantum mechanical (first principles or *ab initio*) calculations were done using VASP (Vienna *Ab initio* Simulation Package) with PW91 GGA functional, known to produce good results with hydrogen-bonded systems. For each structure, we calculate the total energy of the crystal as a function of molar volume (e.g., Fig. 2) and obtain the relevant material parameters by fitting equations of state. Integrated forms of the well-known 3rd-order Birch-Murnaghan equation of state (BMEOS3) [4] and of the 4th-order logarithmic equation of state (LNEOS4) [5] are fitted to the $E(V)$ points to determine the zero-pressure volume, V_0 , the zero-pressure bulk modulus, K_0 , its first pressure derivative, $(dK/dP)_0$ or K_0' , and in the case of LNEOS4, the second pressure derivative, K_0'' .

Experimental results: Figure 1 shows the volume thermal expansivity of mirabilite [6] and meridianiite [7] as determined by fitting the neutron data with Debye and Einstein models of the crystals' internal energy. The volume thermal expansion of both phases is similar to that of epsomite [8], and considerably smaller than that of ice Ih [9].

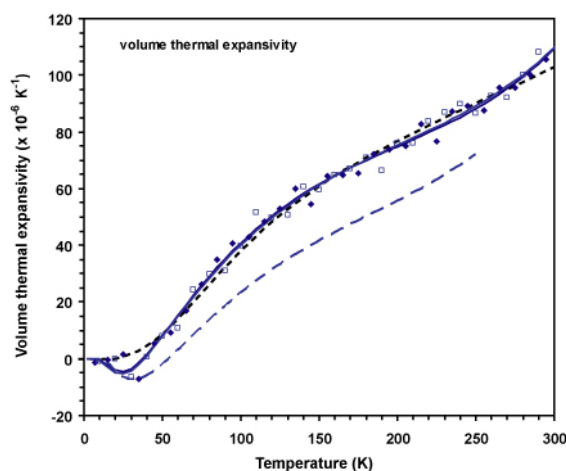


Figure 1. Comparison of the volume thermal expansion coefficient α_V , for deuterated mirabilite from Debye (solid line) and Einstein (dotted line) models. The dashed line shows the volume thermal expansion of meridianiite [7] for comparison.

Our analysis of the thermal expansion in relation to structural elements in both crystals reveals that hydro-

gen-bonding is responsible for the magnitude and orientation of the expansion tensors as a function of temperature (and, in all probability, pressure as well). In mirabilite, the two interstitial water molecules appear to dominate, and in meridianiite it is the bifurcated interlayer hydrogen bond. Although we intend to explore the thermoelastic behaviour using high-pressure neutron diffraction during 2008, we have already acquired a detailed understanding of how these hydrogen-bonds affect the bulk crystal properties using quantum mechanical calculations.

Computational results: Figure 2 shows the calculated $E(V)$ curve for mirabilite, fitted with equations of state; parameters obtained from these fits (for both mirabilite and meridianiite) are given in Table 1. In both cases the difference between the calculated and measured V_0 is $\sim 3\%$, which is typical of these types of calculations.

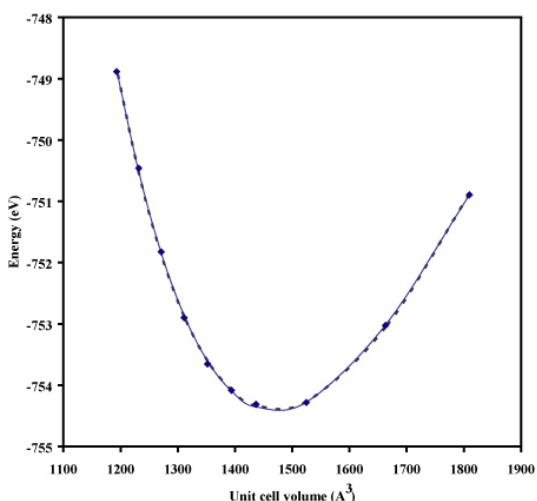


Figure 2. The *ab initio* $E(V)$ curve for mirabilite. The points are the calculations, the solid line is a LNEOS4 fit and the dotted line a BMEOS3 fit. The fit parameters are given in Table 1.

It is of some interest to note that the calculated bulk moduli of mirabilite, meridianiite, and epsomite [8] are all identical (within errors), despite major differences in intermolecular bonding. Both mirabilite and meridianiite exhibit major discontinuities in their elastic properties at high pressure (~ 5 GPa) which are the

result of very small changes in the hydrogen-bond network. In the case of meridianiite, we find that changes in the bifurcated h-bond result in rotation of the $\text{Mg}(\text{H}_2\text{O})_6$ octahedra, such that a *single* hydrogen-bond donated to a sulfate tetrahedron breaks, and reforms to a $\text{Mg}(\text{H}_2\text{O})_6$ octahedron. Such small structural changes would be a challenge to observe experimentally at present, illustrating the value and complementarity of computational mineral physics in the study of planetary ices.

Summary: The evolution and dynamics of the icy satellites are governed by the behaviour of the constituent materials of the satellites. Modelling of these planetary bodies requires a combination of experimental and computational techniques to obtain the necessary thermoelastic properties and polymorphic phase behaviour. Quantum mechanical calculations make a significant contribution to this effort, allowing the rapid determination of physical properties for the kinds of complex low-symmetry salt hydrates that may comprise such moons. The results we have obtained here give us the confidence to tackle much more difficult problems, using the *ab initio* method, such as calculation of diffusion coefficients as a route to understanding diffusion creep processes in these crystals.

References: [1] Kargel, J. S. (1991) *Icarus* **94**, 368. [2] Dalton *et al.* (2005) *Icarus* **177**, 472. [3] Orlando *et al.* (2005) *Icarus* **177**, 528. [4] Birch, F. (1952) *J. Geophys. Res.* **57**, 227 [5] Poirier, J.P. and A.Tarantola (1998) *Phys. Earth Planet. Int.* **109**, 1. [6] Brand *et al.*, submitted. [7] Fortes *et al.* (2008) *Phys. Chem. Min.*, doi:10.1007/s00269-008-0214-x [8] Fortes *et al.* (2006) *Eur. J. Min.* **18**, 449 [9] Röttger *et al.*, (1994) *Acta Cryst. B* **50**, 644.

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Table 1. Fitted thermoelastic parameters for mirabilite and meridianiite from *ab initio* simulation.

	Mirabilite		Meridianiite	
	BMEOS3	LNEOS4	BMEOS3	LNEOS4
V_0 (\AA^3)	1471(2)	1470(2)	722.0(3)	722.1(3)
E_0 (eV per unit cell)	-754.392(2)	-754.411(3)	-403.667(2)	-403.667(2)
K_0 (GPa)	22.1(2)	23.3(8)	23.1(1)	22.8(6)
K'	5.2(3)	5.1(2)	2.9(3)	2.9(3)
K'' (GPa^{-1})	-	0.7(3)	-	0.4(12)