ISIS Experimental Report

Rutherford Appleton Laboratory

		RB Number:	510036
		Date of Report:	July 2006
Title of Experiment:	The incompressibility and high-pressure behaviour of anhydrous $MgSO_4$.	**Local Contact:**	R. I. Smith
Principal Proposer:	A. D. Fortes	**Instrument:**	POLARIS
Affiliation:	University College London		
Experimental Team:	A. D. Fortes, I. G. Wood	**Date of Experiment:**	3-6/07/2006

Introduction: The aim of this experiment was to measure the bulk and axial incompressibility of anhydrous $MgSO_4$ at room temperature up to 1 GPa, and then to observe the phase behaviour of the sample upon heating to 1000 K at 1 GPa. This work is intended to complement our work on anhydrous $MgSO_4$ at atmospheric pressure (RB510035 and 610130), allowing us to derive improved Mg-O and S-O interatomic potentials for use in molecular dynamics calculations. These calculations provide the basis for extending our studies of hydrous $MgSO_4$ salts, such as $MgSO_4.7H_2O$ (RB14491) and $MgSO_4.11H_2O$ (RB15133), which are thought to be major rock-forming minerals inide the large icy moons of the outer solar system (see ISIS Science Highlights, 2004).

There are three known polymorphs of $MgSO_4$; α-$MgSO_4$ has the $CrVO_4$-type structure [1]; β-$MgSO_4$ has the $ZnSO_4$-type structure [2]; the structure of γ-$MgSO_4$, which exists only above ~1000°C [3,4] is unknown. Very little work exists on the bulk properties of $MgSO_4$ and its phase transition behaviour at high pressure.

Experimental method: α-$MgSO_4$ was was synthesized from MgO and H_2SO_4 and dried for 24 hours at 200°C; the material we used here is from the same batch prepared for our earlier work (RB510035). The powder sample was pressed into a platinum canister under a load of 0.5 tons and then mounted inside a high P,T Gardner cell [5]. We found that the scattering from the sample was extremely weak, and the observation of parasitic scattering from the graphite heaters in the diffraction pattern suggested that there was some problem with the alignment or collimation of the cell. Counting times suitable for fitting a unit cell to the diffraction data proved to be ~ 6 hours; comparison with the results of other studies using the same cell indicated to us that this was anomalously long. Furthermore, we found that load was not being applied to the sample – even though the gauge connected to the hydraulic ram appeared to be functioning properly. It is possible that both the weak scattering and failure to transmit load are symptoms of the same problem. The net gain from this work was the collection of 5573 μAhr of data essentially at atmospheric pressure.

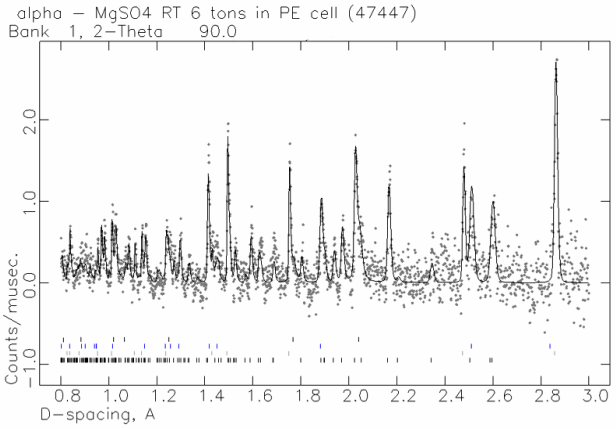
After abandoning the Gardner cell, we loaded a Paris-Edinburgh cell with α-$MgSO_4$, Pb pressure marker, and MeOD/EtOD pressure transmitting fluid. Data were collected at room temperature, and we found again that the sample was scattering far more weakly than expected. Comparison of the Pb (111) reflection in our patterns with those from a previous user (the lead foils used are a 'standard' size) indicated that our count rate was too low by a factor of about three. Time constraints thus allowed us to collect data at just three loads; 6 tons (12.6 hours), 30 tons (12.7 hours), and 60 tons (22.5 hours).

Results: The GSAS package was used to determine the lattice parameters of α-$MgSO_4$ and Pb. From the three measured diffractions patterns we obtained the unit cell dimensions as a function of pressure; [0.00(10) GPa] a = 5.1821(9) Å, b = 7.8845(14) Å, c = 6.4994(12) Å, V = 265.55(5) Å^3; [2.52(11) GPa], a = 5.1586(10) Å, b = 7.7870(16) Å, c = 6.3807(13) Å, V = 256.31(6) Å^3; [6.36(11) GPa], a = 5.1301(14) Å, b = 7.6693(23) Å, c = 6.2250(19) Å, V = 245.70(8) Å^3. These results were fitted with a 3rd order Birch-Murnaghan equation of state for comparison with the density functional theory values (Table I). Since there are only three data points, and two variables in the fitted equation, then the fit is unrealistically good (i.e., R^2 = 1.0) and there are no standard errors on the fitted parameters presented in Table 1; had we been able to collect more data then we would be able to present estimates of the uncertainty in V_0, K_0 and K'.

Table I. Comparison of the calculated (DFT, unpublished) and experimentally measured (powder neutron diffraction) values for the elastic properties of β- and α-$MgSO_4$.

	β-$MgSO_4$ (DFT)	α-$MgSO_4$ (DFT)	α-$MgSO_4$ (exp)
V_0 (Å^3)	285.00(12)	276.47(15)	265.553
K_0 (GPa)	62.3(5)	61.2(6)	64.11
K'	3.98(5)	4.68(8)	5.90
E_0 (eV)	-148.384(6)	-148.389(7)	-
K_a (GPa)	59.5(20)	160(12)	168.13
K'$_a$	3.02(11)	12.5(14)	14.32
K_b (GPa)	172(10)	69(5)	61.68
K'$_b$	17.6(14)	3.9(4)	4.83
K_c (GPa)	41.9(5)	39.6(12)	40.57
K'$_c$	3.16(3)	3.33(7)	4.22

Figure 1. The powder neutron diffraction pattern acquired under a load of 6 tons in the P-E cell after an integration time of 12.5 hours (2150 μA hr). Tic marks are, from the top down, nickel, tungsten carbide, lead, and α-$MgSO_4$.



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