

ISIS Experimental Report

Rutherford Appleton Laboratory

Title of Experiment: Ab initio solution of the crystal structure of magnesium sulfate dodecahydrate.

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Instrument: HRPD

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Introduction

The dodecahydrate of MgSO_4 , which we call Fritzsche's salt, was first identified 167 years ago [1], and yet essentially nothing is known about it today. This substance has a limited region of stability in equilibrium with its aqueous solution, dehydrating to $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (the mineral epsomite) above $\sim 2^\circ\text{C}$. Fritzsche's salt has garnered the interest of planetary scientists, however, over the past 15 years since a combination of modelling and spectroscopic evidence suggested that it could be a major rock-forming mineral in the outer solar system's icy moons. Indeed the dehydration reaction has been implicated in the global-scale rifting of Jupiter's moon Ganymede.

One of the first steps in characterising this material is to determine its crystal structure. The presence of a significant quantity of bound water in the crystal dictates that neutron diffraction is the method of choice for structural study, and since indexing relies on accurate high-resolution data, we chose to conduct a powder diffraction experiment on HRPD.

Experimental

The sample was made by flash-freezing a stoichiometric solution (33.4wt% MgSO_4 in D_2O) in liquid nitrogen. The sample was then broken up and powdered under air at -10°C in the ISIS cold room. This method has been demonstrated to form a fine polycrystalline mass which transforms to acicular epsomite crystals upon warming, identical to the behaviour we have observed in single crystals of hydrogenous Fritzsche's salt grown from solution in our own cold room. 5.1 grams of powdered Fritzsche's salt was loaded into a pre-cooled aluminium slab-can. The sample-can/centre-stick assembly was moved from the cold room in a bucket of dry ice and loaded into a cryostat on the HRPD beam line. Initial data collection at 250 K revealed a unique diffraction pattern containing no reflexions from either ice or epsomite. A full data set was then collected at this temperature for ~ 21 hours (346.7 μA) with the beam choppers phased to provide a wide time-of-flight window, 30-230ms, at half the normal flux (i.e., 5 Hz pulse frequency). The great advantage of this was to allow access to longer d-spacings; in the forward scattering banks it was possible to see out to d-spacings of 17 \AA . In the 'normal' t-o-f window, 60-160ms, data were then collected at 5 K intervals upon cooling from 250 K to 4 K (~ 20 minutes each), with the objective of characterising

the thermal expansivity once the pattern was indexed. At 4.2 K, another low-noise data set was collected, ~ 7 hours (177.9 μA) in the 30-130ms window, and ~ 19 hours (312.1 μA) in the 30-230ms window.

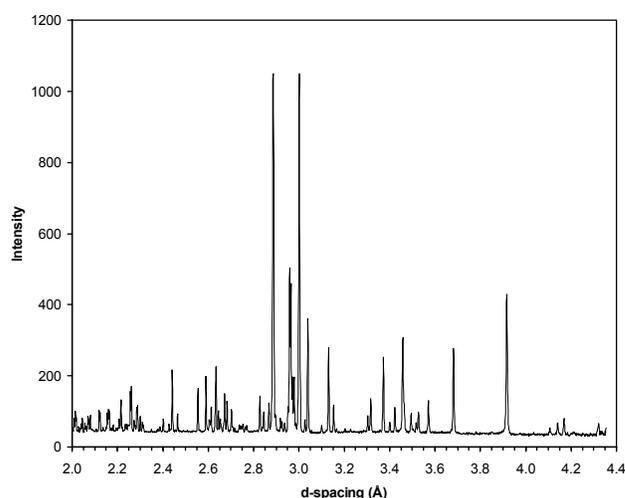


Figure 1. Normalised diffraction pattern of Fritzsche's salt collected in the backscattering banks at 250 K.

References

[1] Fritzsche (1837) Bulletin scientifique publié par l'Académie Impériale des Sciences de St. Pétersbourg **2**, 193-196.