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Neutron Diffraction Refinement of the Structure of Gypsum, $CaSO_4.2H_2O$

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Abstract

The crystal structure of gypsum, $CaSO_4.2H_2O$, has been refined to $R_w = 0{\cdot}023$ and $R = 0{\cdot}036$ for 610 neutron diffraction intensities collected at room temperature (294 K) for a unit cell with $a = 5{\cdot}679$ (5), $b = 15{\cdot}202$ (14), $c = 6{\cdot}522$ (6) Å, $\beta = 118{\cdot}43$ (4)°, and space group $I2/a$, $Z = 4$, $V = 495{\cdot}2$ Å^3, $d_c = 2{\cdot}3$ g cm^{-3}. The refinement was based on a model with anisotropic thermal motion for all atoms, and an isotropic secondary-extinction coefficient. The O—H bonds of the water molecule are 0·942 (3) and 0·959 (3) Å and hence significantly different. The difference, 0·017 (4) Å, is in accordance with spectroscopic stretching-frequency differences for the two O—H bonds. The water molecule donates two hydrogen bonds of 1·856 (2) and 1·941 (2) Å to sulfate O atoms. The shortest hydrogen bond is not linear, the O—H···O angle being 170·9 (2)°, whereas the other bond has an angle of 177·2 (2)°. H—H is 1·533 (3) Å and H—O—H 107·5 (2)°. The sulfate ion is definitely not a regular tetrahedron. The S—O distances are equal [1·474 (1) and 1·471 (1) Å], but the O—S—O angles are not [111·1 (1), 111·0 (1), 111·1 (1) and 106·3 (1)°], leading to differences in the O—O tetrahedral edges [2·429 (1), 2·432 (2), 2·426 (2) and 2·357 (1) Å]. The shortest edge is shared between the sulfate tetrahedron and the square-bipyramidal CaO_8 group.

Introduction

The crystal structure of gypsum ($CaSO_4.2H_2O$) has been the subject of several refinement studies since it was first determined from two-dimensional X-ray data by Wooster (1936). The structure was refined from two-dimensional neutron data by Atoji & Rundle (1958), and from three-dimensional X-ray data by Cole & Lancucki (1974). The latter authors also carried out a refinement based on the neutron diffraction intensities of Atoji & Rundle (1958). However, the refinement could not be carried beyond an isotropic model.

Gypsum has also been extensively studied by spectroscopic methods (Behrenblut, Dawson & Wilkinson, 1973; Fokushima & Yanagida, 1972; McKnett, Dybowski & Vaughan, 1975) and of particular interest is the IR investigation performed by Seidl, Knop & Falk (1969) who found that the water molecules in gypsum are asymmetric. The extent of the asymmetry was measured by the difference between the two OH stretching frequencies of HDO molecules; this was found to be 90 cm^{-1}, corresponding to a difference of 0·02 Å in the O···O distance of the two hydrogen bonds. Although available structural data give similar indications only conclusions of marginal significance may be drawn. Many of the properties of gypsum are related to the presence and arrangement of the water molecules within the structure, and in order to study the dynamics of the water in gypsum in detail we found that a refinement based on three-dimensional neutron diffraction data was needed. The result of this work is reported here. Advantage has been taken of better scattering lengths and more modern methods for the treatment of absorption and extinction effects.

Experimental

Different unit cells have been chosen for gypsum (Bragg, 1937), and in order to facilitate comparison

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Table 1. *Additional crystal data*

Space group $I2/a$ (non-standard setting of $C2/c$, No. 15)
Equivalent positions $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2})$
$x,y,z;\ \frac{1}{2}+x,\ \frac{1}{2}-y,\ z$
$\bar{x},\bar{y},\bar{z};\ \frac{1}{2}-x,\ \frac{1}{2}+y,\ \bar{z}$
Systematic absences
hkl: $h+k+l=2n+1$
$h0l$: $h=2n+1,\ (l=2n+1)$
Crystal mass: 13·95 mg
Absorption coefficient, μ: 1·38 cm^{-1}
Volume of crystal: measured 65 mm^3; calculated 68 mm^3

Faces	*h k l*	*d* (cm)*	*h k l*	*d* (cm)*
	$0\,1\,0$	0·15	$\bar{1}\,0\,1$	0·205
	$0\,\bar{1}\,0$	0·15	$1\,\bar{2}\,\bar{1}$	0·26
	$4\,0\,\bar{7}$	0·26	$1\,2\,\bar{1}$	0·215
	$\bar{4}\,0\,\bar{7}$	0·26		

* Distance from arbitrary origin inside crystal.

Table 2. *Refinement parameters*

Number of reflections measured	611
$\sin\theta/\lambda$ (max.) (Å^{-1})	0·61
Number of parameters refined	57
$R(F^2)=\sum\lvert F_o^2-k^2\lvert F_c\rvert^2\rvert^2/\sum F_o^2$	0·037
$R_w(F^2)=\lvert\sum w(F_o^2-k^2\lvert F_c\rvert^2)^2/\sum wF_o^4\rvert^{1/2}$	0·043
$R(F)=\sum\lvert F_o-k\lvert F_c\rvert\rvert/\sum F_o$	0·036
$R_w(F)=\lvert\sum w(F_o-k\lvert F_c\rvert)^2/\sum wF_o^2\rvert^{1/2}$	0·023
$S=\lvert\sum w(F_o^2-k^2\lvert F_c\rvert^2)^2/(m-n)\rvert^{1/2}$	1·28

with previous structure determinations (Atoji & Rundle, 1958; Cole & Lancucki, 1974) we have used the non-standard setting $I2/a$ instead of $C2/c$ (see Table 1).

A suitable crystal was cut from a larger sample of the mineral from Hampshire, England, obtained from Ward's Natural Science Establishment, Inc., Rochester, New York. Care was taken in order to obtain a uniform transparent specimen, and faces perpendicular to the (010) plane were polished with fine-grain sand paper. The volume calculated on the basis of the weight and density agrees well with that determined from measurements of the crystal faces. The crystal was arbitrarily mounted and data were collected on the automatic four-circle diffractometer CIRCUS at the reactor JEEP II at IFE, Kjeller. The diffractometer was operated under a control system developed by Tressum (1975). Cell parameters were determined by least-squares refinement based on the setting angles of 20 reflections with $2\theta > 40°$. The values are in good agreement with those reported previously, and are given in the *Abstract*; see Table 1 for other crystal data. The neutron wavelength, 1·255 (1) Å, was determined by measurements of reflections from a standard NaCl crystal. Intensity data were collected in the θ–2θ scanning mode. The scan width was determined from the relation $\Delta 2\theta = (2{\cdot}15 + 0{\cdot}95\ \text{tg}\ \theta)°$ for $2\theta > 40°$ and a fixed scan width of 64 steps was utilized for $2\theta < 40°$. For all measurements a fixed monitor setting and a step size of 0·08° in 2θ was used. Data were collected in one hemisphere of reciprocal space out to $2\theta_{\max} = 100°$. All systematic extinctions were checked prior to data collection. Raw step-scan intensity profiles were analyzed, the peaks being located as described by Lehmann & Larsen (1974) with a program written by Groth (1976). Absorption corrections were calculated by the method of de Meulenaer & Tompa (1965), as modified by Templeton & Templeton (1973). The linear absorption coefficient was determined from measurements of the transmission through a plate-like crystal of known thickness, and agrees well with the value given by Atoji & Rundle (1958). Squared structure amplitudes were obtained as $F_o^2 = I \sin 2\theta$; their standard deviations were calculated from counting statistics, and a 2% uncertainty in instrument stability was included.

Structure refinement

The starting parameters for the refinement of the structure were those given by Atoji & Rundle (1958). The structure was refined with a local version of the least-squares program *LINEX* 74 (Becker & Coppens, 1975), adapted to the crystallographic computing system at the Department of Chemistry of the University of Oslo (Groth, 1973). The function minimized was $\sum w(F_o^2 - k\lvert F_c\rvert^2)^2$ where k is the overall scale factor and the weights, w, were given by $w^{-1} = [\sigma(F_o^2) + (0{\cdot}01F_o^2)^2 + 2500]^2$. The constant term was introduced in order to give lower weights to weak reflections, most of which had F_o^2 greater than F_c^2. All measurements with $F_o^2 > 0$ were included in the refinements. A summary of refinement parameters is given in Table 2. The neutron scattering lengths used for O and H atoms were 5·80 and −3·74 fm (Bacon, 1978). Those of Ca and S were refined and found to be 4·74 (2) and 2·87 (1) fm, respectively, in agreement with the values given by Bacon (1977). In the final cycle all positional and thermal parameters were refined and an isotropic secondary-extinction parameter was also included.

Discussion

Coordinates of atomic positions are given in Table 3,* anisotropic thermal parameters in Table 4, and relevant interatomic distances and angles in Table 5.

There is, in general, good agreement with the positional parameters from the previous X-ray study (Cole & Lancucki, 1974). The maximum differences in the x, y, and z parameters for the non-hydrogen atoms

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36479 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Positional parameters*

	x	y	z
Ca	0·5	0·07967 (9)	0·25
S	0·0	0·07705 (13)	0·75
O(1)	0·96320 (15)	0·13190 (5)	0·55047 (13)
O(2)	0·75822 (15)	0·02226 (5)	0·66709 (13)
O(*W*)	0·37960 (21)	0·18212 (7)	0·45881 (16)
H(1)	0·25112 (41)	0·16158 (11)	0·50372 (35)
H(2)	0·40458 (36)	0·24275 (13)	0·49217 (31)

Table 4. *Anisotropic thermal parameters* (Å^2 × 10^4)

The anisotropic thermal parameters are of the form

$$\exp\{-2\pi^2(U_{11}a^{*2}h^2+\ldots+2U_{23}b^*c^*kl)\}.$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	207 (8)	258 (8)	195 (8)	0	81 (6)	0
S	190 (11)	204 (10)	192 (11)	0	86 (10)	0
O(1)	262 (4)	279 (4)	243 (4)	−11 (4)	123 (3)	44 (3)
O(2)	222 (4)	270 (4)	254 (3)	−46 4)	92 (3)	8 (3)
O(*W*)	391 (5)	294 (6)	391 (5)	1 (5)	253 (4)	−38 (4)
H(1)	599 (10)	464 (9)	632 (10)	−12 (9)	432 (9)	18 (8)
H(2)	596 (10)	383 (9)	714 (11)	−39 (11)	384 (9)	−85 (10)

Table 5. *Interatomic distances* (Å) *and bond angles* (°)

Sulfate ion	
S–O(1)	1·474 (1)
S–O(2)	1·471 (1)
O(1)–O(1′)	2·432 (2)
O(1)–O(2)	2·357 (1)
O(2)–O(2′)	2·426 (2)
O(1)–O(2′)	2·429 (1)
O(1)–S–O(1′)	111·11 (14)
O(2)–S–O(2′)	111·04 (14)
O(1)–S–O(2)	106·29 (4)
O(1)–S–O(2′)	111·09 (4)
Ca···O distances	
Ca···O(1)	2·546 (1)
Ca···O(2)	2·552 (1)
Ca···O(2‴)	2·366 (1)
Ca···O(*W*)	2·374 (1)

Water molecule	
O(*W*)–H(1)	0·959 (3)
O(*W*)–H(2)	0·942 (3)
H(1)···H(2)	1·533 (3)
H(1)–O(*W*)–H(2)	107·51 (17)
Hydrogen bond	
O(*W*)···O(1)	2·807 (1)
O(*W*)···O(1″)	2·882 (1)
O(1)···H(1)	1·856 (2)
O(1)···H(2)	1·941 (2)
O(1)···H(1)–O(*W*)	170·92 (18)
O(1′)···H(2)–O(*W*)	177·20 (17)

Symmetry code

(′) $\bar{x}, y, \frac{1}{2}-z$
(″) $\frac{1}{2}+x, \frac{1}{2}-y, z$
(‴) $\bar{x}, \bar{y}, \bar{z}$

are 0·014, 0·011 and 0·009 Å, all occurring in the positional parameters of the atom O(1). The average absolute discrepancies are 0·010, 0·004 and 0·005 Å for x, y and z, respectively. Moderately good agreement also exists with the re-refined positional parameters of the H atoms [results based on the refinement of the neutron data of Atoji & Rundle (1958)]. The standard deviations in the latter parameters have, however, been lowered by a factor of 10 in the present investigation compared to the previous work.

The magnitudes of the thermal parameters from this investigation exceed those previously reported roughly by a factor of two, indicating sources of systematic errors in one or both studies (Abrahams, Hamilton & Mathieson, 1970; Hamilton & Abrahams, 1970).

As described previously, gypsum has a layer structure, the layers being parallel to the (010) face. Two sheets of sulfate ions are intimately bound together by calcium ions so as to form a strong double sheet. These double sheets are separated by sheets of water molecules. Each calcium ion is eight coordinated, by six O atoms belonging to sulfate groups, and by two water molecules. The Ca–O distances range from 2·552 (1) to 2·366 (1) Å. Each water molecule links a calcium atom both to an oxygen in the same double sheet 2·81 Å away and to one in a neighboring sheet 2·88 Å away. This relatively weak hydrogen bonding explains the easy cleavage along (010) planes.

The arrangement of the square-antiprismatic CaO_8 groups and sulfate tetrahedra consists of centrosymmetric pairs of chains along [101]. The arrangement is nearly identical to that found in the *ac* projection of the anhydrite structure in its *Amma* setting (see below) (Kirfel & Will, 1980).

The tetrahedral sulfate group is not regular. The space-group requirement is a twofold axis only (C_2 site symmetry). The O–O distances are 2·426, 2·429, 2·432 and 2·357 (1) Å and the respective angles are 111·1, 111·1, 111·0 and 106·3 (1)°. The two S–O distances are equal within standard deviations: 1·474 (1) and 1·471 (1) Å. The length compares well with corresponding distances in a recent neutron study of anhydrite (Kirfel & Will, 1980), and with results given by Baur (1970). That the SO_4^{2-} ion deviates from regularity has been known for some time from observations of splittings of fundamental frequencies in Raman and IR spectra of gypsum (Hass & Sutherland, 1956; Rousset & Lochet, 1945; Seidl, Knop & Falk, 1969).

The two non-equivalent O atoms in the SO_4^{2-} tetrahedron have different crystallographic environments. O(1) is hydrogen-bonded to two water molecules and coordinated to one Ca^{2+} ion at 2·546 (1) Å, and one water O at 2·374 (1) Å. O(2), on the other hand, is coordinated to two Ca^{2+} ions at 2·552 (1) and 2·366 (1) Å. It is well known that energy gain from packing can lead to relaxation of internal symmetry restrictions of molecules and ions and also that bond angles are more easily deformed than bond distances, in accordance with our findings.

The most interesting result, however, from this investigation concerns the dimensions of the water molecule and the geometry of the hydrogen bonding in gypsum (Fig. 1). There are no symmetry restrictions on the water molecules in the structure as it is situated in a general position in the unit cell. Accordingly, the two OH bonds are, in principle, non-equivalent. Our results give OH(1) = 0·959 (3) and OH(2) = 0·942 (3) Å, and a difference of 0·017 (4) Å, which is highly significant. The distances from the H atoms to the hydrogen-bond acceptors, H(1)···O(1) = 1·856 (2) and H(2)···O(1) = 1·941 (2) Å, are in accordance with expectations: The shorter is the H···O distance, the longer the OH distance (Olovsson & Jønsson, 1976). The hydro-

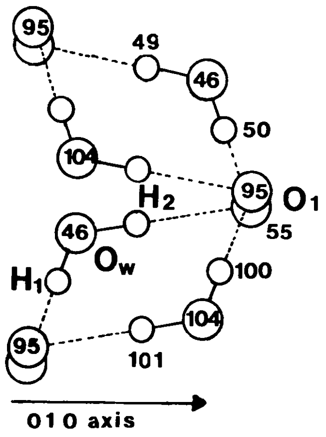

Fig. 1. The water molecule of gypsum projected on the (001) plane.

gen-bond angles are 170·9 (2) and 177·2 (2)°, the longest hydrogen bond being more nearly linear. The H—O—H angle is 107·5 (2)° and the intermolecular H—H distance is 1·533 (3) Å. The dimensions of an unperturbed water molecule in the gas phase are 105·54° and $r_e = 0{\cdot}984$ Å. No thermal correction has been applied to our results and a detailed comparison is therefore not warranted. However, the angle has increased by approximately 3°, as commonly observed (Falk & Knop, 1973).

Another interesting feature concerns the channels of water molecules formed along the [101] direction, which may be related to the near 'zeolitic' (Ramsdell & Partridge, 1929) nature of the material and its ability to form anhydrite as a secondary mineral. Water molecules can presumably migrate along this direction. In this connection, Atoji's (1959) finding that anhydrite micro-crystals are formed along this direction on dehydration of single gypsum crystals is interesting. He found that the direction corresponding to the *c* axis in the *Amma* setting for anhydrite was preserved, while the two other axes were randomly oriented.

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