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ANHYDROUS SULPHATES. II. REFINEMENT OF THE CRYSTAL STRUCTURE OF ANHYDRITE

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ABSTRACT

Three-dimensional counter-diffractometer data and a full- matrix least-squares method have been used to refine the crystal structure of anhydrite, $CaSO_4$, $a = 6.993(2)$, $b = 6.995(2)$, $c = 6.245(1)$Å, in the space group *Amma*. The final *R*-factor for 284 observed reflections was 1.6%.

Although the point symmetry of the SO_4^{2-} group is *mm*, it is distorted only slightly from an ideal tetragonal disphenoid and all S-O bond lengths are statistically equal. The Ca is surrounded by eight oxygens between 2.34 and 2.56Å, which form a distorted triangular dodecahedron. These two polyhedra link together to form alternating edge-sharing chains that are parallel to the *c*-axis in this orientation. Identical chains also occur in the structure of gypsum, running parallel to (101) in the *I*2/*c* orientation. This suggests that the chains are preserved in the high-temperature dehydration of gypsum → anhydrite, and accounts for the oriented nature of this reaction (Atoji 1959).

INTRODUCTION

Anhydrite ($CaSO_4$) is one of the principal sulphate minerals and exhibits a wide variety of parageneses. It is a major constituent of evaporite deposits, being typically associated with gypsum, alkali halides and carbonates. Anhydrite is also an important constituent of fumarolic deposits (Stoiber & Rose 1974), being associated with a wide variety of sulphates, sulphides, oxides and chlorides.

The crystal structure of anhydrite was first investigated by Wasastjerna (1925) and Dickinson & Binks (1926). The structural arrangements proposed by these investigators were similar, but the values of the *z*-coordinates (in the orientation *Amma)* differed systematically by 0.05 between the two solutions. Later work by Cheng & Zussman (1963) and Höhne (1961, 1962) confirmed the structure proposed by Wasastjerna (1925). Höhne (1961, 1962) reported parameters in the noncentric space group $Bm2_1b$ but stated that the deviations from centricity were small. Many different orientations have been used for the anhydrite cell for which the standard setting is *Cmcm;* however, the setting *Amma* best shows the relations between anhydrite and its hydrates and this orientation is used in this study.

EXPERIMENTAL

The crystals used in this investigation were from Leopoldshall, East Germany. Fragments were examined optically for the presence of twinning or alteration to gypsum, but neither was found. Single-crystal precession photographs exhibited an *A*-centred orthorhombic lattice with additional extinctions *h0l*, $h = 2n$; this is compatible with the space group *Amma* proposed by Cheng & Zussman (1963). Cell dimensions were determined by least-squares refinement of 15 reflections automatically aligned on a 4-circle diffractometer, giving the following values: $a = 6.993(2)$, $b = 6.995(2)$, $c = 6.245(1)$Å, $V = 309.70$Å^3.

An irregular equidimensional crystal of ~0.20 mm average dimension was used to collect the intensity data using Mo*K*α radiation and a Syntex P$\bar{1}$ automatic diffractometer according to the experimental procedure described by Hawthorne & Ferguson (1975). The data correspond closely to the values given by previous workers, and the stoichiometric composition was assumed for the purposes of the refinement.

A total of 552 reflections was collected over two asymmetric units out to a value of 65°2*θ*. Because of the equidimensional shape and low absorption coefficient of the crystal, no absorption corrections were considered necessary. The data were corrected for Lorentz, polarization and background effects and averaged to produce an asymmetric set. A reflection was considered as observed if its magnitude exceeded three standard deviations based on counting statistics. This resulted in 330 unique reflections of which 284 were considered as observed.

REFINEMENT

Neutral scattering factors were taken from Cromer & Mann (1968) with anomalous dispersion corrections from Cromer (1965). The final atomic parameters of Cheng & Zussman (1963) were used to initiate the refinement which was performed with the least-squares program RFINE (Finger 1969). Full-matrix refinement of all variables for an isotropic thermal model results in convergence at R- and R_w-factors* of 3.8 and 4.1% respectively (observed data only). Temperature factors were converted to anisotropic of the form

$$\exp\left[-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}\right]$$

and a correction was made for (isotropic) extinction (Zachariasen 1968) with the extinction coefficient included as a variable in the refinement. Refinement of all variables resulted in convergence at R-factors of 1.6% (observed) and 1.8% (all data) and R_w-factors of 1.8% (observed) and 1.9% (all data). In view of the good agreement obtained in the centrosymmetric space group, no attempt was made to refine the structure in *Am*2₁*a*, and the space group *Amma* is considered as established by the refinement. Observed and calculated structure factors are listed in Table 1**, atomic coordinates and equivalent isotropic temperature factors in Table 2, and anisotropic temperature factor coefficients in Table 3. Interatomic distances and angles, and the magnitudes and orientations of the principal axes of the thermal ellipsoids were calculated with the program ERRORS (L. W. Finger, personal communication) and are presented in Tables 4 and 5 respectively.

TABLE 2. POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR ANHYDRITE.

	x	*y*	*z*	$B_{equiv.}$
Ca	3/4	0	0.34760(7)	0.65(1)Å^2
S	1/4	0	0.15556(8)	0.55(1)
01	1/4	0.1699(1)	0.0162(2)	0.99(2)
02	0.0819(2)	0	0.2975(2)	0.94(2)

TABLE 3. ANISOTROPIC TEMPERATURE FACTORS FOR ANHYDRITE

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	0.00343(8)	0.00377(8)	0.00354(9)	0	0	0
S	0.00338(9)	D.00270(9)	0.00296(11)	0	0	0
01	0.00786(22)	0.00337(19)	0.00486(23)	0	0	0.00105(19)
02	0.00351(19)	0.00679(21)	0.00513(24)	0	0.00121(19)	0

TABLE 4. SELECTED BOND LENGTHS AND ANGLES FOR ANHYORITE

S-01	x 2	1.473(1)Å	Ca-01e	x 2	2.564(1)Å
S-02d	x 2	1.474(1)	Ca-01j	x 2	2.461(1)
S-0		1.473	Ca-02	x 2	2.345(1)
			Ca-02a	x 2	2.510(1)
			Ca-0		2.470
01-01d	x 1	2.376(2)^s	01-S-01d		107.55(8)°
01-02d	x 4	2.426(1)	01-S-02d		110.81(4)
02-02d	x 1	2.355(2)^s	02-S-02d		106.08(7)
0-0		2.406	0-S-0		109.48
01-01b	x 1	2.376(2)^s	01-Ca-01b		55.22(5)
01-01g	x 2	3.318(1)	01-Ca-01g		82.61(2)
01-02c	x 4	3.264(1)	01-Ca-02c		83.21(3)
01-02h	x 4	3.477(1)	01-Ca-02h		92.65(1)
01-02i	x 4	2.930(1)	01-Ca-02i		77.22(3)
02-02c	x 2	2.778(2)	02-Ca-02c		69.69(5)
02-02f	x 1	2.355(2)^s	02-Ca-02f		55.96(6)
		3.089			79.34

Equivalent Positions a = $\bar{x}, \bar{y}, \bar{z}$; b = $x, \bar{y}, z$; c = $\bar{x}, y, \bar{z}$;
d = $1/2-x, \bar{y}, z$; e = $1/2+x, y, \bar{z}$; f = $1/2-x, y, z$;
g = $x, 1/2-y, 1/2+z$; h = $\bar{x}, 1/2+y, 1/2-z$; i = $x, 1/2-y, z-1/2$;
j = $\bar{x}, y-1/2, 1/2-z$.

^{s}denotes edge shared between SO_4 and Ca polyhedra.

TABLE 5. MAGNITUOE AND ORIENTATION OF THE PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS FOR ANHYDRITE.

	R.M.S. Displacement, Å^2	Angle to *a*-axis in Degrees	Angle to *b*-axis in Degrees	Angle to *c*-axis in Degrees
Ca	0.084(1)	90	90	0
	0.092(1)	0	90	90
	0.097(1)	90	0	90
S	0.076(1)	90	90	0
	0.082(1)	90	0	90
	0.092(1)	0	90	90
01	0.081(3)	90	37(4)	127(4)
	0.107(2)	90	127(4)	143(4)
	0.140(2)	0	90	90
02	0.082(3)	38(4)	90	128(4)
	0.110(3)	128(4)	90	142(4)
	0.130(2)	90	0	90

DISCUSSION

The dominant motif of the anhydrite structure is the chain of alternating edge-sharing S and Ca polyhedra. The point symmetry of the sulphate tetrahedron is *mm*, resulting in two unique S-O bonds; these are equal and thus there is no bond-length distortion of the tetrahedron. However, the tetrahedral bond angles subtended by edges shared with the Ca polyhedron are contracted in agreement with Pauling's 3rd rule (Pauling 1960), and the SO_4 group is actually a slightly distorted tetragonal disphenoid. The Ca site also has point symmetry *mm* and shows a fairly regular coordination by eight oxygen atoms at distances between 2.345 and 2.564Å, forming a distorted triangular dodecahedron. Edge lengths and angles involved in the edge-sharing with the SO_4 group are strongly contracted due both to the disparate size of the two polyhedra and to cation-cation repulsion. The edge-sharing chains extend in the

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*$R = \Sigma \left| |F_{obs}| - |F_{cal}| \right| / \Sigma |F_{obs}|$; $R_w = \left| \Sigma w \left| |F_{obs}| - |F_{cal}| \right|^2 / \Sigma w F_{obs}^2 \right|^{1/2}$, $w = 1$

**Table 1 has been deposited with the Depository of Unpublished Data. Copies may be obtained on request to: Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Ontario, Canada.

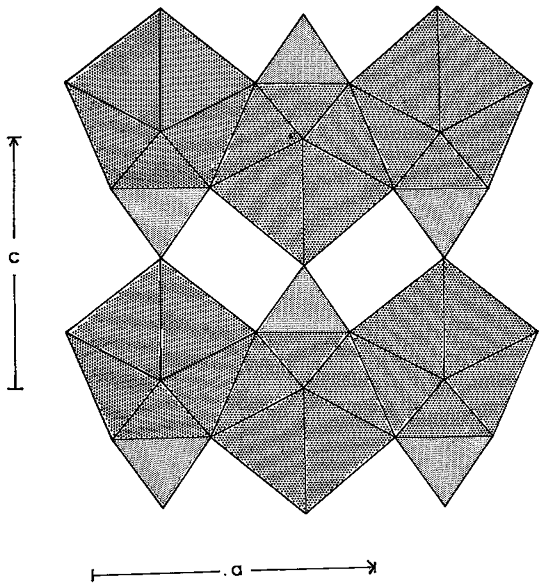

FIG. 1. Polyhedral representation of the anhydrite structure viewed along the *b*-axis. The Ca dodecahedra (large dots) and the S tetrahedra (small dots) form alternating edge-sharing chains parallel to the *c* axis; these link along *a* by edge-sharing of the dodecahedra.

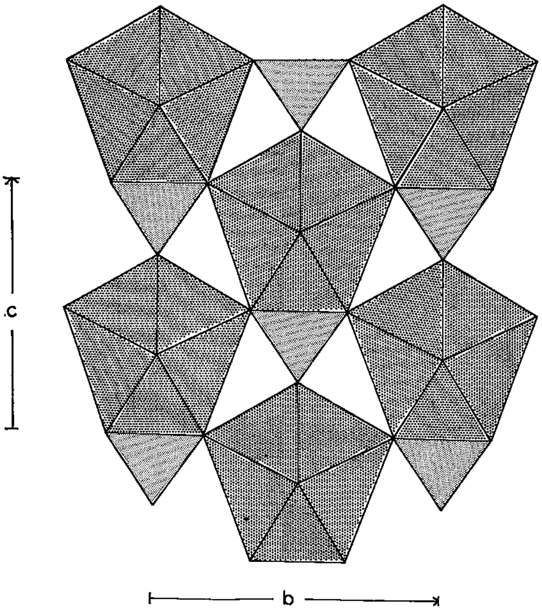

FIG. 2. Polyhedral representation of the anhydrite structure viewed down the *a* axis. In this orientation, it can be seen that the alternating edge-sharing chains link along *b* by corner-sharing between polyhedra.

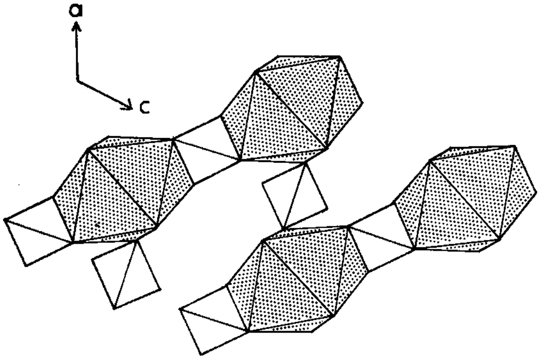

FIG. 3. Polyhedral representation of the gypsum structure viewed along the *b* axis. The Ca dodecahedra (shaded) and S tetrahedra (unshaded) form alternating edge-sharing chains extending along (101).

c-direction and link in the *a*-direction by edge-sharing between adjacent CaO_8 dodecahedra and corner-sharing between the SO_4 tetrahedra and the CaO_8 dodecahedra (see Fig. 1). In this orientation, the structure appears identical to that of zircon (Robinson *et al.* 1971); the anhydrite cell dimensions are pseudo-tetragonal and Wyckoff (1965) indicates that anhydrite is actually an orthorhombic distortion of the zircon structure. This is not the case; in the zircon structure, the edge-sharing SiO_4-ZrO_8 chains are linked in both the *a*- and *b*-directions by edge-sharing of the triangular dodecahedra, forming edge-sharing dodecahedral chains parallel to *X* and *Y*. In anhydrite, this type of linkage occurs only in the *X* direction; in the *Y* direction, interchain linkage is accomplished by corner-sharing between the various polyhedra, as shown in Figure 2.

Examination of the hydrates of $CaSO_4$ shows that the alternating edge-sharing SO_4-CaO_8 chain is a dominant feature in each structure. Figure 3 shows an *a-c* projection of the structure of gypsum ($CaSO_4 \cdot 2H_2O$) using the atomic coordinates given by Cole & Lancucki (1974); similar edge-sharing chains run parallel to 101 in this structure .The strictly-oriented transformation of gypsum to anhydrite during high-temperature dehydration (Atoji 1959) is presumably controlled by the orientation of these chains in each structure.

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