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CRYSTAL STRUCTURES AND MINERAL CHEMISTRY OF DOUBLE-SALT HYDRATES: II. THE CRYSTAL STRUCTURE OF LOEWEITE

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ABSTRACT

The crystal structure of loeweite, $6Na_2SO_4 \cdot 7MgSO_4 \cdot 15H_2O$, has been solved by reiterative application of Sayre's equation yielding a final R factor of 6.2%. The structure is unusual in that one of the three independent sulphate groups is disordered, giving rise to local noncentrosymmetry.

The structure can be described as corner-sharing zig-zag chains of Mg octahedra and S tetrahedra, emanating in six directions from the corners of the Mg octahedron located at the center of the unit cell. The two non-equivalent Na atoms are in 7-fold coordination with the Na-O distances ranging from 2.31 to 2.87 Å. The Mg-O distances vary within a small range of 2.01 to 2.12 Å. The S-O distances in the two independent SO_4 groups average 1.47 and 1.48 Å respectively, while the mean distance in the disordered SO_4 group is 1.60 Å.

INTRODUCTION

Loeweite is a sodium-magnesium sulphate hydrate, found only in salt deposits of oceanic origin. Table 1 summarizes the conflicting views of various authors with regard to its stoichiometry. As can be seen from the table, there are essentially two uncertainties:

(1) The number of water molecules in the unit cell, and

(2) The ratio of $Na_2SO_4/MgSO_4$ in the formula.

In order to resolve this stoichiometric problem, as well as to continue our study of double sulphate hydrate minerals, we undertook this investigation.

EXPERIMENTAL

Both natural and synthetic crystals were used in intensity measurements. Synthetic crystals were grown by us, according to the method described by Kühn and Ritter (1958). Natural loeweite, from the Hattorf mine, Philippsthal, Germany, was kindly sent to us by Dr. Kühn. The composition, optics and cell dimensions of the synthetic and natural crystals are in complete agreement.

Symmetry and Cell Dimensions. The cell parameters of loeweite are: $a = 11.769 \pm .009$ Å and $\alpha = 106.5 \pm .2°$, in excellent agreement with those given by Schneider and Zemann (1969). The cell parameters were obtained from precession films and by direct measurement with a Buerger diffractometer. Diffraction symmetry is $\bar{3}R-$, indicating the space group of $R\bar{3}$ if centric or $R3$ if acentric. $R\bar{3}$ was finally chosen based on (1) piezoelectric measurements, (2) intensity statistics, and (3) least-squares refinement. The density was measured by the sink-float method yielding a value 2.36 ± 0.01 g/cm³, in good agreement with the calculated value of 2.35 g/cm³, assuming a unit $6Na_2SO_4 \cdot 7MgSO_4 \cdot 15H_2O$ to be present in the cell, as proposed by Kühn and Ritter (1958) and confirmed by the results of the present structural investigation.

TABLE 1. CHEMICAL COMPOSITIONS PROPOSED FOR LOEWEITE

$Na_2SO_4 \cdot MgSO_4 \cdot 2\frac{1}{2}H_2O$ or $6Na_2SO_4 \cdot 6MgSO_4 \cdot 15H_2O$	Dana (1951)
$Na_2SO_4 \cdot MgSO_4 \cdot 2H_2O$ or $6Na_2SO_4 \cdot 6MgSO_4 \cdot 12H_2O$	Strunz (1957)
$6Na_2SO_4 \cdot 7MgSO_4 \cdot 15H_2O$	Kühn and Ritter (1958), also Schneider and Zemann (1959)
$4Na_2SO_4 \cdot 4MgSO_4 \cdot 9H_2O$	Heide (1966)

Intensity measurements and corrections. Three dimensional data were collected utilizing an automated Buerger diffractometer. The synthetic crystal used in the analysis was a parallelepiped with dimensions $0.2 \times 0.3 \times 0.3$ mm while the natural crystal was ground into a 0.25 mm diameter sphere. The crystals were mounted on the hexagonal c axis, and CuKα radiation was used with a proportional counter and pulse height analyzer. Several standard reflections, weak as well as strong, were monitored at the beginning and end of each level to check against any crystal misorientation and/or instability of the system. A total of 9 levels was measured, yielding approximately 4500 reflections. However, after averaging the 3 equivalents for each reflection and omitting those reflections which were considered unobservable 1075 nonequivalent reflections resulted. The intensities were corrected for Lp, with no absorption correction. After collection of the natural loeweite data, considerable nonlinearity was discovered in the detector used. Therefore, the synthetic loeweite data was used in all stages of the structure determination.

DETERMINATION OF THE STRUCTURE

From the chemical composition, the mineral appears to be an equal-atom structure, conducive to solution by the direct method. Since no other structure with so high a symmetry as loeweite had previously been solved by the direct method, we were somewhat dubious about its effectiveness at the start. Notwithstanding, normalized structure factors were calculated and the distribution statistics are shown in Table 2.

The structure was then solved by applying Sayre's equation, employing an unpublished program written by R. E. Long, details of the program having been described in our previous paper (Robinson and Fang, 1969). An E map was made using the solution having the highest consistency index. All atoms, save three, were obtained from the E map and the first structure factor calculation gave an R factor of 22 percent. The remaining three atoms were located by the difference Fourier technique.

TABLE 2. EXPERIMENTAL AND THEORETICAL VALUES OF NORMALIZED STRUCTURE FACTORS

	Exp.	Centro.	Non-centro.
$\langle \lvert E \rvert \rangle$	0.763	0.798	0.886
$\langle E^2 - 1 \rangle$	0.899	0.968	0.736
$\lvert E \rvert \geq 3.0$	0.14%	0.3%	0.01%
$\lvert E \rvert \geq 2.0$	3.4%	5.0%	1.8%
$\lvert E \rvert \geq 1.0$	28.4%	32.0%	37.0%

REFINEMENT

Refinement was carried out with the BNLSI program (a modified version of ORFLS, kindly supplied by W. C. Hamilton of Brookhaven National Laboratory). Scattering curves were obtained from the International Tables for Crystallography and the atomic parameters used were obtained from the Fourier and difference Fourier maps. The refinement converged to yield an *R* factor of 13.2 percent in three cycles. At this point, an electron density map was made using all 1075 reflections. The map showed that all atoms were correctly placed with proper relative peak heights, except for that of S(3) which occupies a special position, (xxx). This peak height is only about half that of S(1) and S(2), both in general positions. Three possible explanations exist; (1) that loeweite has a S-deficient structure, with a half occupancy of the S(3) atom. This assumption leads to the formation of a discrete pyrosulphate group, centered at the corners of the unit cell, (2) that the sulphate group containing S(3) is disordered, and therefore, the S(3)O_4 tetrahedron occupies the two equivalent sites only 50 percent of the time, and (3) that the space group is actually *R*3. In the noncentrosymmetric space group, S(3) would still occupy the special position at xxx, except that there would be no requirement for another S at $(\bar{x}\bar{x}\bar{x})$. This, of course, would obviate the necessity for postulating a defect or disordered structure. Therefore, the last hypothesis was first tested by performing a least-squares refinement in space group *R*3. The result was that all pairs of atoms related by the center of symmetry gave extremely high correlation coefficients (0.95 to 0.99) and no improvement in the *R* factor was achieved. Thus, the third assumption was eliminated. Next, structure factors were recalculated with a half occupancy of S(3). The *R*-factor dropped by 3 percent, from 13 to 10 percent. The $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$ and $\frac{3}{4}$ occupancies of S(3) were also tried, but they gave higher *R* factors than that of the $\frac{1}{2}$ occupancy. Hypothesis one was rejected because of the fact that it leads to a discrete pyrosulphate group, a situation which, from chemical considerations, is highly unlikely. It also leads to an incorrect number of H_2O molecules in the cell.

Therefore, it was concluded that the structure is a disordered one with S(3) statistically divided between the two symmetry equivalent sites. Thus, our structural investigation fully confirms the composition of loeweite, as proposed by Kühn & Ritter (1958) and Schneider & Zemann (1959)

The refinement was continued and the final *R* factor is 6.2 percent. The weighting scheme and rejection test of our previous paper (Robinson and Fang, 1969) and individual isotropic temperature factors were used. An attempt to locate hydrogen positions in the structure was unsuccessful. Table 3 gives the final atomic parameters of synthetic loeweite. The atomic parameters of the natural material are in reasonably good agreement, although with higher standard deviations due to inferior data as discussed earlier, and could not be refined below 8.7 percent. The observed and calculated structure factors for synthetic loeweite are listed in Table 4 which has been deposited with the American Society for Information Science, The National Auxiliary Publications Service.[1]

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Figure 1 is a polyhedral representation of the loeweite structure, which can be described as a linkage of alternate Mg octahedra and S tetrahedra,

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[1] For detailed paper, extended version, or supplementary material, order NAPS Document No. 00748 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, N. Y. 10001; remitting $1.00 for microfiche or $3.00 for photocopies.

TABLE 3. ATOMIC COORDINATES, TEMPERATURE FACTORS AND STANDARD ERRORS[a]

Atom	No. of Positions, Wyckoff Notation	x	y	z	$B(\text{Å}^2)$
Na(1)	6*f*	0.9103 (3)	0.5064 (3)	0.3569 (3)	1.54 (6)
Na(2)	6*f*	.3121 (3)	.4552 (3)	.1928 (3)	1.79 (7)
Mg(1)	6*f*	.6890 (2)	.2068 (2)	.1214 (2)	0.55 (5)
Mg(2)	1*b*	1/2	1/2	1/2	0.49 (10)
S(1)	6*f*	.8328 (2)	.4537 (2)	.0535 (2)	0.49 (3)
S(2)	6*f*	.5647 (2)	.4112 (2)	.2335 (2)	0.49 (4)
S(3)	2*c*/2	.1195	x	x	1.04 (18)
O(1)	6*f*	.6210 (5)	.0255 (5)	.1152 (5)	1.28 (10)
O(2)	6*f*	.7861 (6)	.3817 (7)	.1269 (7)	1.51 (11)
O(3)	6*f*	.8511 (6)	.0657 (6)	.4220 (6)	1.61 (11)
O(4)	6*f*	.5255 (6)	.0269 (6)	.2721 (6)	2.27 (12)
O(5)	6*f*	.6942 (5)	.5151 (5)	.3116 (5)	1.08 (10)
O(6)	6*f*	.4874 (5)	.4095 (5)	.3135 (5)	0.90 (9)
O(7)	6*f*	.4977 (5)	.4319 (5)	.1189 (5)	0.96 (9)
O(8)	6*f*	.5734 (5)	.2841 (5)	.1942 (5)	0.89 (9)
O(9)	1*a*	0	0	0	3.75 (41)
Ow(1)	6*f*	.8120 (5)	.2764 (5)	.3161 (5)	1.22 (10)
Ow(2)	6*f*	.8350 (7)	.1634 (6)	.0701 (7)	2.57 (13)
O, Ow(1)	6*f*	.1620 (11)	.2367 (11)	.0762 (10)	6.96 (29)

[a] In parentheses

each sharing corners and emanating radially from the six corners of the Mg(2) octahedron located at the center of the cell. The linkage goes through S(2), Mg(1), S(1), Mg(1), S(2) and then back to Mg(2) in the next cell. All six chains are identical. While the Mg(2) octahedron is surrounded by six S(2) tetrahedra, the Mg(1) octahedron is shared with only four S tetrahedra, three S(1) and one S(2), for the remaining two corners are occupied by water molecules. The S(3) tetrahedron is isolated from the above linkage, located at the corner of the cell with one apex at the cell origin and the S lying on the 3-fold axis. This SO_4 group is, as mentioned in the REFINEMENT, disordered and will be further discussed below. Na(1) (not shown) has seven nearest neighbors, sharing three corners with S(1) tetrahedra (two corners to an S(1) tetrahedron, the third with another S(1) tetrahedron), three corners with S(2) tetrahedra, (the same as with S(1) tetrahedra), and the seventh with a Mg octahedron through Ow(1) which is a water molecule. Na(2) (also absent from the drawing) is likewise seven-coordinated, sharing corners with the oxygens of all three SO_4 groups. Thus, the Na atoms serve to join the six octahedron-tetrahedron chains, and the bonding shows no particular plane of weakness, giving rise to a conchoidal fracture.

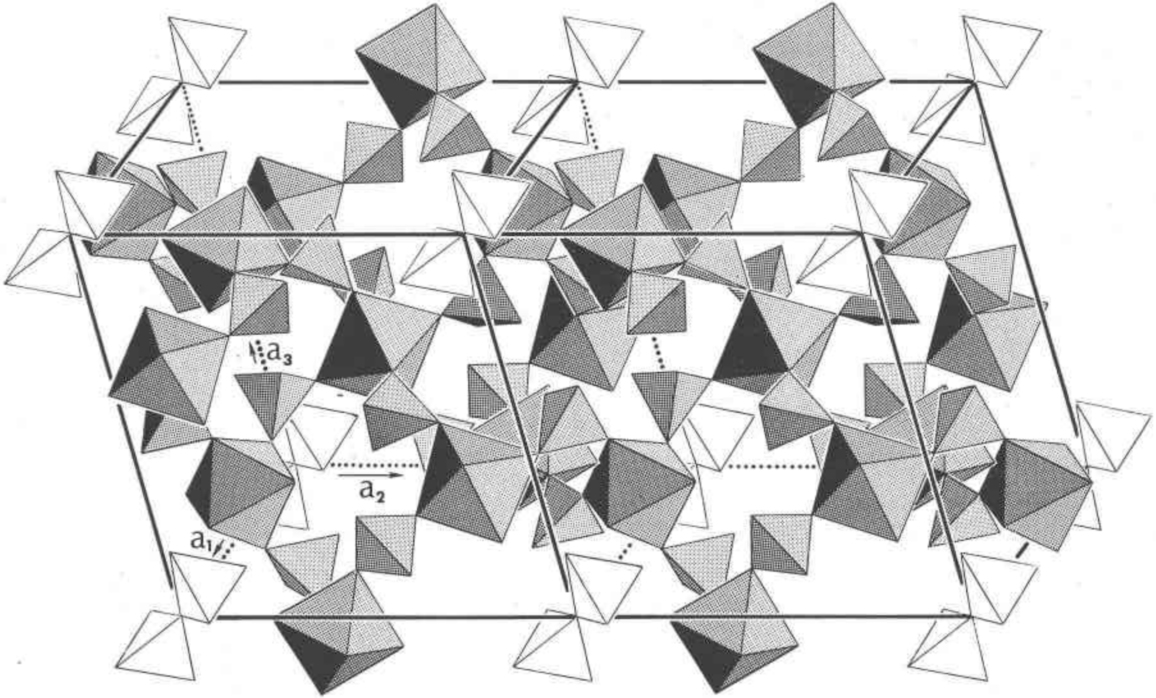

FIG. 1. Two rhombohedral unit cells of loeweite. The disordered nature of the sulfate group around the origin is depicted by the unshaded tetrahedra. Note that when an SO_4 group is present on one side of the origin, the other side is always occupied by an empty tetrahedron (actually nothing more than a triangle of water molecules and the oxygen at the origin).

Disordered sulphate group The sulphate group, composed of S(3) (at a special 2-fold position), O,Ow(1) (at a general 6-fold position) and O(9) (at the origin), all located from difference maps, would appear to form a perfect S_2O_7 group around the origin, were it not for its disordered character. During the course of refinement, the positional parameter of S(3) oscillated between narrow limits ($x=0.1190$ to 0.1198) with a higher standard error than the other atoms. Coupled with this, the B's of S(3), O,Ow(1) and O(9) were much higher than the B's of other comparable atoms. This suggested a disordered SO_4 group, namely the half occupancy of S at each of the two sites related by the center of symmetry. The disorder also affects the O,Ow(1) position, making it necessary for the O,Ow(1) to be an H_2O molecule when the S(3) atom is not present (which forms an empty tetrahedron composed of three O,Ow(1) water molecules and one O(9) oxygen), and a normal oxygen atom when the S(3) is present. Since the stoichiometry demands 15 H_2O molecules (as reported by Kühn and Ritter, 1958 and confirmed by our own T. G. A. experiment) the combination of two 6-fold water molecules, Ow(1) and Ow(2), plus the 3 waters derived from the O, Ow(1) position complete this requirement. Therefore, the S(3) sulphate group can be depicted as shifting its location from one side of the origin to the other, along the 3-fold axis of the unit cell but is never present on both sides simultaneously. This is an example of local asymmetry, although the overall structure is centrosymmetric from a statistical point of view.

TABLE 5. INTERATOMIC DISTANCES (IN Å)[a]

Tetrahedral coordination around S					
S(1) *tetrahedron*		S(2) *tetrahedron*		S(3) *tetrahedron*	
S(1)–O(1)	1.476 (6)	S(2)–O(5)	1.473 (6)	S(3)–O(9)	1.601 (2)
–O(2)	1.480 (6)	–O(6)	1.485 (6)	–O, Ow(1)	1.601 (13)
–O(3)	1.463 (6)	–O(7)	1.481 (6)	–O, Ow(1)	1.601 (13)
–O(4)	1.455 (6)	–O(8)	1.478 (6)	–O, Ow(1)	1.601 (13)
Mean	1.469		1.479		1.601
O(1)–O(2)	2.396 (8)	O(5)–O(6)	2.408 (7)	O(9)–O, Ow(1)	2.606 (12)
O(1)–O(3)	2.419 (8)	O(5)–O(7)	2.434 (8)	O(9)–O, Ow(1)	2.606 (12)
O(1)–O(4)	2.417 (9)	O(5)–O(8)	2.425 (7)	O(9)–O, Ow(1)	2.606 (12)
O(2)–O(3)	2.358 (8)	O(6)–O(7)	2.411 (8)	O, Ow(1)–O, Ow(1)	2.624 (22)
O(2)–O(4)	2.405 (8)	O(6)–O(8)	2.379 (7)	O, Ow(1)–O, Ow(1)	2.624 (22)
O(3)–O(4)	2.387 (9)	O(7)–O(8)	2.432 (7)	O, Ow(1)–O, Ow(1)	2.624 (22)
Mean	2.397	Mean	2.415	Mean	2.615

Table 5—(*continued*)

Octahedral coordination around Mg

Mg(1) *octahedron*		Mg(2) *octahedron*	
Mg(1)–Ow(1)	2.096 (6)	Mg(2)–O(6)	2.090 (5)
–O(1)	2.026 (6)	–O(6)	2.090 (5)
–O(2)	2.023 (6)	–O(6)	2.090 (5)
–O(3)	2.007 (6)	–O(6)	2.090 (5)
–O(8)	2.082 (6)	–O(6)	2.090 (5)
–Ow(2)	2.119 (8)	–O(6)	2.090 (5)
Mean	2.059	Mean	2.090
Ow(1)–O(1)	2.934 (8)	O(6)–O(6)	2.844 (9)
Ow(1)–O(2)	2.825 (8)	O(6)–O(6)	2.844 (9)
Ow(1)–O(8)	2.806 (8)	O(6)–O(6)	2.844 (9)
Ow(1)–Ow(2)	2.947 (9)	O(6)–O(6)	2.844 (9)
O(1)–O(3)	2.909 (8)	O(6)–O(6)	2.844 (9)
O(1)–O(8)	3.177 (8)	O(6)–O(6)	2.844 (9)
O(1)–Ow(2)	2.861 (9)	O(6)–O(6)	3.064 (9)
O(2)–O(3)	2.855 (8)	O(6)–O(6)	3.064 (9)
O(2)–O(8)	2.867 (8)	O(6)–O(6)	3.064 (9)
O(2)–Ow(2)	2.731 (9)	O(6)–O(6)	3.064 (9)
O(3)–O(8)	3.045 (8)	O(6)–O(6)	3.064 (9)
O(3)–Ow(2)	2.922 (9)	O(6)–O(6)	3.064 (9)
Mean	2.907	Mean	2.954
Ow(1)–O(3)	4.101	O(6)–O(6)	4.181
O(1)–O(2)	4.032	O(6)–O(6)	4.181
O(8)–Ow(2)	4.181	O(6)–O(6)	4.181
Mean	4.105	Mean	4.181

Coordination around Na

Na(1)–O(5)	2.485 (6)	Na(2)–O(5)	2.580 (6)
–Ow(1)	2.462 (6)	–O(6)	2.441 (6)
–O(7)	2.404 (6)	–O(6)	2.464 (6)
–O(7)	2.616 (6)	–O(7)	2.624 (6)
–O(2)	2.428 (6)	–O(4)	2.310 (8)
–O(3)	2.866 (6)	–O(8)	2.473 (6)
–O(4)	2.352 (6)	O, Ow(1)	2.378 (12)
Mean	2.516	Mean	2.467

[a] Standard deviations are in parentheses.

TABLE 6. SELECTED BOND ANGLES (IN DEGREES)
Standard Deviations Range from 0.1° to 0.5°

Tetrahedral angles around S

S(1) tetrahedron		*S(2) tetrahedron*		*S(3) tetrahedron*	
O(1)–S(1)–O(2)	108.3	O(5)–S(2)–O(6)	109.0	O(9)–S(3)–O, Ow(1)	108.9
O(1)– –O(3)	110.9	O(5)– –O(7)	111.0	O(5)– –O, Ow(1)	108.9
O(1)– –O(4)	111.1	O(5)– –O(7)	110.5	O(5)– –O, Ow(1)	108.9
O(2)– –O(3)	106.5	O(6)– –O(7)	108.8	O, Ow(1)– –O, Ow(1)	110.0
O(2)– –O(4)	110.1	O(6)– –O(8)	106.8	O, Ow(1)– –O, Ow(1)	110.0
O(3)– –O(4)	109.8	O(7)– –O(8)	110.5	O, Ow(1)– –O, Ow(1)	110.0
Mean	109.5	Mean	109.4	Mean	109.5

Octahedral angles around Mg

Mg(1) octahedron		*Mg(2) octahedron*	
Ow(1)–Mg–O(1)	90.7	O(6)–Mg(2)–O(6)	85.7
Ow(1)– –O(2)	86.6	O(6)–Mg(2)–O(6)	85.7
Ow(1)– –O(8)	84.4	O(6)–Mg(2)–O(6)	85.7
Ow(1)– –Ow(2)	88.7	O(6)–Mg(2)–O(6)	85.7
O(1)– –O(3)	92.3	O(6)–Mg(2)–O(6)	85.7
O(1)– –O(8)	101.3	O(6)–Mg(2)–O(6)	85.7
O(1)– –Ow(2)	87.2	O(6)–Mg(2)–O(6)	94.3
O(2)– –O(3)	90.2	O(6)–Mg(2)–O(6)	94.3
O(2)– –O(8)	88.6	O(6)–Mg(2)–O(6)	94.3
O(2)– –Ow(2)	82.5	O(6)–Mg(2)–O(6)	94.3
O(3)– –O(8)	96.2	O(6)–Mg(2)–O(6)	94.3
O(3)– –Ow(2)	90.2	O(6)–Mg(2)–O(6)	94.3
Mean	89.9	Mean	90.0
Ow(1)– –O(3)	176.7	O(6)– –O(6)	180.0
O(1)– –O(2)	169.4	O(6)– –O(6)	180.0
O(8)– –Ow(2)	169.1	O(6)– –O(6)	180.0
Mean	171.7	Mean	180.0

Bond Lengths and Angles. Table 5 gives interatomic distances and Table 6 lists selected bond angles, calculated from the final parameters of synthetic loeweite. The S(1) and S(2) tetrahedra are quite regular, the S-O distances falling within a narrow 1.455 to 1.485 Å range, with average distances of 1.469 Å and 1.479 Å respectively. No tetrahedral angles deviate more than 3° from the ideal. The S(3)-O distances are all 1.601 Å, longer by 0.1 Å than accepted S-O distances. However, this can be easily explained by the disorder of the S(3) and O,Ow(1) atoms of the group. The Mg-O distances in the Mg(1) octahedron range from 2.007 Å to 2.119 Å and average 2.059 Å. The Mg-O distances in the Mg(2) octahedron are all 2.090 Å, required by symmetry. Only slight distortions of the octahedra occur. The average distances of Na(1)-O and Na(2)-O are 2.516 Å and 2.467 Å respectively. As expected, these are slightly larger than the average value of 2.41 Å found in six-coordinated Na-O distances.

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