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# REFINEMENT OF THE CRYSTAL STRUCTURE OF A GLAUBERITE

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## Abstract

The structure of a glauberite crystal from Imperial County, California has been determined and refined from three-dimensional diffractometer intensities obtained with a double-filter technique. The model refined by successive Fourier syntheses and least-squares techniques confirms that published by Cocco *et al.* (1965) at the time when this investigation was approaching completion. Anisotropic temperature factors and interatomic distances were calculated and a final $R$ factor of 6.4% was obtained.

Glauberite is a well-known and reasonably widespread mineral in saline deposits (Palache 1951). Its composition is $CaNa_2(SO_4)_2$ and it forms characteristic thin, tabular, prismatic, and monoclinic crystals.

A prismatic fragment was cleaved from a large crystal of glauberite from Imperial County, California, for the determination of its structure. The initial lattice constants of $a=10.13$, $b=8.32$, $c=8.52\pm0.02$ Å. and $\beta=112.22\pm0.05°$ were obtained from precession and Weissenberg photographs. These constants were later refined with Britton's (unpublished) least-squares program using data obtained from a powder diffractometer pattern of glauberite containing silicon for internal standard. The final values were obtained as: $a=10.129\pm0.002$ $b=8.306\pm0.002$ $c=8.533\pm0.002$ Å, $\beta=112.19\pm0.01°$.

A larger crystal of glauberite displaying no visible impurities was selected from the same specimen for density determination using a Berman micro-balance and toluene. The average density obtained was 2.80 gm/cm$^3$, while the same calculated from the unit cell dimensions and the stoichiometric chemical formula is 2.78 gm/cm$^3$.

The pattern of systematic reflections in the single crystal photographs indicated the possible space groups of $C2/c$ and $Cc$. On the basis of morphological observations the presence of an inversion-center has been assumed and the space group of $C2/c$ has been used throughout this investigation. The centric space group was also confirmed by Cocco *et al.* (1965).

Three-dimensional intensities were collected by a scintillation counter using an equi-inclination single-crystal diffractometer, MoK$\alpha$ radiation and a pair of balanced Zr-Y filters. The intensities were corrected for Lorentz-polarization and for absorption with the aid of C. W. Burnham's (1964) computer program. No corrections for extinctions were applied. A total of 1,176 independent reflections were measured up to $\sin\theta/\lambda=0.75$.

The Minimum Function Method was adopted for the solution of the

TABLE 1. FINAL ATOMIC COORDINATES IN GLAUBERITE

| Atom | x | y | z | σ(x) | σ(y) | σ(z) |
|---|---|---|---|---|---|---|
| Ca 4e | 1/2<br>(1/2) | .4356<br>(.4360) | 1/4<br>(1/4) | 0<br>(0) | .0001<br>(.0003) | 0<br>(0) |
| Na 8f | .1371<br>(.1379) | .4445<br>(.4450) | .4394<br>(.4403) | .0002<br>(.0005) | .0003<br>(.0006) | .0003<br>(.0006) |
| S 8f | .1856<br>(.1847) | .2143<br>(.2142) | .1888<br>(.1874) | .0001<br>(.0002) | .0001<br>(.0002) | .0001<br>(.0003) |
| O(1) 8f | .1252<br>(.1259) | .0894<br>(.0878) | .0583<br>(.0589) | .0004<br>(.0009) | .0003<br>(.0010) | .0004<br>(.0010) |
| O(2) 8f | .1616<br>(.1629) | .1633<br>(.1621) | .3399<br>(.3421) | .0004<br>(.0008) | .0004<br>(.0008) | .0004<br>(.0009) |
| O(3) 8f | .3400<br>(.3382) | .2294<br>(.2257) | .2303<br>(.2265) | .0004<br>(.0008) | .0004<br>(.0008) | .0005<br>(.0009) |
| O(4) 8f | .1134<br>(.1157) | .3697<br>(.3695) | .1325<br>(.1365) | .0004<br>(.0009) | .0003<br>(.0010) | .0005<br>(.0010) |

Numbers in parentheses are corresponding data from Cocco *et al.* (1965).

three-dimensional Patterson syntheses. Correlation maps located three inversion points from peaks presumed to represent S-S, Ca-S, and Ca-Na vectors. The use of these inversion peaks lead to the construction of $M_6$ maps which revealed the location of all the atoms.

This model was subsequently refined through a set of Fourier syntheses and full-matrix least-squares refinement using Larry W. Finger's (unpublished) least squares and Fourier program and the University's Control Data Corp. 1604 computer. In the refinement of the atomic coordinates, all 1,176 reflections were included. In the last three cycles of the least-squares refinement anisotropic temperature factors were determined, and unreasonably low and occasionally negative values were obtained. However, after discarding those 42 reflections whose $\sin\theta/\lambda$ were lower than 0.25, the temperature factors refined to more reliable values. The omission of these reflections was justified by the principle that the low angle reflections are more liable to primary extinction and are affected more by change in the atomic scattering factors due to the partial ionization of the atoms than higher angle reflections.

In the above calculations, unobserved reflections were assigned a value equal to the square root of the lowest observed structure factors in the

TABLE 2. FINAL ANISOTROPIC TEMPERATURE FACTORS (STANDARD DEVIATIONS ON LOWER ROWS)

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Ca | .00080 | .00053 | .00181 | 0 | −.00010 | 0 |
| | .00015 | .00012 | .00020 | 0 | .00014 | 0 |
| Na | .00332 | .00675 | .00490 | .00031 | .00056 | −.00355 |
| | .00025 | .00026 | .00035 | .00023 | .00023 | .00028 |
| S | .00087 | .00071 | .00110 | −.00052 | .00046 | −.00014 |
| | .00012 | .00010 | .00016 | .00011 | .00011 | .00012 |
| O(1) | .00417 | .00198 | .00377 | −.00123 | .00048 | −.00065 |
| | .00044 | .00037 | .00055 | .00033 | .00040 | .00038 |
| O(2) | .00457 | .00335 | .00227 | −.00055 | .00258 | .00075 |
| | .00043 | .00034 | .00053 | .00034 | .00041 | .00039 |
| O(3) | .00403 | .00423 | .00808 | −.00177 | .00371 | .00079 |
| | .00043 | .00038 | .00067 | .00039 | .00046 | .00048 |
| O(4) | .00316 | .00120 | .00532 | .00134 | .00134 | .00188 |
| | .00041 | .00031 | .00060 | .00032 | .00042 | .00039 |

The definition of the temperature factor is:

$$\exp-[\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl]$$

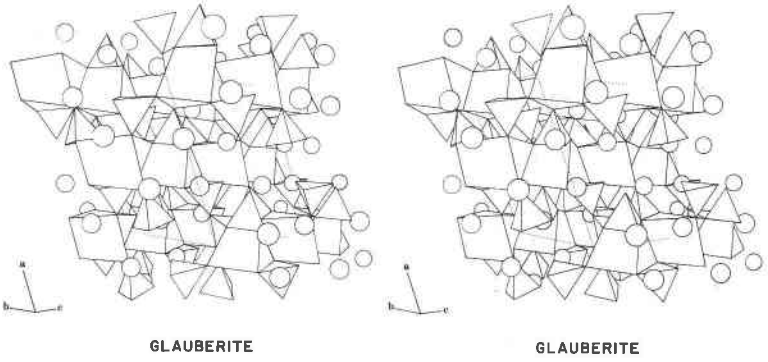

FIG. 1. Stereoscopic drawing of the crystal structure of glauberite. The white tetrahedra represent $SO_4$ and the gray, distorted cubes $CaO_8$ coordination polyhedra. The circles represent the sites of the 7-coordinated Na atoms.

TABLE 3. ELLIPSOIDS OF THERMAL VIBRATION

| Atom | *B* | r | $\mu$(r) (Å) | $\phi$(a) | $\phi$(b) | $\phi$(c) |
|---|---|---|---|---|---|---|
| Ca | 0.34 ±.02 | 1 | .043±.005 | 90° | 0° | 90° |
| | (0.55 ±.03) | 2 | .053±.006 | 136±5 | 90 | 111±5 |
| | | 3 | .091±.003 | 133±5 | 90 | 21±5 |
| Na | 1.50 ±.04 | 1 | .084±.006 | 92±6 | 54±3 | 41±2 |
| | (1.63 ±.08) | 2 | .122±.005 | 158±3 | 72±4 | 84±5 |
| | | 3 | .187±.003 | 113±3 | 139±2 | 50±2 |
| S | 0.25 ±.02 | 1 | .030±.008 | 53±5 | 37±5 | 101±9 |
| | (0.555±.03) | 2 | .057±.004 | 74±10 | 99±10 | 169±9 |
| | | 3 | .073±.004 | 42±6 | 125±5 | 89±11 |
| O(1) | 1.08 ±.06 | 1 | .068±.010 | 74±4 | 28±8 | 76±8 |
| | (0.81 ±.03) | 2 | .112±.008 | 95±8 | 66±9 | 144±8 |
| | | 3 | .154±.007 | 163±5 | 77±5 | 57±7 |
| O(2) | 0.93 ±.06 | 1 | .039±.019 | 119±4 | 111±6 | 23±6 |
| | (0.81 ±.11) | 2 | .113±.006 | 90±9 | 156±7 | 112±6 |
| | | 3 | .145±.007 | 29±4 | 101±9 | 85±5 |
| O(3) | 1.40 ±.06 | 1 | .063±.013 | 137±4 | 130±4 | 60±4 |
| | (0.42 ±.09) | 2 | .149±.006 | 53±9 | 140±4 | 116±17 |
| | | 3 | .164±.007 | 71±13 | 91±15 | 41±13 |
| O(4) | 0.94 ±.06 | 1 | .028±.023 | 76±5 | 154±4 | 75±4 |
| | (0.74 ±.11) | 2 | .125±.007 | 14±6 | 76±10 | 115±22 |
| | | 3 | .139±.007 | 92±22 | 68±6 | 30±19 |

*B* is the equivalent isotropic temperature factor; $\mu$(r) is the r.m.s. displacement along principal axis, r; the $\phi$'s are the angles between r and the crystallographic axes. *B* in parentheses is from Cocco *et al.* (1965).

corresponding ranges of sin $\theta$. Intensities were weighted in accordance with the reciprocals of the variance of the observed structure factors. The atoms were assumed to be neutral and the appropriate scattering factors of Hanson *el al.* (1964) were used in the structure factor calculations.

The terminal *R*-factor associated with the atomic coordinates and anisotropic temperature factors listed in Tables 1 and 2 was 6.4% for the reflections excluding those with sin $\theta/\lambda<0.25$. When these latter reflections were included in the calculations the reliability factor increased to 7.1%.

Ellipsoids of thermal vibration were calculated using L. W. Finger's

TABLE 4. SELECTED BOND DISTANCES IN GLAUBERITE

| Atoms | Distance (Å) | Std. dev. (Å) | Atoms | Distance (Å) | Std. dev. (Å) |
|---|---|---|---|---|---|
| S—O(1) | 1.475 | .003 | Ca—O(2)$^{2}$ | 2.429 (×2) | .003 |
| S—O(2) | 1.462 | .003 | Ca—O(3) | 2.320 (×2) | .004 |
| S—O(3) | 1.473 | .004 | O(1)—O(1)$^{3}$ | 2.778 | .007 |
| S—O(4) | 1.471 | .003 | O(1)—O(2)$^{7}$ | 2.921 | .004 |
| O(1)—O(2) | 2.370 | .005 | Na—O(1)$^{6}$ | 2.685 | .004 |
| O(1)—O(3) | 2.414 | .005 | Na—O(2) | 2.529 | .004 |
| O(1)—O(4) | 2.427 | .004 | Na—O(2)$^{4}$ | 2.367 | .004 |
| O(2)—O(3) | 2.391 | .005 | Na—O(3)$^{6}$ | 2.829 | .005 |
| O(2)—O(4) | 2.378 | .005 | Na—O(4) | 2.613 | .004 |
| O(3)—O(4) | 2.424 | .005 | Na—O(4)$^{5}$ | 2.454 | .004 |
| Ca—O(1)$^{2}$ | 2.735 (×2) | .003 | Na—O(4)$^{7}$ | 2.335 | .004 |
| Ca—O(1)$^{4}$ | 2.460 (×2) | .004 | | | |

Superscripts identify symmetrically identical atoms in different sites (Superscript 1 is omitted):

$^{1}$ x y z; $^{2}$ $\frac{1}{2}$+x $\frac{1}{2}$+y z; $^{3}$ −x −y −z;
$^{4}$ $\frac{1}{2}$−x $\frac{1}{2}$−y −z; $^{5}$ −x y $\frac{1}{2}$−z; $^{6}$ $\frac{1}{2}$−x $\frac{1}{2}$+y $\frac{1}{2}$−z;
$^{7}$ x −y $\frac{1}{2}$+z; $^{8}$ $\frac{1}{2}$+x $\frac{1}{2}$−y $\frac{1}{2}$+z.

program and are summarized in Table 3. Typical inter-atomic distances and bond angles were also calculated and are listed in Tables 4 and 5. The errors were computed by including the least-squares correlation matrix and standard deviations. In order to save space the list of the observed and calculated structure factors are omitted from this paper. However, they are available from the authors on request.

While this investigation was in progress, Cocco *et al.* (1965) have published the results of their work on the crystal structure determination of a glauberite from Chinchon (Madrid). The difference between the two models is restricted to minor deviations in the atomic coordinates. Those few atomic coordinates which differ by more than the approximate limits of the standard deviations are S, O(3), and O(4), display a maximum disagreement equal four times the standard deviations. The difference between the thermal models are more extensive, our cations have lower and anions higher temperature factors than those given by Cocco *et al.* These differences can probably be attributed to possible minor compositional variations and to differences in the techniques of the collection and estimation of intensities used in the two investigations.

This study was supported by a National Science Foundation grant.

TABLE 5. SELECTED BOND ANGLES IN GLAUBERITE

| Atoms | Angle | Std. dev. | Atom | Angle | Std. dev. |
|---|---|---|---|---|---|
| O(1)—S—O(2) | 107.6° | .2° | O(2)—Na—O(4)$^7$ | 153.7 | .4 |
| O(1)—S—O(3) | 110.0 | .2 | O(2)$^4$—Na—O(3)$^6$ | 120.7 | .2 |
| O(1)—S—O(4) | 110.9 | .2 | O(2)$^4$—Na—O(4) | 115.6 | .2 |
| O(2)—S—O(3) | 109.1 | .2 | O(2)$^4$—Na—O(4)$^5$ | 127.0 | .2 |
| O(2)—S—O(4) | 108.3 | .2 | O(2)$^4$—Na—O(4)$^7$ | 88.6 | .1 |
| O(3)—S—O(4) | 110.8 | .2 | O(3)$^6$—Na—O(4) | 71.3 | .1 |
| O(1)$^2$—Ca—O(1)$^4$ | 64.4 (×2) | .2 | O(3)$^6$—Na—O(4)$^5$ | 111.1 | .2 |
| O(1)$^2$—Ca—O(1)$^6$ | 124.3 | .2 | O(3)$^6$—Na—O(4)$^7$ | 81.9 | .1 |
| O(1)$^2$—Ca—O(1)$^8$ | 120.7 (×2) | .2 | O(4)—Na—O(4)$^5$ | 89.7 | .1 |
| O(1)$^2$—Ca—O(2)$^2$ | 54.2 (×2) | .2 | O(4)—Na—O(4)$^7$ | 150.4 | .3 |
| O(1)$^2$—Ca—O(2)$^6$ | 81.8 (×2) | .1 | O(4)$^5$—Na—O(4)$^7$ | 88.4 | .1 |
| O(1)$^2$—Ca—O(3) | 140.4 (×2) | .3 | S—O(1)—Ca$^2$ | 91.8 | .2 |
| O(1)$^2$—Ca—O(3)$^5$ | 85.4 (×2) | .1 | S—O(1)—Ca$^4$ | 140.0 | .3 |
| O(1)$^4$—Ca—O(1)$^8$ | 170.3 | 1.4 | S—O(1)—Na$^6$ | 101.2 | .2 |
| O(1)$^4$—Ca—O(2)$^2$ | 114.6 (×2) | .1 | Na$^6$—O(1)—Ca$^2$ | 113.8 | .2 |
| O(1)$^4$—Ca—O(2)$^6$ | 73.4 (×2) | .1 | Na$^6$—O(1)—Ca$^4$ | 93.9 | .1 |
| O(1)$^4$—Ca—O(3) | 78.3 (×2) | .1 | Ca$^2$—O(1)—Ca$^4$ | 115.6 | .2 |
| O(1)$^4$—Ca—O(3)$^5$ | 94.5 (×2) | .1 | S—O(2)—Ca$^2$ | 105.3 | .2 |
| O(2)$^2$—Ca—O(2)$^6$ | 77.7 | .2 | S—O(2)—Na | 95.7 | .2 |
| O(2)$^2$—Ca—O(3) | 165.2 (×2) | .6 | S—O(2)—Na$^4$ | 115.5 | .3 |
| O(2)$^2$—Ca—O(3)$^5$ | 100.5 (×2) | .1 | Ca$^2$—O(2)—Na | 133.3 | .3 |
| O(3)—Ca—O(3)$^5$ | 84.8 | .2 | Ca$^2$—O(2)—Na$^4$ | 103.4 | .1 |
| O(1)$^6$—Na—O(2) | 102.4° | .1 | Na—O(2)—Na$^4$ | 104.3 | .2 |
| O(1)$^6$—Na—O(2)$^4$ | 70.3 | .1 | S—O(3)—Ca | 136.8 | .3 |
| O(1)$^6$—Na—O(3)$^6$ | 51.8 | .2 | S—O(3)—Na$^6$ | 95.2 | .2 |
| O(1)$^6$—Na—O(4) | 81.8 | .1 | Na$^6$—O(3)—Ca | 117.7 | .2 |
| O(1)$^6$—Na—O(4)$^5$ | 162.7 | .6 | S—O(4)—Na | 92.0 | .2 |
| O(1)$^6$—Na—O(4)$^7$ | 91.7 | .1 | S—O(4)—Na$^5$ | 130.0 | .3 |
| O(2)—Na—O(2)$^4$ | 75.7 | .2 | S—O(4)—Na$^7$ | 129.7 | .3 |
| O(2)—Na—O(3)$^6$ | 124.3 | .2 | Na—O(4)—Na$^5$ | 83.4 | .1 |
| O(2)—Na—O(4) | 55.1 | .2 | Na—O(4)—Na$^7$ | 123.7 | .2 |
| O(2)—Na—O(4)$^5$ | 84.6 | .1 | Na$^5$—O(4)—Na$^7$ | 91.6 | .1 |

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