I. M. RUMANOVA and G. F. VOLODINA

1958

SovietRxiv

Abstract

Full Text

CRYSTALLOGRAPHY

I. M. RUMANOVA and G. F. VOLODINA

THE CRYSTAL STRUCTURE OF NATROCHALCITE

$NaCu_2(OH)[SO_4]_2 \cdot H_2O = Na[SO_4]_2[Cu_2, OH_2H_2O]$

(Presented by Academician N. V. Belov, 20 VI 1958)

Natrochalcite was first described in 1908 by Palache and Warren (^{1,2}). In 1939 Palache published new data on natrochalcite (^{3}), pointing out errors made in previous works. Thus, the previously reported value of the specific gravity, 2.33 g/cm^3 (^{1}) (2.83 g/cm^3 (^{2})), on more careful determination proved to be (3.49 ± 0.02 g/cm^3 (^{3})). The second error concerned the chemical formula of the mineral: with a correct chemical analysis, in (^{1}) the expression $Na_2SO_4 \cdot Cu_4(OH)_2[SO_4]_2 \cdot 2H_2O$ was erroneously given; the true formula $Na_2SO_4 \cdot Cu_4(OH)_2[SO_4]_3 \cdot 2H_2O$ is given in (^{2,3}). In a number of handbooks the formula of natrochalcite also requires correction: in (^{4,5}) the expression $NaCu(OH)SO_4 \cdot H_2O$ is given, and in (^{6,7}) the expression $NaCu(OH)[SO_4]_2 \cdot H_2O$.

The first X-ray study of natrochalcite was carried out by Richmond (^{3}), who gave the unit-cell parameters cited in all known handbooks: $a = 8.74$ Å, $b = 6.15$ Å, $c = 6.53$ Å, $\beta = 118°42.5'$. These results do not agree with the axial ratios found goniometrically, $a : b : c = 1.423 : 1 : 1.214$ at $\beta = 118°42.5'$ (^{1,2,3}); from these ratios follows a value $c = 7.46$ Å.

The objects of our study were crystals from the Chilean deposit of Chuquicamata. Rotation photographs about a, b, and c were taken with Mo radiation, as well as X-ray goniometric layer-line developments of the $(0, 1, 2)$ lines of rotation about a and b. In addition, a zero-level rotation development about b was obtained with Cu radiation. To determine the intensities of the reflections, the photographic "multiple-film" method was used; estimation was made visually by means of a blackening scale. The parameters found for the monoclinic cell, $a = 8.75$ Å, $b = 6.16$ Å, $c = 7.44$ Å, $\beta = 118°40'$, agree well with the data of optical goniometry ($^{1-3}$). The value of c proves to be sharply different from that reported by Richmond; his value, 6.53 Å, corresponds to the interplanar spacing $d_{001} = c \sin\beta$. The unit cell ($V = 351$ Å^3) contains two formula units of $NaCu_2(OH)[SO_4]_2 \cdot H_2O$.

From the extinction analysis, three monoclinic space groups are possible: $C2$, Cm, and $C2/m$. The data of optical goniometry ($^{1-3}$) indicate the presence of

Fig. 1. Weighted projection of electron density

Figure 1: Fig. 1. Weighted projection of electron density

a center of symmetry, as do measurements of the piezoelectric effect, which gave a negative result. Therefore the space group may be taken as $C2/m = C_{2h}^3$.

The structure determination was carried out by the heavy-atom method, the role of which is played by Cu. On the rotation photographs about a and b, the intensities of the odd layer lines proved to be much weaker than those of the even ones. This is naturally explained by the fact that the four Cu atoms present in the cell make no contributions to the structure factors of hkl reflections with $h = 2n + 1$ ($k = 2n + 1$). And indeed, in the cell there are two equivalent quadruples of positions at centers of symmetry (e) (1/4, 1/4, 0) and (f) (1/4, 1/4, 1/2), which (by co-

ordinates) give precisely such an effect. We placed Cu in (e) and thereby fixed the origin of the cell.

First, the projection of the electron density $\sigma(y, z)$ was constructed, the signs of the 83 nonzero F_{0kl} for which were calculated from the adopted Cu coordinates. In the synthesis, in addition to the specified Cu atoms, other maxima appeared, which were identified with S, Na, and O. All peaks, with the exception of one, proved to be located on the line $y = 0$, from which it is evident that most atoms are situated in the mirror planes of symmetry in the fourfold positions $(i)\,(x, 0, z)$. The Na atoms, according to their number in the unit cell, occupy twofold positions at centers of symmetry $(c)\,(0, 0, \frac{1}{2})$ or $(d)\,(0, \frac{1}{2}, \frac{1}{2})$. The next projection of the electron density $\sigma(x, z)$, whose signs S_{h0l} were likewise determined from the Cu coordinates, made it possible approximately to outline the x- and z-coordinates of all atoms. In the synthesis $\sigma(x, z)$, constructed from 190 nonzero F_{h0l}, the parasite peaks did not exceed 50% of the O peaks in magnitude. The location of the Na atoms at centers of symmetry (c) or (d), and of S, O_{I}, O_{II}, and OH (H_2O) in the symmetry planes (i), was confirmed; the atom O_{III},

Fig. 1. Weighted projection of the electron density

$$C_1(x, z) = \int_0^b \rho(x, y, z) \cos 2\pi y \, dy$$

(negative regions are hatched). Contours are drawn at intervals of $3e/\mathring{A}^2$.

to which a peak of double height corresponded, must occupy a general position with three parameters. Although the unit cell contains two OH groups and two H_2O groups, they are not in free twofold positions, as follows from the syntheses constructed, but jointly occupy one fourfold position (i). The arrangement of atoms along y was determined from the weighted Patterson projection

$$C_1(u,w) = \int_0^b P(u,v,w)\cos 2\pi v\, dv = \frac{1}{A}\sum_{h,l=-\infty}^{\infty} F_{h1l}^2 \cos 2\pi\left(\frac{hu}{a}+\frac{lw}{c}\right).$$

It should be especially emphasized that the heavy Cu cations make no contributions to F_{h1l}^2, and this made it possible clearly to reveal interatomic distances corresponding to the lighter atoms. The synthesis $C_1(u,w)$ confirmed the results obtained from $\sigma(x,z)$ and gave the y-coordinates (0 or $\frac{1}{2}$) of atoms in the mirror planes of symmetry. Thus, the Na atoms lie in (d), not in (c). The structural model was thereby elucidated. The missing $y_{\mathrm{O_{III}}}$ was determined from crystal-chemical considerations: since $\mathrm{O}_{\mathrm{III}a}$ and the mirror-plane-related $\mathrm{O}_{\mathrm{III}b}$ form an edge of the SO_4 tetrahedron, $\mathrm{O}_{\mathrm{III}a}$—$\mathrm{O}_{\mathrm{III}b} = 2.46$ Å, then

$$y/b = (\mathrm{O}_{\mathrm{III}a} - \mathrm{O}_{\mathrm{III}b})/2b = 0.200.$$

The next stage of the investigation was the refinement of the coordinates of the completed

model from the weighted projection $C_1(x,z) = \int_0^b \rho(x,y,z)\cos 2\pi y\, dy$, on which the Cu cations are absent and do not exert a distorting influence on the lighter atoms; on the other hand, the latter, being located in the planes $y = 0$ and $y = 1/2$, are well revealed on $C_1(x,z)$. The signs of 105 nonzero F_{h1l} were initially calculated from the coordinates of S, Na, and $\mathrm{O_{III}}$. From the constructed synthesis, the x, z-coordinates of S and $\mathrm{O_{III}}$ were refined, and the positions of $\mathrm{O_I}$, $\mathrm{O_{II}}$, and OH (H_2O), close to those obtained earlier, were also determined.

Table 1

Coordinates of the basis atoms of the structure of natrochalcite

Atoms and their number in the cell	Position and point symmetry	x/a	y/b	z/c
4 Cu	(e) $\bar{1}$	0.25	0.25	0
2 Na	(d) $2/m$	0	0.5	0.5
4 S	(i) m	0.090	0	0.300
4 $\mathrm{O_I}$	(i) m	0.192	0	0.191
4 $\mathrm{O_{II}}$	(i) m	0.207	0	0.518
8 $\mathrm{O_{III}}$	(j) 1	−0.017	0.200	0.250
4 OH (H_2O)	(i) m	0.157	0.5	0.074

Further refinement was carried out by the method of successive $C_1(x,z)$-syntheses. As a result, on the finally refined projection $C_1(x,z)$ (Fig. 1), the

Fig. 2. Projection of the structure of natrochalcite on the xz plane in coordination polyhedra

Figure 2: Fig. 2. Projection of the structure of natrochalcite on the xz plane in coordination polyhedra

few parasitic peaks do not exceed 20% in magnitude of the O peaks, whose heights differ from one another by no more than 9% (apart from 2 O_{III}). The coordinates of the basis atoms found from this projection are collected in Table 1.

The discrepancy coefficient calculated from 105 nonzero F_{h1l} is $R_{h1l} = 13.9\%$. Taking into account zero F_{h1l} up to $\sin\vartheta/\lambda = 0.8$ Å^{-1}, we obtain 19.2%. It made no sense to calculate R_{h0l} and R_{h2l}, since the main contribution to F_{h0l} and F_{h2l} is made by the heavy Cu atoms, lying at centers of symmetry and strongly lowering R.

Fig. 2. Projection of the structure of natrochalcite on the *xz* plane in coordination polyhedra.

Figure 2 shows a projection of the structure of natrochalcite onto the *xz* plane. In it, each Cu atom is located at the center of a somewhat distorted oxygen octahedron, and each S lies in an almost regular O-tetrahedron. The Cu-octahedra are linked into columns extending parallel to *b*, with two such Cu-octahedra per cell along *b*, joined by a common (O − OH) edge. Two Cu-columns, displaced relative to one another by $a/2$, are connected with each other by two individual SO_4-tetrahedra. Together, the Cu-columns and the SO_4-tetrahedra linking them form layers parallel to (001). The Na cations, situated between the layers at centers of symmetry, are in oxygen eight-vertices.

We give the most important interatomic distances in the structure of natrochalcite (oxygen atoms are denoted by Roman numerals; the subscripts *a* and *b* correspond to atoms related by the mirror plane of symmetry; a prime denotes an atom related by a base-centered center of symmetry in (*e*) or (*f*); double primes denote an atom related by a base-centered center of symmetry in (*b*) or (*d*)):

SO_4-tetrahedron: $\mathrm{S} - \mathrm{I}$ 1.47 Å, $\mathrm{S} - \mathrm{II}$ 1.44 Å, $\mathrm{S} - \mathrm{III}_a, \mathrm{III}_b$ 1.48 Å, $\mathrm{I} - \mathrm{II}$ 2.36 Å, $\mathrm{I} - \mathrm{III}_a, \mathrm{III}_b$ 2.42 Å, $\mathrm{II} - \mathrm{III}_a, \mathrm{III}_b$ 2.39 Å, $\mathrm{III}_a - \mathrm{III}_b$ 2.46 Å.

Na-polyhedron: $\mathrm{Na} - \mathrm{I}, \mathrm{I}''$ 2.57 Å, $\mathrm{Na} - \mathrm{II}, \mathrm{II}''$ 2.63 Å, $\mathrm{Na} - \mathrm{III}_a, \mathrm{III}_b, \mathrm{III}''_a, \mathrm{III}''_b$ 2.58 Å.

Cu-octahedron: $\mathrm{Cu} - \mathrm{I}, \mathrm{I}'$ 2.30 Å, $\mathrm{Cu} - \mathrm{III}, \mathrm{III}'$ 2.02 Å, $\mathrm{Cu} - \mathrm{OH}, \mathrm{OH}'$ 1.94 Å, $\mathrm{I} - \mathrm{III}$ 3.01 Å, $\mathrm{I} - \mathrm{III}'$ 3.12 Å, $\mathrm{I} - \mathrm{OH}$ 3.17 Å, $\mathrm{I} - \mathrm{OH}'$ 2.85 Å, $\mathrm{OH} - \mathrm{III}$ 2.78 Å, $\mathrm{OH}' - \mathrm{III}$ 2.80 Å.

$\mathrm{OH}(\mathrm{H_2O}) - \mathrm{OH}''(\mathrm{H_2O}'')$ 2.42 Å.

The Cu–O and S–O distances agree well with those found in other structures. The increase in the Na–O distances in comparison with the standard values and with the distances in astrakhanite (8) is apparently associated with the eightfold (as against sixfold in astrakhanite) coordination of Na in natrochalcite. Noteworthy is the distance between the $OH(H_2O)$ groups related by the center of symmetry in (b), $OH(H_2O)-OH''(H_2O'')$ (in Fig. 2 it is indicated by arrows). Its value, 2.42 Å, indicates the presence of a hydrogen bond (9). Apparently, one of the positions is occupied by an OH group and the other by H_2O, with a hydrogen bond of the type HO ... HOH between them. Since both positions in the structure are equivalent, the arrangement of OH and H_2O in it may be regarded as disordered in accordance with the space group $C2/m$, the H atom being distributed between two equivalent positions on the line $OH - OH''$.

Natrochalcite is characterized by perfect cleavage along (001) (1,2). This property is well explained by the structure found. The rupture plane passes through the Na eight-vertices parallel to the layers of Cu-octahedra and SO_4-tetrahedra. The weak strength of the bonds within the Na-polyhedra is a consequence of the small charge of the Na cation and the large Na–O distances (2.57–2.64 Å).

The positive optical sign of natrochalcite ($2V = 36°52'$) (1,2) is in full agreement with chains of heavy Cu atoms parallel to b.

The authors express their deep gratitude to Academician N. V. Belov for valuable comments.

Institute of Crystallography
Academy of Sciences of the USSR

Received
17 VI 1958

REFERENCES

1. C. Palache, C. H. Warren, *Am. J. Sci.*, **26**, 342 (1908).
2. C. Palache, C. H. Warren, *Zs. Krist.*, **45**, 534 (1908).
3. C. Palache, *Am. J. Sci.*, **237**, 447 (1939).
4. R. W. G. Wyckoff, *Crystal Structures*, **2**, 1951.
5. A. G. Betekhtin, *Mineralogy*, 1950, p. 577.
6. *Strukturbericht*, **7**, 137 (1943).
7. J. D. H. Donnay, W. Nowacki, *Crystal Data*, 1954, p. 214.

8. I. M. Rumanova, DAN, **118**, No. 1, 84 (1958).
9. B. K. Weinstein, *Crystallography*, **3**, No. 3, 293 (1958).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.