THE CRYSTAL STRUCTURE OF ASTRACHANITE

1958

SovietRxiv

Abstract

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CRYSTALLOGRAPHY

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THE CRYSTAL STRUCTURE OF ASTRACHANITE

(Presented by Academician N. V. Belov, 11 VII 1957)

Astrachanite $Na_2Mg(SO_4)_2 \cdot 4H_2O$ was first investigated radiographically in 1940 by Lauro ([1]), who obtained the parameters of the monoclinic cell ($a = 11.04$ Å, $b = 8.15$ Å, $c = 5.49$ Å, $\beta = 100^\circ 39'$) and determined the space group of the crystal.

The object of our study was colorless transparent grains, the orientation of which was achieved with the aid of Laue photographs. On Mo radiation, rotation photographs about a, b, and c were obtained, and then goniometric recordings of the zero and also the layer $(1, 2)$ rotation lines about b and c. In sufficient agreement with the previous data, $a = 11.03$ Å, $b = 8.14$ Å, $c = 5.49$ Å, $\beta = 100^\circ 40'$, with two molecules of $Na_2Mg(SO_4)_2 \cdot 4H_2O$ in the cell. The space group is $C_{2h}^5 = P2_1/a$, with a center of symmetry that is beyond doubt on the basis of the radiogoniometric data alone.

First of all we turned to the projection of the electron density xy, as corresponding to the shortest period c. Having 150 reflections of the $hk0$ zone, we were able to apply the statistical method ([2]) for determining the signs. The reference group of signs, which included 30% of all $hk0$ reflections with the largest unit amplitudes, was found by comparing the signs of reflections and by constructing, from the compared pairs, chains of signs ([3–5]). Assigning in the chains two signs fixing the origin of the cell at one of the four centers of symmetry of the projection xy, and using the relation
$S_H = S(S_{K_i} \cdot S_{H+K_i})$, we found the signs of all 45 reflections of the reference group. The signs of the remaining reflections were determined from the reference ones by means of the same relation. Of the 150 S_{hk0}, 17 S_{hk0} remained undetermined.

From the 133 F_{hk0} supplied with signs, a projection of the structure was constructed, from which, in the first approximation, the coordinates x and y of all atoms were determined, with the exception of O_4, which in this projection overlaps the S atom. In Fig. 1 a Fourier synthesis is given, with clearly emerging peaks of the atoms and with very insignificant parasitic peaks. To establish the coordinates z, and for more exact fixation of the position of the overlapping atoms S and O_4, 249 hkl reflections were used, the signs of which were found by the same direct methods; both S_{hk0} and S_{hk2} were used. As a result, the signs

Fig. 1. Projection of electron density onto the xy plane

Figure 1: Fig. 1. Projection of electron density onto the xy plane

of 21 reflections could not be determined. From the 228 F_{hkl}, syntheses were constructed

$$\int_0^1 \rho(x,\ y,\ z)\sin 2\pi z\,dz, \qquad \int_0^1 \rho(x,\ y,\ z)\cos 2\pi z\,dz,$$

$$\int_0^1 \rho(x,\ y,\ z)(\cos 2\pi z + \sin 2\pi z)\,dz, \qquad \int_0^1 \rho(x,\ y,\ z)(\cos 2\pi z - \sin 2\pi z)\,dz.$$

From these syntheses all the z-coordinates of the atoms were approximately determined, and, in addition, on these syntheses the atom O_4, merged in the xy projection with S, was revealed, which at the same time made it possible to refine the x- and

y-coordinates of both atoms. All the x and y coordinates of the atoms from the complete and weighted projections proved to be very close; the final values of x and y were adopted on the basis of both projections. The z coordinates were refined from the xz projection and from the set of syntheses

Fig. 1. Projection of electron density onto the xy plane

$$\int_0^1 \rho(x,y,z)\sin 2\pi y\,dy, \qquad \int_0^1 \rho(x,y,z)\cos 2\pi y\,dy, \qquad \int_0^1 \rho(x,y,z)(\cos 2\pi y{+}\sin 2\pi y)\,dy$$

and

$$\int_0^1 \rho(x,y,z)(\cos 2\pi y - \sin 2\pi y)\,dy;$$

in the latter, the peaks of atoms overlapping in the xz projection are resolved (Na with $(H_2O)_I$, O_3 with $(H_2O)_{II}$).

The signs S_{h0l} and S_{h1l} for these syntheses were also found statistically, but the reference group of signs in the case of the $h0l$ zone was determined using the Harker–Kasper inequality method ([6]). In the case of the projection of the astrakhanite structure onto the xy plane, this method could not be used because of the absence of a sufficient number of large unit structural amplitudes U_{hk0}. However, for the xz projection the number

Fig. 2. Projection of the structure onto the xy plane in coordination polyhedra. The numbers next to the cations correspond to the values $100\,z/c$.

Figure 2: Fig. 2. Projection of the structure onto the xy plane in coordination polyhedra. The numbers next to the cations correspond to the values $100\,z/c$.

large U_{h0l} proved sufficient because, for the space group $C_{2h}^5 = P2_1/a$, the relation $\sigma_{h0l}^2 = 2\sigma_{hk0}^2$ is valid if the atoms do not overlap in the projections (7) (σ is the root-mean-square value of the unit structural amplitudes).

Table 1

Coordinates of the basis atoms of the astrakhanite structure

Atoms	Number of atoms in the cell	$\frac{x}{a}\cdot 100$	$\frac{y}{b}\cdot 100$	$\frac{z}{c}\cdot 100$
S	4	13.7	29.0	37.0
Mg	2	0	0	0
Na	4	36.1	7.0	14.0
O_1	4	26.8	27.8	33.4
O_2	4	6.9	13.5	30.7
O_3	4	7.6	43.0	20.9
O_4	4	13.1	33.2	63.3
$(H_2O)_I$	4	15.8	3.5	86.9
$(H_2O)_{II}$	4	41.9	28.8	83.4

The finally selected coordinates of the basis atoms are collected in Table 1. Only the Mg atoms at the centers of symmetry (000) and $\left(\frac{1}{2}\,\frac{1}{2}\,0\right)$ have no parameters. All the others are in general (fourfold) positions, and the entire structure is characterized by 24 parameters. Figure 2 shows the projection of the astrakhanite structure onto the xy plane, with the oxygen tetrahedra around S, the nearly regular small Mg octahedra, and the large, but somewhat deformed, Na octahedra singled out.

Each S atom is located at the center of a regular tetrahedron of oxygen atoms; the S–O distances do not go beyond the narrow limits 1.48-1.52 Å, and the edges of the tetrahedra (O–O) lie within 2.44-2.47 Å. The octahedra around Mg are formed by four H_2O molecules and two O atoms; the Mg–H_2O distances are 2.03-2.08 Å, Mg–O 2.03 Å; the edges of the Mg octahedron lie within 2.83-2.98 Å. Each Na atom is in an octahedron of four O and two H_2O, with Na–O distances from 2.30 to 2.44 Å, and Na–H_2O 2.48 and 2.60 Å.

Fig. 2. Projection of the structure onto the xy plane in coordination polyhedra. The numbers next to the cations correspond to the values $100\,z/c$.

The structure of astrakhanite may be described as composed of infinite chains of octahedra of two types. The chains are parallel to the a axis, and in them single Mg-octahedra alternate with paired Na-octahedra. The latter pair has a common (O–O) edge; with the Mg-octahedron from the same chain each Na-octahedron is connected by a common H_2O vertex. The separate chains are joined to one another in their plane through common H_2O vertices of Mg- and Na-octahedra and thus form not very dense nets of octahedra. These nets, more or less flat, parallel to the xy plane and along the z axis, are connected with one another by SO_4 tetrahedra.

Each H_2O molecule is part of the coordination polyhedra, being bonded in this case to one Mg atom and one Na atom; the bond angle Mg—$(H_2O)_I$—Na is 121°; Mg—$(H_2O)_{II}$—Na is 115°. The H_2O molecule is surrounded by the nearest 6 O atoms and 2 neighboring H_2O, so that the tetrahedral character of the environment of the H_2O particle is not expressed, and one may speak of a joint, more or less dense packing of O atoms and H_2O particles, in the voids of which S, Mg, and Na are located.

The nets of octahedra determine the optically negative character of astrakhanite; the low density of these nets and the well-pronounced chains reduce this negative character to a minimum ($N_g - N_p = 0.004$).

I take this opportunity to express my deep gratitude to Academician N. V. Belov for his attention to the work, and also to N. A. Kushnarev, who performed a number of calculations.

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Received
8 VII 1957

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