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THE ORIGIN OF SATELLITES IN THE RECIPROCAL LATTICE OF CYMRITE

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It was found that cymrite has an orthorhombic unit cell (a = 5.33, b = 36.65, and c = 7.65 Å), and that its space group is $P22_12$. The presence of additional reflections in the x-ray patterns of cymrite, which causes the existence of superperiod along the b axis, is related to regular displacements of atoms from their average positions in direction of the x axis, with a repeat period along the y axis. The method of successive approximations was used to obtain more accurate values of the x and y coordinates of the atoms in the structure; R = 18.5%.

It was shown in [1] that the crystalline structure of cymrite can be regarded as a hydrated form of α-celsian [2, 3]. However, such a structural model should be considered as rather rudimentary and ideal, since some of its details, in particular the Ba–O distance, largely contradict the available crystallochemical data. This may be explained by the fact that in interpreting the cymrite structure, only reflections of the average structure were used; this structure is characterized by hexagonal symmetry and the following parameters of the orthohexagonal setting: a = 5.335, b = 9.190, and c = 7.677 Å. Furthermore, additional reflections were observed in the x-ray patterns of all cymrite specimens investigated [1, 4, 5], indicating the existence of a superperiod along the b axis (b = 4b' = 36.76 Å). These additional reflections may be considered as satellites, since they are observed only near the fundamental reflections.

It is evident that to establish the true cymrite structure, we have to elucidate the nature of those distortions of the ideal lattice which are responsible for the appearance of the satellites in the x-ray patterns of cymrite.

We investigated these satellites in the x-ray patterns of cymrite from the Baikal region [1] and Alaska [6] (Mo radiation, RKOP, RKV, and KFOR cameras).

Investigations of single crystal cymrite from Alaska showed that this mineral has orthorhombic symmetry with the following cell parameters: a = 5.33, b = 36.76, and c = 7.65 Å. The geometry of the reflection positions in the x-ray patterns indicated that each h and k reflection with k = 4n (n integral) is accompanied by satellites with indices h, k ± 1 and sometimes h, k ± 2 (Fig. 1). It should be noted that the satellites are absent between (0k0) reflections, which indicates extinction of the (0k0) reflections with k = 2n ± 1. The reflections with h = 2n ± 1 are absent between the (h0l) reflections. However, these extinctions are misleading, since they are due to the pseudohexagonal character of the structure. Thus the space group may be considered $P22_12$.

A comparison of the x-ray patterns of cymrite from Alaska and from the Baikal region showed that all single crystals from the Baikal region are in fact triplets whose individuals have identical dimensions and are oriented in the basal plane at multiples of 60 or 120°. It is quite natural that the symmetry of these crystals is "raised" to hexagonal, and the cell parameters are as follows: $a = 8a'$ = 42.68 Å; b = $a\sqrt{3}$ = 73.836 Å. This tripling effect was also noted in Alaskan cymrite single crystals; however, for these specimens the dimensions of the individuals composing the triplets were greatly divergent. Therefore, we did not observe the hexagonal symmetry in the satellite-intensity distribution for the Alaskan specimens; this fact allowed us to demonstrate

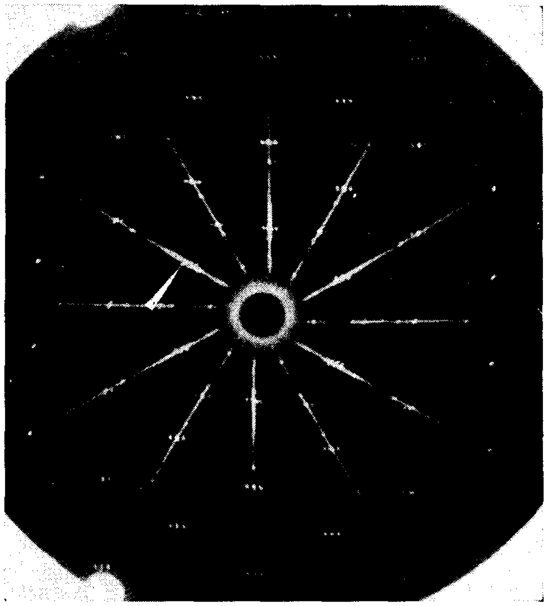

Fig. 1. X-ray pattern of cymrite, (hk0) reflections (KFOR camera).

the tripling effect in cymrite and to determine the true symmetry of this mineral. From the Alaskan cymrite specimens we succeeded in cleaving only one crystal with dimensions of several tenths of a millimeter and totally free of tripling.

In connection with the above, in further investigations we used only experimental data which were obtained from this Alaskan cymrite crystal. First of all, we tried to determine the structure directly by the usual methods of structural analysis. Thus, we constructed two projections of the Patterson function using the independent reflections of the (hk0) type (51 reflections of the average structure and 64 satellites): in calculating one of these projections we used F_f^2 and F_s^2 as the coefficients of the Fourier series, and for the other F_s^2 and $(F_f^2 - F_f^2{}_{cal})$. Here F_s^2 and F_f^2 are the experimental values of the squares of the structure factors for satellites and fundamental reflections, respectively, and $F_f^2{}_{cal}$ are the squares of the structural amplitudes calculated for the average structure. The characteristic feature of the syntheses obtained (see Fig. 2) consists in the fact that the peaks corresponding to the interatomic Ba–Ba distance are of decreasing height and are smeared out along the x axis with increasing y. Initially, it was assumed that the decrease in the Ba–Ba peak height is related to isomorphous replacement of Ba by $(H_3O)^+$ in the structure. This assumption appeared quite natural, since there is presently both theoretical support and experimental evidence for the existence of distortions of the average structure related to periodically varying distances between atomic planes and/or to the periodically changing scattering power (structural amplitude) of these planes [7, 8]. Thus by calculating F_{cal} we checked the different structural models in which the parameters of neighboring cells vary due to the regular distribution of Si and Al in the tetrahedra, and in which variations in the structure factor are caused by the replacement of Ba^{2+} by $(H_3O)^+$. However, testing the different variants of such models did not lead to any positive results.

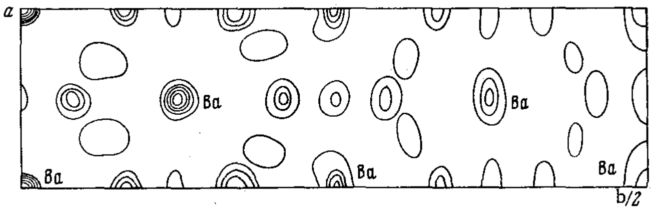

Fig. 2. Projection of the Patterson function along the z axis.

If we assume that the smearing of the peaks and the decrease in their height in the Patterson syntheses are related to regular displacements of atoms from their average positions along the x axis with a period along the y axis, we can then explain the essential features of the diffraction patterns for cymrite and obtain satisfactory agreement between the calculated and experimental data.

We consider a crystal with a certain unit cell (a, b, c) in which the values of the x coordinates of the atoms are shifted from the average positions with a period (λ) along the b axis. Under these conditions the x and y coordinates of an arbitrary R-th atom can be written in the following form:

$$x_R = n_1 a + x_j + \Delta_j \sin 2\pi y_R / \lambda, \qquad y_R = n_2 b + y_j,$$

where n_1 and n_2 are the coordinates of the origin of the n-th cell (containing the atom under consideration) with respect to the origin of the nondistorted lattice; x_j and y_j are the coordinates of the atom with respect to the origin of the nondistorted unit cell; Δ_j is the displacement amplitude of atoms of the j-th type. In order to simplify matters, we suppose that all atoms with $y = 0$ have x coordinates which coincide for the distorted and average structures. In other words, the wavelike distortions of the structure are coherent for all types of atoms and differ only in the amplitude of their deviation from the average positions. In reciprocal space the reflection amplitude is given as a function of the h, k coordinates in the following form:

$$\left.\begin{aligned} A(hk) &= \sum_{R} f_R \exp\left[2\pi i\left(h\frac{x_R}{a}+k\frac{y_R}{b}\right)\right] \\ &= \sum_{j}\sum_{n} f_j \exp\left\{2\pi i\left[hn_1+kn_2+\frac{hx_j}{a}\right.\right. \\ &\quad \left.\left.+\frac{h\Delta_j}{a}\sin\frac{2\pi}{\lambda}(n_2b+y_j)+k\frac{y_j}{b}\right]\right\} \end{aligned}\right\} \quad (1)$$

If we assume Δ_j to be small compared to a, we can replace the exponential whose index contains $\sin 2\pi y_R/\lambda$ by the first two terms of the power series into which it may be decomposed, and represent it by the half-sum of the corresponding exponential functions. Under these conditions we obtain

$$\left.\begin{aligned} A(hk) &= \sum_{n}\sum_{j} f_j \exp\left[2\pi i\left(hn_1+kn_2+h\frac{x_j}{a}+k\frac{y_j}{b}\right)\right] \\ &\pm\frac{\pi h}{a}\sum_{n}\sum_{j} f_j\Delta_j \exp\left\{2\pi i\left[hn_1+\left(k\pm\frac{b}{\lambda}\right)n_2+\frac{hx_j}{a}\right.\right. \\ &\left.\left.+\left(k\pm\frac{b}{\lambda}\right)\frac{y_j}{b}\right]\right\} = F(hk)\sum_{n}\exp[2\pi i(hn_1+kn_2)] \\ &\pm\frac{\pi h}{a}F\left(h,k\pm\frac{b}{\lambda}\right)\sum_{n}\exp\left\{2\pi i\left[hn_1+\left(k\pm\frac{b}{\lambda}\right)n_2\right]\right\}. \end{aligned}\right\} (2)$$

In the first term of the above equation the amplitude maximum is proportional to F for h and k integrals. Analogously, the integrals h, k ± b/λ correspond to the maximum values of the other two terms.

Thus in the reciprocal cymrite lattice two additional points arise in the neighborhood of each point having the coordinates h, k: their distance from the latter point is ± b/λ, and they correspond to the satellites. It should be noted that in spite of their distribution along the y axis, the "weight" of these satellites is proportional to h^2.

To evaluate the order of magnitude of Δ, we assume that in the model considered here a displacement of the cells along the x axis occurs while the relative geometric arrangement of the atoms is maintained within the limits of each cell. Then expression (2) can be rewritten in the following form:

$$A(h,k) = F(hk)\left\{\sum_{n}\exp[2\pi i(hn_1+kn_2)] \pm\frac{\pi h\Delta}{a}\sum_{n}\exp 2\pi i[hn_1+(k\pm b/\lambda)n_2]\right\}$$

and from the following relationship:

$$F_s^{\,2} : F_o^{\,2} = (\pi h\Delta/a)^2 \qquad (3)$$

TABLE 1. Experimental and Calculated Values F(hk0).

$hk0$	F_{exp}	F_{cal}	$hk0$	F_{exp}	F_{cal}	$hk0$	E_{exp}	F_{cal}	$hk0$	F_{exp}	F_{cal}
0.8.0	121	132	2.56.0	55	67	4.48.0	174	152	8.2.0	43	71
0.16.0	475	389	3.3.0	85	76	4.49.0	31	--77	8.15.0	44	47
0.24.0	610	557	3.4.0	91	80	5.3.0	90	45	8.23.0	99	92
0.32.0	216	188	3.5.0	59	--23	5.4.0	72	69	8.24.0	20	48
0.40.0	150	144	3.11.0	206	183	5.5.0	56	--58	8.25.0	25	--80
0.48.0	274	256	3.12.0	505	471	5.10.0	23	77	8.47.0	75	47
0.56.0	62	98	3.13.0	206	--208	5.11.0	222	211	8.48.0	19	28
0.64.0	43	43	3.19.0	26	70	5.12.0	246	178	8.49.0	44	--58
1.3.0	30	3	3.20.0	50	37	5.13.0	224	--181			
1.4.0	124	125	3.21.0	71	--60	5.14.0	23	66			
1.11.0	126	154	3.27.0	45	5	5.19.0	35	42			
1.12.0	554	653	3.28.0	105	121	5.20.0	71	81			
1.13.0	136	--145	3.35.0	113	134	5.21.0	71	--76			
1.20.0	154	142	3.36.0	255	213	5.35.0	139	123			
1.27.0	20	60	3.37.0	116	--125	5.36.0	146	156			
1.23.0	88	64	3.44.0	42	90	5.37.0	116	--128			
1.29.0	40	--43	3.52.0	33	32	6.0.0	197	189			
1.36.0	202	360	3.60.0	93	121	6.1.0	197	--158			
1.44.0	65	68	4.0.0	520	435	6.7.0	56	68			
1.52.0	59	68	4.1.0	240	--288	6.8.0	45	68			
1.60.0	161	136	4.2.0	49	67	6.9.0	81	--86			
2.0.0	520	678	4.3.0	17	--35	6.23.0	183	152			
2.1.0	125	--130	4.8.0	109	141	6.24.0	155	127			
2.7.0	108	101	4.15.0	117	89	6.25.0	159	--155			
2.8.0	389	380	4.16.0	162	156	6.42.0	45	--78			
2.9.0	108	--99	4.17.0	44	--56	6.47.0	62	82			
2.16.0	133	142	4.23.0	208	147	6.48.0	32	70			
2.23.0	136	162	4.24.0	298	296	7.3.0	49	67			
2.24.0	573	555	4.25.0	200	--157	7.10.0	36	65			
2.25.0	143	--140	4.31.0	37	58	7.11.0	144	134			
2.32.0	119	126	4.32.0	98	105	7.12.0	81	65			
2.40.0	127	112	4.33.0	18	--55	7.13.0	145	--153			
2.47.0	58	59	4.39.0	26	25	7.14.0	36	72			
2.48.0	243	235	4.40.0	26	83	7.36.0	40	92			
2.49.0	59	--66	4.47.0	86	82	8.1.0	142	--113			

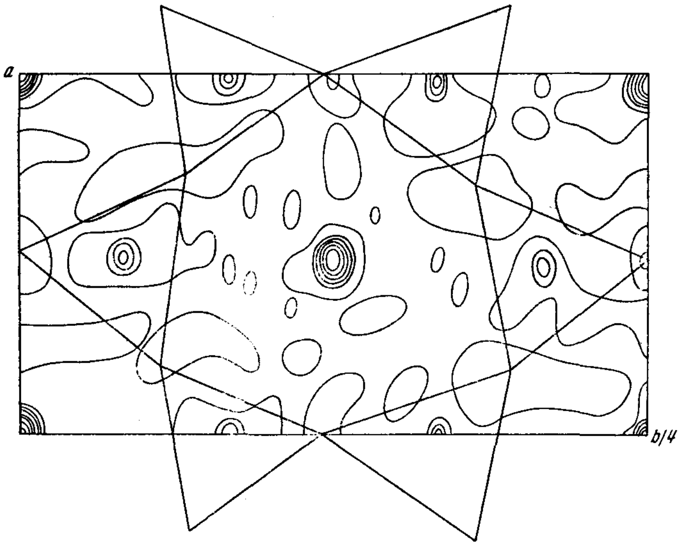

Fig. 3. Electron-density projection of the cymrite structure along the z axis.

TABLE 2. Atomic x and y Coordinates in the Cymrite Structure.

Atom	x	y	Atom	x	y
Ba_1	0	0	O_5	0,500	0
Ba_2	0.530	0.125	O_6	0,282	0,067
Ba_3	0,033	0,250	O_7	0.792	0.060
Si_1	0.022	0,083	O_8	0.797	0.193
Si_2	0.035	0.165	O_9	0,295	0.181
Si_3	0.522	0,042	O_{10}	0,500	0.250
Si_4	0.540	0.210	O_{11}	0,008	0.123
O_1	0,022	0.083	$(H_2O)_1$	0	0
O_2	0,035	0.165	$(H_2O)_2$	0,530	0.125
O_3	0.522	0,042	$(H_2O)_3$	0,033	0.250
O_4	0.540	0.210			

we can readily determine the magnitude of Δ/a.

When Δ/a is not too small, the exponential coefficient in Eq. (1) may be decomposed into a series by use of the Bessel functions. In this case each point of the reciprocal lattice along the b axis is accompanied by a series of satellites at the following distances $\pm b/\lambda$, $\pm 2b/\lambda$ ...

An analysis shows that the regular intensity distribution of the satellites in the cymrite x-ray patterns is in good agreement with the ratios obtained.

It is seen from Table 1 that with rare exceptions the ratio (F_s^2/F_f^2) is proportional to h^2. In particular, the satellites are absent between the (0k) reflections. Furthermore, several reflections have satellites at distances of $\pm 2b/\lambda$ and $\pm 3b/\lambda$.

In accordance with the above results we studied a structural model in which the Ba atoms are regularly displaced along the x axis with a period equal to 4b'. The displacement amplitude Δ, determined from Eq. (3), was found to be close to the values which were obtained from the Patterson syntheses for the Ba atoms. Figure 3 shows the projection of the electron density $\rho(x, y)$, clearly characterized by atom displacements from the average positions. It is seen from this figure that the S–O ring is distorted with respect to the hexagonal form. The atomic coordinates (Table 2) were more accurately defined by subsequent syntheses of $\rho(x,y)$. The values F_{cal} calculated according to the data of this projection are in satisfactory agreement with the experimental values F_{exp} (see Table 1).

When establishing a common scale for F_{exp} and F_{cal}, it appeared initially that the intensities of the 10 strongest reflections were reduced with respect to the others. This may be explained by the fact that in the first stages of the analysis, we used overexposed films to obtain full visualization: the blackening of the strongest reflections was therefore no longer proportional to the logarithm of the intensity. Thus it was convenient to use the intensities from two x-ray patterns with different exposure. The following values were obtained: $R = 18.5\%$; $B = -1.0$ Å^2; $\sin \nu/\lambda < 0.9$.

The data obtained do not allow us to establish definitely the nature of the atomic displacements. This phenomenon may be due to the orderly arrangement of the Si and Al cations. This assumption is supported by the fact that satellites are absent from the x-ray patterns of annealed cymrite. It is evident that the order in the distribution of Si and Al is destroyed by heat treatment, a conclusion supported by the establishment of this phenomenon for the case of feldspar. At the present time we are refining the structure from three-dimensional data.

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