X-ray examination of aramayoite.

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AN attempt was made to determine the true symmetry of the cleavage flakes of aramayoite by means of the Laue photographic method. Since X-ray diffraction takes place within the crystal, the lack of well-developed faces other than main cleavage faces was no disadvantage. One feature, however, which did prove a difficulty, was the pliability of thin cleavage flakes referred to by Dr. Spencer.[1] It was essential that the whole of the main cleavage face upon which the X-ray beam was incident should be strictly perpendicular to that beam. In order to ensure this, only those flakes were used which gave a single optical reflection, and two distinct methods of setting were resorted to. In the first case the slit (circular aperture) was used vertically; the flat end of the slit system was ground truly perpendicular to the slit itself and was thus horizontal. The crystal flake was laid on a glass coverslip so as to cover the upper end of the slit and it was then assumed that the cleavage face should be perpendicular to the slit and therefore to the X-ray beam (fig. 1 *b*). The Laue photograph obtained on a plate supported parallel to the flat end of the slit system showed no symmetry whatever. A second method of setting was then employed; a fine pencil of light was sent down the slit (used horizontally) and made to impinge on a crystal flake at about 6 mm. from the opposite end. The flake was adjusted until the reflected beam returned exactly along the path of the incident beam (fig. 1 *a*). In that position the flake was perpendicular to the beam of light and therefore to the X-ray beam which was afterwards substituted. The photographs obtained from this setting with various specimens were entirely similar to those previously obtained by means of the first method. By tilting the flake a photograph showing pseudo-tetragonal symmetry could be obtained, but a flake properly set with the main cleavage face normal to the beam gave a completely asymmetric picture (fig. 2). The inference was, therefore,

[1] L. J. Spencer, Aramayoite, a new mineral, from Bolivia. This vol., p. 156.

that perpendicular to the main cleavage plane there were no elements of symmetry whatever. A Laue photograph taken in that direction could, of course, give no information as to the existence of a symmetry plane parallel to the main cleavage itself.

In view of the fact that so far the examination had revealed none of the symmetry suspected by Dr. Spencer, the investigation was extended still farther. A quantity of the mineral was ground as finely as possible in an agate mortar, and a photograph was taken using the

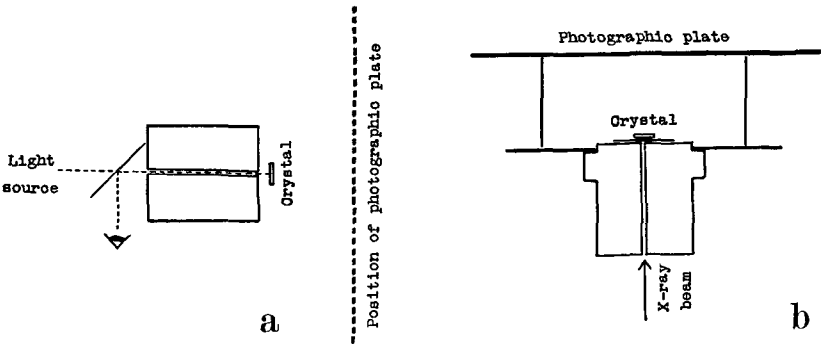

FIG. 1. Arrangement of apparatus for X-ray Laue photographs.
(*a*) Slit horizontal; (*b*) slit vertical.

resulting powder. In order to avoid orientation of the powder, the latter was mixed with a little water and a strip of paper was dipped into the mixture. When the water had dried off, the paper was covered with a fine layer of the powder and the subsequent photographs showed clear but broad lines corresponding to the following mean spacings (Cu radiation).

Spacing.	Intensity.	Spacing.	Intensity.
3·89	very weak	2·06	mod. weak
3·43	moderate	1·94	mod. weak
3·20	moderate	1·76	weak
2·83	strong	1·71	weak

These lines are not consistent with a tetragonal cell of the relative dimensions $a : c = 1 : 1{\cdot}44$, nor do they, in fact, correspond very closely with a tetragonal cell of any axial ratio whatever.[1]

[1] Cf. A. W. Hull and W. P. Davey, Physical Rev., 1921, vol. 17, p. 549.

Finally, the mineral was examined on the Bragg ionization spectrometer, and the spacings of and angles between a considerable number of planes were measured. These results showed beyond doubt that the mineral is triclinic and explained some of the inconsistencies mentioned by Dr. Spencer. The reflections from the main cleavage face were comparatively small, the first order observed being less than one-third as intense as those from some other planes in the crystal. This is unusual,

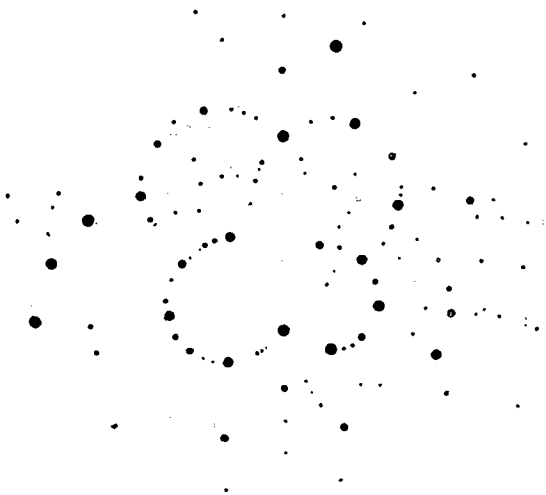

FIG. 2. Laue diagram of aramayoite. X-ray beam perpendicular to (001); (110) vertical.

since in such crystals as calcite and mica the main cleavage face gives quite the most intense reflection of all. Reflections from planes in four zones were measured, each of the zone-axes lying in the cleavage plane (001). Thus although accurate measurements could be obtained of the angles between the basal plane and the various pyramid and prism faces, no direct measurements of angles between side planes were made. Knowing the spacings of these side planes, however, the angles between them could be calculated fairly accurately from the formula

$$\left(\frac{1}{d_{hk0}}\right)^2 \quad \left(\frac{h}{d_{100}}\right)^2 + \left(\frac{k}{d_{010}}\right)^2 - \frac{2hk \cdot \cos(100:010)}{d_{100} \cdot d_{010}}.$$

The experimental results lead to a minimum unit cell of the dimensions

$$a = 5{\cdot}672 \text{ Å.U.} \qquad \alpha = 86° 55'$$
$$b = 5{\cdot}688 \qquad \beta = 90\ 53$$
$$c = 5{\cdot}623 \qquad \gamma = 93\ 18$$

Hence $a : b : c = 0{\cdot}9972 : 1 : 0{\cdot}9886$.

This cell would contain two molecules of the constitution $Ag(Sb,Bi)S_2$, or one molecule of $Ag_2S.(Sb,Bi)_2S_3$, the proportion of Sb to Bi being taken as that given by Mr. Mountain's analysis. No reflections were observed that would indicate a larger cell than the above, and the observed reflections eliminate all smaller cells. The experimental results are tabulated below. No fifth-order reflections were observed, but there was one sixth-order reflection (intensity 5) from the plane (001).

			Angle to	Relative intensities of orders			
(*hkl*).	*d* (calc.).	*d* (obs.).	(001) (obs.).	I.	II.	III.	IV.
(100)	5·662	5·64	91° 4′	—	170	—	37
(010)	5·670	5·67	86 52	—	180	—	34
(001)	5·614	5·61	0	—	52	—	23
(110)	3·899	3·89	88 38	—	92	—	3
($\bar{1}10$)	4·127	4·13	86 36	4	134	—	14
(101)	3·962	3·94	44 4	17	100	7	9
(10$\bar{1}$)	4·013	4·04	44 59	—	95	—	8
(201)	2·516	2·51	62 16	—	22	—	—
(20$\bar{1}$)	2·541	2·55	64 9	—	20	—	—
(102)	2·503	2·50	25 56	—	16	—	—
(10$\bar{2}$)	2·526	2·54	26 34	—	15	—	—
(301)	1·783	1·78	70 24	16	—	—	—
(30$\bar{1}$)	1·795	$1{\cdot}79_5$	72 19	9	—	—	—
(011)	4·102	4·09	46 16	—	110	—	—
(01$\bar{1}$)	3·888	3·88	43 4	?	115	—	4
(012)	2·572	2·57	26 52	—	15	—	—
(01$\bar{2}$)	2·465	2·48	25 42	—	14	—	—
(021)	2·588	2·58	65 43	—	27	—	—
(02$\bar{1}$)	2·473	2·50	60 44½	—	21	—	—
(111)	3·246	3·24	56 10	100	56	5	—
(11$\bar{1}$)	3·164	$3{\cdot}16_5$	54 20	108	54	7	—
(113)	1·707	$1{\cdot}70_5$	25 58	25	—	—	—
(11$\bar{3}$)	1·669	$1{\cdot}67_5$	25 26	25	—	—	—
(331)	1·274	1·27	78 18	17	—	—	—
(33$\bar{1}$)	1·258	1·26	75 44	18	—	—	—
($\bar{1}11$)	3·404	$3{\cdot}42_5$	55 41	165	77	22	5
($\bar{1}1\bar{1}$)	3·252	3·23	51 28	124	65	15	—
($\bar{1}13$)	1·736	1·73	24 49	30	—	—	—
($\bar{2}2\bar{1}$)	1·911	1·91	66 51	—	12	—	—
($\bar{3}1\bar{3}$)	1·351	$1{\cdot}35_5$	79 7	37	—	—	—
($\bar{3}3\bar{1}$)	1·322	1·32	73 8	33	—	—	—

The planes (110), ($\bar{1}$10), and (001) in the above cell correspond to Dr. Spencer's three axial planes ((100), (010), and (001) respectively), the difference in orientation being given by a rotation of approximately 45° about the *c*-axis. The small odd-order reflections observed from the (101) and other 'mixed indices' planes show, however, that his cell, which is nearly tetragonal in shape, is not a possible minimum cell. The prominent cleavages and pyramidal facets observed at angles

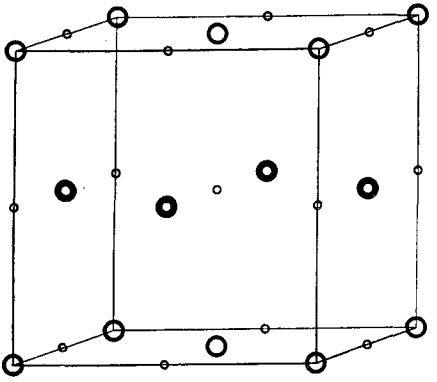

FIG. 3. Lattice of aramayoite, $Ag(Sb,Bi)S_2$.

varying from 73° to 80° from the basal plane would correspond to the planes (33$\bar{1}$), (33$\bar{1}$), (331), and ($\bar{3}$31). The angles made by these planes with (001), when measured on the X-ray spectrometer, were found to be 73° 8′, 75° 44′, 78° 18′, 79° 7′ respectively. The goniometrical results, therefore, which appeared to be inconsistent on the hypothesis of a tetragonal cell, become perfectly consistent when considered in the light of the X-ray analysis. Again it may be noticed, however, that the X-ray reflections from these planes are by no means among the most intense that were observed. The occasional optical reflections at about 55° and 90° are easily explicable on the basis of the triclinic cell, and the reflections at about 40°, while not corresponding to any plane from which X-ray reflections were actually observed, may quite possibly be due to the (33$\bar{5}$) or the ($\bar{2}$23) or some more complex plane. The powder photograph lines are completely accounted for by reference to the table of results, though many of the weaker reflections could not

be seen on the photograph. The majority of the lines are due to more than one reflection and are consequently broad.

The intensities given in the table are extremely interesting. The only planes for which comparatively large first-orders were found are those all of whose indices are odd. In nearly all other cases the odd orders were either absent (that is, too weak for observation) or very small compared with the even orders. This shows that the cell is very nearly face-centred, and since there are only four heavy atoms in the cell, those four must lie at or very near the positions (000) $(0\frac{1}{2}\frac{1}{2})$ $(\frac{1}{2}0\frac{1}{2})$ $(\frac{1}{2}\frac{1}{2}0)$. The similarities between the intensities of reflection from, and the spacings of, the planes (100) and (010) point to an arrangement in which Sb(Bi) atoms lie at (000) $(\frac{1}{2}\frac{1}{2}0)$ and Ag atoms at $(0\frac{1}{2}\frac{1}{2})$ $(\frac{1}{2}0\frac{1}{2})$. The main cleavage planes, (001), would then consist of alternate layers of Sb and Ag atoms, whereas in the (100) and (010) planes the Sb and Ag are coplanar. The positions of the S atoms are not so clearly indicated, but various possibilities may be eliminated by a consideration of the relative intensities of the different order reflections. Thus the diamond arrangement may be dismissed because it would lead to a (400) reflection strong compared with the (200), and a (222) reflection weak compared with the (111). The reverse is actually the case, when allowance is made for the 'normal' falling-off of intensities. The NaCl arrangement (Sb and Ag replacing 2Na, and S replacing Cl) is a more probable one, but is not altogether satisfactory. In that case the S atoms would be located at the points $(\frac{1}{2}00)$ $(0\frac{1}{2}0)$ $(00\frac{1}{2})$ $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ (fig. 3). It is doubtful whether the results obtained from a more detailed analysis of the intensity data would at present justify the time and labour involved.