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The Crystal Structure of Iron Lazulite, a Synthetic Mineral Related to Lazulite

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The crystal structure of iron lazulite, a basic iron phosphate related to lazulite, has been determined.

Interpretation of single-crystal photographs indicates the space group D_4^{10}–$I4_12$ (except for three very faint reflections, the space group is D_{4h}^{19}–$I4/a\,md$) with $a = 5{\cdot}37$, $c = 12{\cdot}81$ A. Atomic positions are 4 P in 4 (*a*); 4 'OH' in 4 (*b*); about 7 Fe randomly situated in 8 (*f*) with $x = 0{\cdot}49$; 16 'O' in 16 (*g*) with $x = 0{\cdot}24$, $y = 0{\cdot}02$, $z = 0{\cdot}07$.

The phosphorus atoms are surrounded by slightly distorted oxygen tetrahedra; the iron atoms are surrounded by distorted oxygen octahedra sharing faces. The distortion of the phosphate groups from tetrahedral symmetry largely accounts for the appearance of the three faint reflections which prevent the space group from being $I4/a\,md$.

Introduction

Iron lazulite is a synthetic mineral so named because of its high iron content and its similarity in crystal shape and X-ray powder pattern to the naturally occurring mineral, lazulite [$(Fe, Mg)\,O\,.\,Al_2O_3\,.\,P_2O_5\,.\,H_2O$]. It was prepared by Prof. J. W. Gruner of the University of Minnesota as a result of a $FePO_4$, $HFeO_2$, water, 'contamination' heated to 170° at about 400 lb./in.^{2} pressure in a bomb. Because of its evident similarity to lazulite it is hoped that the determination of its structure will lead to the structures of the latter and of the related minerals as well.

Crystal data

The crystals were a shiny, jewel-like black in color. Some were shaped very nearly like octahedra with two opposite edges bevelled, a shape common also to lazulite. Their density, determined by a sink-or-float method in a thallium malonate–thallium formate solution, was 3·8 g.cm.$^{-3}$. A complete chemical analysis was not possible, but Dr Gruner reported that phosphate was the only important anion present. The black color was an indication that the iron was present in both valence states. This is also indicated by the fact that the iron presumably assumes the roles of magnesium and aluminium in lazulite.

The space group, unit cell, and approximate structure

For the purpose of this investigation, a single crystal of the described octahedral shape, having a maximum dimension of about 0·15 mm., was selected. Though lazulite is monoclinic (Dana, 1892; Berry, 1948), iron lazulite proved to be tetragonal. Zero-, first-, and second-level Weissenbergs were taken about [010] and [001] using Mo *K* radiation. The systematic extinctions showed that the unit cell selected was body-centered, showed the presence of a fourfold screw axis, and placed the structure unequivocally in D_4^{10}–$I4_12$. Except for very faint (110), (310) and (114) reflections the space group would have been D_{4h}^{19}–$I4/a\,md$. The unit-cell dimensions are

$$a = 5{\cdot}37, \quad c = 12{\cdot}81 \text{ A}.$$

The structural problem was rather unusual, since the chemical composition was known only qualitatively. The determination served to solve simultaneously the problems of structure and composition.

The molecular weight was taken to be one-quarter of the total of the atomic weights per unit cell (minimum multiplicity for this space group is 4) and was computed to be 211 from the observed density.

Except for a choice of origin, the 4 (*a*) and 4 (*b*) positions of D_4^{10} are equivalent. As a first step, phosphorus atoms were put, arbitrarily, in 4 (*a*), i.e. at $0, 0, 0;\ 0, \frac{1}{2}, \frac{1}{4};\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2};\ \frac{1}{2}, 0, \frac{3}{4}$. In order to place four oxygens tetrahedrally about each of the four phosphorus atoms, it was necessary to use the 16-fold general positions ($x, y, z;\ \bar{x}, \bar{y}, z;\ \bar{x}, \frac{1}{2}+y, \frac{1}{4}-z;\ x, \frac{1}{2}-y, \frac{1}{4}-z;\ y, x, \bar{z};\ \bar{y}, \bar{x}, \bar{z};\ \bar{y}, \frac{1}{2}+x, \frac{1}{4}+z;\ y, \frac{1}{2}-x, \frac{1}{4}+z$; plus the corresponding body centering positions). Inspection showed that there were only two ways in which the oxygens could be placed in 16 (*g*) without squashing the phosphate tetrahedra. These correspond to $x_O, y_O, z_O \doteqdot \frac{1}{4}, 0, \frac{1}{13}$ and $0, \frac{1}{4}, \frac{1}{13}$. The second leads to a sterically impossible situation, since it would result in an O–O distance of about 1·2 A. The first set leads to no such difficulty.

Large holes in the structure remained at the other fourfold positions 4 (*b*): $0, 0, \frac{1}{2};\ 0, \frac{1}{2}, \frac{3}{4};\ \frac{1}{2}, \frac{1}{2}, 0;\ \frac{1}{2}, 0, \frac{1}{4}$. Now, oxygen has the largest crystal radius of the atoms in iron lazulite, a situation which holds in most light minerals, so that the structures are mainly determined by the packing of oxygens (Bragg, 1937). It was therefore reasonable to put oxygen in the second fourfold positions. Subsequent application of Pauling's electrostatic valency rule indicated that these were OH groups.

With the two fourfold positions filled in the manner indicated, the structure was closely similar to that of scheelite, $CaWO_4$. Indeed, $BaMoO_4$, another compound with the scheelite structure, would be expected to have the same dimensions as iron lazulite since barium, which occupies the position of the fourfold oxygen in iron lazulite, has a crystal radius of 1·35 A. as compared with 1·40 A. for the radius of oxygen (Pauling, 1940). The comparison is as follows:

$BaMoO_4$: $a = 5{\cdot}56$, $c = 12{\cdot}76$ A.

Iron lazulite: $a = 5{\cdot}37$, $c = 12{\cdot}81$ A.

The remaining task was to fix the positions of the iron atoms. The 99 molecular weight units remaining indicate that there are very nearly 1·75 iron atoms per 'molecule' or 7 per unit cell. Such a defect structure was to be anticipated, for, indeed, strict analogy with the formula of lazulite would indicate 6 iron atoms per unit cell. In order to find the eightfold positions over which these iron atoms are distributed, the structure factors for the ($h00$) and (110) reflections were plotted as functions of the single iron parameter in each of the eightfold positions (assuming the other parameters to be as stated above). Only in 8(f) could the structure factors stand in the ratio of those for these reflections. These positions are: $x, \frac{1}{4}, \frac{1}{8}$; $\bar{x}, \frac{3}{4}, \frac{1}{8}$; $\frac{1}{4}, x, \frac{7}{8}$; $\frac{3}{4}, \bar{x}, \frac{7}{8}$; plus the corresponding body centering positions. The plot further showed that the value of x had to be about 0·5 or 0·0, the latter being eliminated by comparison of general (hkl) reflections.

Some refinement of the parameters

Intensities were measured visually by comparison with a strip of standard spots. They were reduced to structure factors without correction for absorption—a correction made unnecessary by the small crystal size and the use of molybdenum radiation. Structure-factor calculations on the basis of the approximate structure showed that the assumed parameters were very close to the truth. However, the calculated structure factors for (110), (310) and (114) were zero. To account for these faint, but definitely present, reflections, it was necessary to distort the phosphate tetrahedra slightly, to displace the iron slightly, or both. The method used for determining the type of parameter refinements can be outlined as follows: The observed ($hk0$) structure factors were put on the scale of the calculated ones. Assuming a P–O distance of 1·58 A. and a regular PO_4 tetrahedron, x_O was found to be 0·24. This value would not be appreciably changed with small distortions. Then the calculated structure factor for (110) was written as a function of x_{Fe} and y_O and equated to the scaled observed structure factor. (Reflection (110) was the most easily measurable of those reflections which necessitated the parameter refinements.) This equation indicated the values of x_{Fe} and y_O which would together satisfy the value for F_{110} observed. A similar treatment with the (310) reflection did not serve to limit this set, but a consideration of (510), for which an upper bound could be established, showed that the major change must come in y_O. This was also expected from the agreement of structure factors for the high-order reflections.

The last reflection used to fix these two parameters was (600). Here the observed intensity was definitely greater than that calculated, and it was therefore held reasonable to maximize the calculated structure factor on the set of values determined by (110). This process led to the numerical assignment $x_{\mathrm{Fe}} = 0{\cdot}49$ and $y_O = 0{\cdot}02$. A more accurate assignment could have been made on the basis of the entire set of reflections, of course, but, it was felt even this procedure would have yielded values within 0·005 of the above.

By assuming the P–O distance of 1·58 A. and a regular tetrahedron of oxygen atoms, the z_O parameter was found to be 0·07. This figure was independently arrived at by plotting the ($00l$) reflections as functions of z_O. The proper interrelationship was found to hold best at this value. Some support for the oxygen x parameter is obtained from the oxygen diameter of 2·8 A. (Pauling, 1940), which also leads to $x_O = 0{\cdot}24$.

The structure factors (Table 1) were calculated on the basis of this set of parameters, which are, in summary:

4 P atoms in 4(a);

4 OH groups in 4(b);

7 Fe distributed randomly in 8(f) with $x_{\mathrm{Fe}} = 0{\cdot}49$;

and 16 O in 16(g) with $x_O = 0{\cdot}24$, $y_O = 0{\cdot}02$, and $z_O = 0{\cdot}07$.

Discussion of co-ordination

The co-ordination of atoms in the lower half of the unit cell of iron lazulite is indicated in Fig. 1. Double lines indicate the P–O bonding in the phosphate tetrahedra.

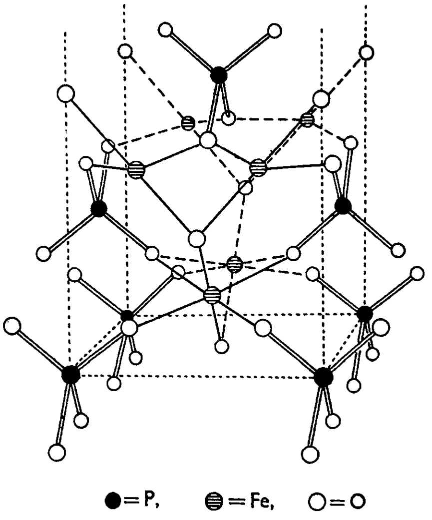

Fig. 1. Lower half of unit cell.

The distorted, face-sharing, oxygen octahedra about the iron atoms can be picked out by following the solid Fe–O lines emanating from iron atoms in the forward half of the unit cell and the broken Fe–O lines from iron atoms in the rear half of the cell.

For the purpose of checking the electrostatic valency rule, let us for the moment ignore the defect structure and assume that there is a doubly positive iron atom at each of the eightfold positions. A phosphate oxygen may then be thought of as co-ordinated to one phosphorus atom and two iron atoms. The phosphorus atom with its 4 co-ordination contributes $\frac{5}{4}$ of an electrostatic bond to a phosphate oxygen, and the two irons contribute $\frac{1}{3}$ each for a total of $\frac{23}{12}$. The oxygen atoms in the fourfold positions have four iron atoms as their nearest cationic neighbors, which contribute a total of $\frac{4}{3}$ of an electrostatic bond. It is thus necessary to postulate O–H groups at the fourfold positions, yielding a total of $\frac{7}{3}$. Two considerations indicate that the totals for both the sixteenfold oxygens and the fourfold oxygens are more nearly 2. First, the Fe–O distance for the sixteenfold oxygens is about 0·1 A. shorter than the Fe–O distance for the fourfold oxygens (1·96 *v.* 2·09 A.). Secondly, we have made the calculation assuming that all the hydrogen charge contributed to the total for the oxygens of the O–H groups alone, whereas some effect on the phosphate oxygens would also be expected.

Table 1. *Structure factors*

Symbols: NOF = not on film, i.e. either blocked by beam stopper or outside oscillation range. B = background too heavy to permit estimation of spot.

hkl	$\lvert F_o \rvert$	$\lvert F_c \rvert$	α (°)
004	74	85	180
008	92	101	180
0,0,12	31	29	0
0,0,16	91	118	0
101	49	37	225
103	89	127	315
105	48	37	45
107	77	65	135
109	55	37	225
1,0,11	55	46	315
1,0,13	74	68	45
200	75	63	0
202	71	63	90
204	57	56	0
206	120	137	270
208	60	43	0
2,0,10	108	127	90
2,0,12	45	34	0
2,0,14	55	70	270
301	54	38	225
303	88	94	315
305	51	39	45
307	54	44	135
309	29	26	225
3,0,11	39	40	315
3,0,13	49	65	45
400	136	183	0
402	< 27	0·1	270
404	57	58	180
406	< 29	2	90
408	80	87	0
4,0,10	< 34	3	270
4,0,12	< 37	27	180
4,0,14	< 39	0·9	90
501	< 31	17	225
503	65	62	315
505	43	38	45
507	< 39	37	135
509	< 35	28	225
5,0,11	37	39	315
5,0,13	44	51	45
600	48	27	0
602	46	54	90
604	35	39	0
606	68	80	270
608	41	51	0
6,0,10	53	82	90
701	< 39	23	225
703	59	50	315
705	43	29	45
707	< 41	15	135
800	84	97	0
011	NOF	NOF	NOF
013	> 88	127	44·9
015	50	37	315
017	73	64	225
019	51	37	135
0,1,11	50	46	45
0,1,13	59	68	315
110	26	23	180
112	68	75	0
114	< 14	10	0
116	57	49	0
118	< 20	0·2	180
1,1,10	48	39	0
1,1,12	< 25	3	0
1,1,14	34	33	0
211	61	65	320
213	79	82	214
215	21	11	132
217	78	81	37
219	63	58	321
2,1,11	25	19	244
2,1,13	33	42	147
310	< 18	14	180
312	54	46	326
314	< 20	10	316
316	52	48	22
318	< 23	1	139
3,1,10	39	40	333
3,1,12	< 49	4	49
3,1,14	< 29	28	16
411	25	27	116
413	74	79	60
415	40	39	313
417	32	45	246
419	30	29	117
4,1,11	35	40	51
4,1,13	43	58	300
510	25	28	180
512	41	39	354
514	< 26	18	14
516	30	31	25
518	< 28	4	199
5,1,10	30	31	332
020	NOF	NOF	NOF
022	NOF	NOF	NOF
024	61	56	0
026	99	138	90
028	55	43	0
0,2,10	106	126	90
0,2,12	37	34	0
0,2,14	47	70	90
121	52	65	42
123	66	81	146
125	21	11	229
127	73	81	323
129	64	58	39
1,2,11	< 32	19	144
1,2,13	35	42	213
220	NOF	NOF	NOF
222	< 17	1	180
224	106	166	0
226	< 21	1	0
228	< 24	14	180
2,2,10	< 27	0·4	0
2,2,12	81	93	0
321	59	51	51
323	61	55	123
325	< 23	13	225
327	76	75	312
329	62	56	49
420	NOF	NOF	NOF
422	61	60	270
424	45	37	4
426	86	98	90
428	32	33	359
4,2,10	76	98	270
521	NOF	NOF	NOF
523	NOF	NOF	NOF
525	< 32	12	218
527	45	52	324
529	44	40	37
110	24	23	180
130	20	14	180
150	B	B	B
170	B	B	B
200	69	63	0
220	128	128	180
240	40	42	0
260	58	63	180
280	< 35	30	0
310	NOF	NOF	NOF
330	B	B	B
350	B	B	B
370	B	B	B
400	150	183	0
440	113	136	0
460	41	24	0
480	63	85	0
550	B	B	B
600	48	27	0
800	69	96	0
011	46	37	135
031	43	38	135
051	25	17	135
121	60	65	42
141	24	27	244
161	36	46	33
231	51	51	312
251	49	51	318

The packing of oxygens has each O–H group centering a tetrahedron of the four nearest oxygens at about 2·70 A., and a rectangular antiprism of the eight next nearest at about 3·06 A.

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The Structure of Dimethylberyllium*

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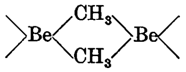
Dimethylberyllium is body-centered orthorhombic, with $a_0=6{\cdot}13$, $b_0=11{\cdot}53$, $c_0=4{\cdot}18$ A., and a structure similar to SiS_2. In the



chains, the C–Be–C angle within the four-membered ring is somewhat greater than tetrahedral, and the Be–C–Be angle is only 66°. The electron-deficient Be–C bonds are 1·93 A. in length.

This structure is in agreement with the rule that electron-deficient bonding results from the tendency of metals, with fewer valence electrons than low-energy orbitals, to use all their low-energy orbitals in forming bonds, even though combined with elements or groups containing no unshared pairs.

Introduction

Compounds in which the number of bonds exceeds the number of electron pairs, historically limited to the boron hydrides and other third-group hydrides and alkyl compounds, have presented a difficult problem in chemical valence. The discovery of similar electron-deficient bonding in tetramethylplatinum (Rundle & Sturdivant, 1947) made it clear that this valence anomaly was not limited to compounds involving third-group elements. It has been suggested, and given some theoretical justification (Rundle, 1947, 1949), that metals tend to use all their low-energy orbitals in bond formation, even if this requires delocalization of bonding, so that one electron pair serves for more than one interatomic link. This rule not only accounts for the known 'electron-deficient' compounds, but predicts that metals with more low-energy orbitals than valence electrons should form 'electron-deficient' compounds when combined with elements or groups containing no unshared pairs.

Beryllium has four low-energy orbitals, one 2*s* and three 2*p* orbitals, and only two valence electrons. It might be expected to form four tetrahedral interatomic links, even in dimethylberyllium. As a test of the above rule we have determined the structure of dimethylberyllium by X-ray diffraction.

Structure determination

Preparation of the compound

Dimethylberyllium was prepared by the method of Gilman & Schulze (1927), reacting methyl Grignard and anhydrous beryllium chloride in ether solution. The compound, obtained as the ether complex, was freed of ether by subliming repeatedly in a vacuum system.

Dimethylberyllium reacts violently with moisture and air, so that crystals have to be kept in sealed containers. Crystals for single-crystal examination were prepared by subliming excess dimethylberyllium into a thin-walled capillary attached to a vacuum system, sealing off the capillary, and then growing a number of single crystals within the capillary by sublimation under a temperature gradient. In favorable cases this method yielded isolated single crystals suitable for diffraction purposes.

Physical and X-ray data

Dimethylberyllium is a white solid subliming at 200° C. As mentioned above, it forms a crystalline complex with ether. These properties are in agreement with those reported by Gilman & Schulze.

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* Contribution no. 119 from the Institute for Atomic Research and the Department of Chemistry, Iowa State College, Ames, Iowa. This work was performed in the Ames Laboratory of the Atomic Energy Commission.

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