FALSE SYMMETRY OF LAWSONITE

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Pabst [1] deals in detail with the spurious symmetry appearing in the structure of lawsonite $CaAl_2[SiO_7](OH)_2 \cdot H_2O$ in his paper in the Laue Festband of the Zeitschrift für Kristallographie. The reciprocal lattice of that mineral shows clearly absences indicating the holohedral group $D_{2h}^{17} = C\frac{2}{c}\frac{2}{m}\frac{2_1}{m}$, but Pabst sees in the structure only a lower symmetry (the enantiomorphic subgroup) $D_2^5 = C222_1$, he explains the absences in terms of spurious symmetry arising as a result of the Templeton effect [2]. That effect is briefly as follows. If a set of atoms A is related to another set B by glide planes (or screw axes) lying in positions p_1 and p_2 and the remaining atoms are in two sets C and D, connected analogously to symmetry planes (or screw axes), and these latter planes (axes), are found in distinct positions p_1 and p_2, then, although the structure as a whole does not possess those planes, the corresponding planes (axes) of absences will occur. Templeton gives an analytic expression for this effect, but he mentions no actual examples (see Pabst [1]).

Gossner and Mussgnug [3], the pioneers in structure analysis of complex silicates, examined the structure of lawsonite in 1931. They measured the parameters of the orthorhombic unit cell and assigned the mineral to the group D_{2h}^{17} Ccmm on the basis of the absences. In 1947 Wickman gave an analysis of the structure [4], but he considered that the lowest group $D_2^5 = C\ 222_1$, was the one to use; that has no center of symmetry, although his model is clearly centrosymmetric and corresponds exactly to D_{2h}^{17} = Ccmm. Wickman explained his caution on the grounds that the $0k\ell$ reflections were few in number (k = 2 was the largest).

Some of the interatomic distances in Wickman's structure are unsatisfactory, and each Ca atom appears to lie inside a figure composed of five oxygen atoms; in consequence we have reexamined lawsonite in more detail [5], and our results show that the structure was in essence correct, but some coordinates needed substantial revision (Table 1); one result is to place each Ca inside an oxygen octahedron. The symmetry is described by group D_{2h}^{17} = Ccmm without doubt.

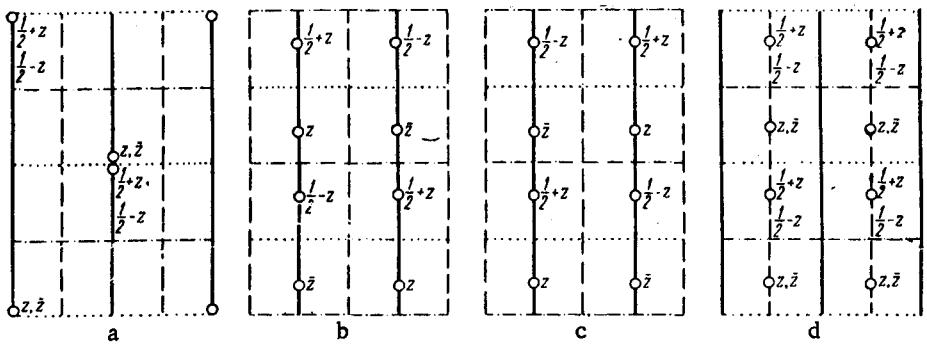
Pabst knew of [3, 4] but not of [5], and overlooked the center of symmetry in Wickman's structure. He recorded Weissenberg photographs with Mo radiation for $0k\ell$ for lawsonite from several different localities and found that spots with $\ell = 2n + 1$ were absent in every case (up to $\ell = 17$ and k = 7), but he did not take these absences as a demonstration of group Ccmm; instead, he ascribed them to a peculiarity of the array of atoms in the unit cell (all the y equal to m/4), which results in the Templeton effect. He divided the atoms into two species, namely those with y equal to 0 or $^1/_2$ (the majority) and those with y equal to $^1/_4$ or $^3/_4$ (O_{II} and O_{IV}, according to [4]). Those of the first kind are related by symmetry elements additional to those in $C222_1$ namely alternating c and n planes, which occupy positions parallel to (100), i.e., 0_{yz} and $^1/_4$ yz (Fig. 1 a shows eight Si atoms related by those planes). The screw axis along the z axis generates m and a planes relating those same atoms; those planes are normal to the ones above; they are parallel to (010) and lie at x0z and $x\,^1/_4\,z$. The atoms of the second kind also are related by extra planes, which again alternate in the same positions, but interchanged [n and c, parallel to (100); a and m, parallel to (010]. Fig. 1 b shows a set of eight O_{II} atoms related in that way. Neither of the sets of planes can perform both functions simultaneously, i.e., they cannot be symmetry elements of the whole structure, although the relations within each group are such as to cause all $0k\ell$ with ℓ odd to be absent, i.e., are such as to cause the Templeton effect.

This argument would be correct if there were only one set of atoms with $y = ^1/_4$ (or $^3/_4$), namely the O_{II}. But, Wickman [4] has shown that there is another such set of the second kind, namely the O_{IV}, which have

Coordinates of Atoms in the Structure of Lawsonite (as 1/100 parts of a,b,c)

Group	Wickman $C222_1$			Revised model Ccmm		
	x	y	z	x	y	z
(4) Ca	32.3	0	1/4	33.8	0	1/4
(4) O_I	2.7	0	1/4	5.1	0	1/4
(4) H_2O	67.0	0	1/4	60.9	0	1/4
(8) Al	25.0	25.0	0.0	1/4	1/4	0
(8) Si	−2.0	0.0	13.5	−2.0	0	13.4
(8) OII	63.5	0.0	5.8	64.0	0	5.8
(8) O_{III}	13.5	0.0	5.8	13.8	0	6.0
(16) (8) O_{II}	39.5	25.0	11.4	37.9	26.3	11.8
(16) (8) O_{IV}	89.5	25.0	11.4			

Note. Wickman's z have been changed to 0.25-z because his origin (near O_I) on a twofold axis is 0.25c away from the inversion center in D_{2h}^{17}. The -z appears on account of the symmetry plane passing through 000 in Wickman's orientation.



Symmetry of the various groups of atoms in the structure of lawsonite. a) Si, b) O_{II}, c) O_{IV}, d) O_{II} and O_{IV} overlapping.

$y = 1/4$ (or $3/4$) and have x coordinates differing from those of the O_{II} by exactly $1/2$ (Fig. 1 c). If we combine the eight-member O_{II} and O_{IV} sets (Fig. 1 d) in a single 16-fold set for group D_{2h}^{17}, we find exactly that extra symmetry assumed for the atoms with $y = 0$ (or $1/2$), i.e., the symmetry of group $C\frac{2}{c}\frac{2}{m}\frac{2_1}{m}$.

Therefore, lawsonite does not show false symmetry*, and so cannot be an illustration of the Templeton effect, because it is known [1, 3-5] that all the atoms have the symmetry of the above group.

LITERATURE CITED

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*The false symmetry demands 21 parameters and an accidental difference of 0.5 between the x coordinates of O_{II} and O_{IV}. The number of parameters in the holohedral structure is 12, i.e., we lose nine parameters accidentally equal to n/4 or to one another. At the same time it becomes impossible to have all the O atoms located at only four levels along the b axis.

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