

The Structure of the High Temperature Modification of Lithium Sulfate *

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The high temperature modification of lithium sulfate has been found to be cubic with a unit cell length of 7.07 Å. The sulfate groups are arranged in a face centered lattice, and the cations can probably exchange between tetrahedral and octahedral positions.

The monoclinic, room-temperature modification of anhydrous lithium sulfate has been studied by Albright¹. At 575 °C a transition takes place. Wyruboff observed that the birefringence disappeared at the transition point and concluded that the high temperature modification was cubic². A cubic symmetry is indicated by the present X-ray investigation.

Table 1 gives observed lines and their relative intensities for lithium sulfate determined from a powder pattern taken at 610 °C with filtered $\text{CuK}\alpha$ radiation. It was noted that the relative X-ray intensities from a sample of the low temperature modification were different before and after being heated above the transition point. Preferred orientation is therefore taking place, and the intensities given in Table 1 cannot be regarded as reliable. Hence no effort was made to use these intensity values for a structure determination.

The observed lines can be indexed by means of a face centered cubic lattice with an edge length:

$$a = 7.07 \text{ \AA}$$

A density of 2.07 corresponds to 4 formula units in the unit cell. The monoclinic modification has a density of 2.22 at room temperature.

From conventional space group considerations a structure of the high temperature lithium sulfate modification can be derived. This structure will

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Table 1. Scattering angles and intensities observed for lithium sulfate at 610° C with $\text{CuK}\alpha$ radiation.

2θ	$\frac{4 \sin^2\theta}{\lambda}$	Int.
21.8	0.0600	24
25.2	0.0803	7
35.9	0.1600	7
42.4	0.2202	7
44.4	0.2404	2
58.4	0.4000	1

be shown to be not quite satisfactory, however, since it does not account for rotation or oscillations of the sulfate groups. By assuming that equivalent atoms take equivalent fixed crystallographic positions, all but two space groups can be ruled out. Only the space groups $F23$ and $F\bar{4}3m$ will simultaneously take 4 sulfur, 8 lithium, and 16 oxygen atoms in one unit cell. With either of these space groups the following coordinates can be assigned to the atoms:

- S 0, 0, 0.
 O $u, u, u; u, \bar{u}, \bar{u}; u, u, \bar{u}; \bar{u}, \bar{u}, u$.
 Li two of the following three coordinates:
 $1/4, 1/4, 1/4; 3/4, 3/4, 3/4; 1/2, 1/2, 1/2$.

If it is assumed that the tetrahedral sulfate group has the usual sulfur-oxygen distance of about 1.50 Å, the parameter u will have the value 0.12. Of the possible lithium positions, those given by the coordinates $1/4, 1/4, 1/4$ and $3/4, 3/4, 3/4$ correspond to a tetrahedral coordination with respect to sulfate groups, though the former gives the cation a 4 coordination and the latter a 12 coordination with respect to oxygen. In the following, however, both these positions shall be referred to as tetrahedral. The position $1/2, 1/2, 1/2$ is 6 coordinated by sulfate groups, and will hence be referred to as octahedral though the coordination number with respect to oxygen is 12.

Except for the positions and numbers of the cations this structure of lithium sulfate appears identical with the structures derived for the high temperature modifications of sodium and potassium perchlorates^{3,4} and borofluorides⁵. The sodium and potassium ions in these structures will occupy the spacious octahedral $1/2, 1/2, 1/2$ positions. This position provides a lithium ion with a too large space. In accordance with this, no analogous cubic high temperature modification has been found for lithium perchlorate and borofluoride.

The structures discussed above lead to some improbable interatomic distances. In lithium sulfate the closest approach of two oxygens belonging to different sulfate groups will be 2.56 Å. Lithium ions in the $1/4, 1/4, 1/4$ positions would be surrounded by oxygen at a lithium-oxygen distance of 1.56 Å. Thus the $1/4, 1/4, 1/4$ lattice sites provide the lithium ions with a too small space. On the other hand, both the $1/2, 1/2, 1/2$ and the $3/4, 3/4, 3/4$ lattice sites provide the lithium ions with a too large space. A rotation of the sulfate

groups through 45° around one axis, however, will increase the previously too short oxygen-oxygen distance of 2.56 Å. The closest distance between oxygens in neighboring sulfate groups will now be 3.18 Å. Now all the lithium ions can occupy tetrahedral positions, four coordinated by oxygen and with a reasonable lithium-oxygen distance of 2.06 Å. Since strong rotational oscillations must be expected for the sulfate groups, the lithium ions most probably can exchange between tetrahedral and octahedral lattice positions. With this high degree of disorder, the given space group can at most be approximately correct. It is even conceivable that the compound has a pseudocubic structure, but any weak reflections which could indicate this would only be noticeable in single crystal exposures.

X-Ray intensities observed for the perchlorates and the borofluorides do not in all cases agree with a reasonable size of the anion group. Finbak and Hassel obtained a better fit of the intensity data by assuming a rotation of the anion group^{5,6}. As in the lithium sulfate, anion groups of acceptable sizes will approach each other too closely when the atoms are in positions prescribed by the adopted space group. Hence a steric hindrance to free rotation is provided. Coupled rotation or strong rotational oscillations must occur, however. In agreement with this, a fairly strong continuous background scattering is observed in lithium sulfate. The scattering has a maximum at $2\theta = 36^\circ$ for the $\text{CuK}\alpha$ radiation employed. This background did not change appreciably in intensity on passing the transition point indicating strong rotational oscillation of the sulfate groups already below the transition point.

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