planes is illustrated in Fig. 8. Its relation to the 4-connected Net 4 of Fig. 6, Part 2, is evident. In this case, also, a series of identical nets can interpenetrate to give a structure containing parallel tunnels and stacks of squares the planes of which are parallel to the faces of a cube.

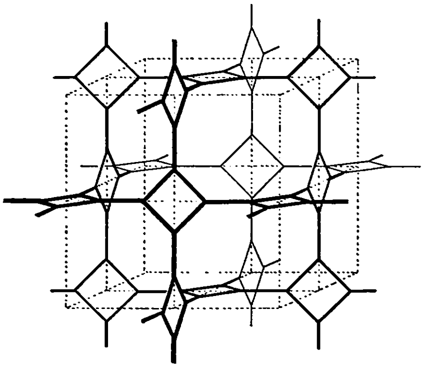
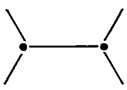


Fig. 8. Three-dimensional 3-connected net containing squares with their planes parallel to {100} planes.

In Part 2 we mentioned that the 3-connected Nets 1 and 2 result from replacing the points in the 4-connected diamond net by the unit



there being two ways of orienting this unit. The same process may be applied to the cubic net of Fig. 18(*b*) of Part 2. If the unit is inserted at each point so that the line joining the two substituting points bisects a pair of opposite 90° angles the net of Fig. 8 is obtained. The alternative is to bisect the pair of opposite 120° angles at each point, when the net of Fig. 9 results. This net has tetrahedral symmetry and contains hexagons with their planes parallel to tetrahedron faces. It is not possible to form a system of interpenetrating nets of this type. The nets of Figs. 5, 8 and 9 form a family of cubic nets all having 24 points in the unit cell. With the coordinates given in Table 1 all links in a net are equal in length.

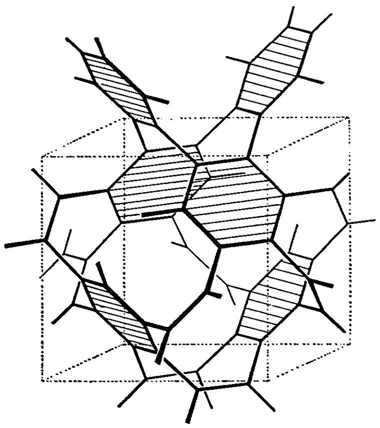


Fig. 9. Three-dimensional 3-connected net containing hexagons having their planes parallel to tetrahedral planes.

Table 1

Figure	Space group	Equivalent position	Angles between links (coplanar) (°)
5	$I4_13$	24(*h*): $x=0{\cdot}058$	60 (1), 150 (2)
8	$Im3m$	24(*g*): $x=0{\cdot}147$	90 (1), 135 (2)
9	$P\bar{4}3m$	24(*j*): $x=\frac{5}{12}$ $y=\frac{3}{12}$ $z=\frac{1}{12}$	120 (3)

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Unit-Cell Dimensions of Lithium Fluoride made from Li^6 and Li^7

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The unit-cell sides of Li^6F and Li^7F are found to be $4{\cdot}0271 \pm 0{\cdot}0001$ Å and $4{\cdot}0263 \pm 0{\cdot}0001$ Å respectively at 25° C., a fractional difference of about 2×10^{-4}. It is considered that this difference arises from the difference in zero-point energy of these materials. It is to be compared with the calculated value of $3{\cdot}3 \times 10^{-4}$, which is, however, in error by an unspecified amount since it applies only to temperatures above the Debye temperature.

Introduction

At the Conference of the X-ray Analysis Group of the Institute of Physics held in Edinburgh in April 1952 the writer reported briefly on some work he had carried out on the unit-cell dimensions of lithium fluoride made from the separated isotopes Li^6 and Li^7. He then stated that differences in the unit cell dimensions had been observed. However, he was not quite satisfied of the purity of the original samples and has repeated all the observations on new material in the preparation of which particular attention has been paid to the methods of purification employed. Happily the final results confirmed those previously reported and it is the purpose of the present paper to give an account of these, together with a reference to their explanation which has been worked out quantitatively by Dr H. London.

Basis for the expectation of a change in unit-cell dimensions

Experimental evidence already exists for the isotopic change of atomic volume in the extreme cases of hydrogen (Megaw, 1934; Zintl & Harder, 1935) and helium (London, 1936, 1938). The volume change for the latter (atomic volume of $He^3 = 37$ cm.^{3} and that of $He^4 = 28$ cm.^{3}) is due to the large zero-point energy, which makes helium much less dense than a consideration of minimum potential energy alone would warrant. The difference in zero-point energy between He^3 and He^4 is then big enough, relative to the potential energy (which is constant) to affect appreciably the densities of these two isotopes, and hence their atomic volumes.

If a similar argument is true for lithium fluoride, then, since the zero-point energy decreases with increasing mass, we should expect the molecular volume of Li^7F to be smaller than that of Li^6F, i.e. the unit-cell dimensions of Li^7F should be smaller than those of Li^6F. The observed values do, in fact, differ in this sense.

For a large effect we require a material with a high Debye characteristic temperature and a large fractional difference in mass between the two isotopic states concerned. Lithium fluoride, with a Debye temperature of 645° K. and a fractional change of molecular mass of 4 % is thus quite a suitable material to examine.

Dr H. London, by minimizing the expression for the free energy, has obtained an expression for the change of molecular volume which leads to the conclusion that the unit-cell side of Li^7F should be smaller than that of Li^6F by $3{\cdot}3\times10^{-4}$. He hopes to publish his calculations in the near future.

Preparation and purification of material

The lithium isotopes were separated electromagnetically through the kindness of Dr R. H. V. M. Dawton and Dr M. L. Smith of the E.M. Group at Harwell. A number of methods of purification were tried by Dr Smith and the resulting products tested for 'structural' purity (i.e. freedom from impurity atoms which replace atoms in the LiF structure, rather than from ordinary chemical impurities) by X-ray examination, a precise determination of the unit-cell dimensions of Li^7F being made in each case and compared with the value for LiF published by Straumanis, Ievinš & Karlsons (1939), and a concordant value obtained by the writer from 'spec-pure' lithium fluoride supplied by Messrs Johnson–Matthey. That this method is feasible arises from the fact that any possible structural impurity atom will have the effect of increasing the unit-cell dimensions. During this work, the precaution was taken of ensuring that the samples of Li^6F and Li^7F on which the purification processes were carried out were of the same size. Thus any impurities that might be introduced during handling would have the same effect on both Li^6F and Li^7F.

After a number of trials it was found that the most satisfactory method of purification was by straightforward recrystallization, the corrected value for the unit-cell side of Li^7F agreeing within experimental error with the value for natural LiF. The correction is necessary since the presence of 7·5 % Li^6 will increase the unit-cell side of LiF over that of Li^7F by 0·00006 Å. The actual figures are:

a_0, according to Straumanis *et al.*, 4·0262 Å at 25° C.

a_0, according to present measurements, 4·0262 Å at 25° C.

a_0 (from Li^7F), according to present measurements, 4·0263 Å at 25° C.

X-ray techniques and results

The two main sources of error which were guarded against were temperature variation and errors in sampling. Lithium fluoride has a linear coefficient of thermal expansion of 34×10^{-6}/°C. (this is given by Straumanis, Ievinš & Karlsons (1938) and has been confirmed during the present work), and a temperature change of 1° C. will produce a change in the value of the unit-cell side of 0·00014 Å. Thermostatically controlled cameras have therefore been employed; by means of these it is possible to control the temperature to within ±0·2° C., and hence the change in unit-cell side to within ±0·00003 Å.

To guard against sampling errors, X-ray photographs were taken of a number of independent specimens, taken from various portions of each batch of lithium fluoride. Two batches of both Li^6F and Li^7F were used and four X-ray specimens were made up from each batch. Eight independent results were therefore available for each substance. In the case of the 'spec-pure' material, however, four specimens only were examined, as the object of this examination was merely to check the published value of Straumanis *et al.*

An ordinary commercial 19 cm. camera was used in which had been built a slit system giving a beam at the specimen of cross-section about 5 mm. × 1 mm. The specimen diameter was about 0·3 mm. in each case, and the specimens were made by rolling to the required size a paste obtained by mixing a small amount of Canada balsam with the lithium fluoride. Copper K radiation was used, with no filter.

No allowance was made for X-ray refraction in this work. Moreover, although the standard errors of the final values for Li^6F and Li^7F are satisfactorily small, they must be regarded as valid only as a measure of the significance of the differences observed, i.e. they are random errors. The total errors, which include errors arising from systematic errors in temperature measurement or camera calibration must be somewhat higher. Uncertainties in the values of the X-ray wavelengths will also contribute to the total error, although this source of error can be evaded by expressing the results on an arbitrary scale. In the present work the value for Cu $K\alpha_1$ has been assumed to be 1·54050 Å.

To obtain the unit-cell size of a sample the usual extrapolation technique, using the Nelson–Riley function, was employed, attention being restricted to reflexions at glancing angles greater than 50°. Allowance was made for the errors in reading the positions of the $K\alpha_1$ and $K\alpha_2$ reflexions, which arise from the proximity of these reflexions and which are the greater the greater this proximity, by carrying out independent extrapolations for the $K\alpha_1$, $K\alpha_2$ and $K\beta$ reflexions.* As expected, the slopes of the three lines were in general different, that for the $K\beta$ reflexions being intermediate between those for the $K\alpha_1$ and $K\alpha_2$. The mean of the three extrapolated values was then taken as the value appropriate to the specimen in question. Two separate measurements of each film were carried out in this way and the mean of the two results was taken as the final value. The actual figures are given in Table 1.

Table 1. *Unit-cell sides of* Li^6F *and* Li^7F

Specimen number	Li^6F a_0, corrected to 25° C.	Li^7F a_0, corrected to 25° C.
1	4·02703 Å	4·02617 Å
2	4·02704	4·02628
3	4·02710	4·02618
4	4·02713	4·02614
5	4·02718	4·02638
6	4·02701	4·02635
7	4·02705	4·02627
8	4·02723	4·02645
Mean	4·02710	4·02628
Standard error	0·00003	0·00004

It will be seen from Table 1 that the unit-cell side of Li^7F is fractionally smaller than that of Li^6F by about 2×10^{-4}. This is to be compared with the calculated value mentioned above, based on the Debye theory of solids, of $3{\cdot}3\times10^{-4}$. It will be seen that the observed value is somewhat less than that calculated, but it should be noted that the latter value is valid only for temperatures above the Debye characteristic temperature, and that the temperature of the present experiments was only about half the Debye temperature. The error thus introduced is difficult to assess and some discrepancy between the observed and calculated values is to be expected.

As already mentioned, the standard errors quoted in Table 1 are random errors only. A systematic error of 0·2° C. in temperature measurement would lead, according to the figures already given, to an error of 0·00003 Å, and in this case the error could, of course, be in either sense. Similarly any systematic error in camera calibration, which could also be in either sense, might be expected to affect the fifth place of decimals, although it is not easy to estimate the magnitude of this effect. The observed standard errors for Li^6F and Li^7F correspond to limiting errors of 0·00006 Å and 0·00008 Å respectively, and it is considered that the limiting error is best rounded off to 0·0001 Å in each case, so that the unit-cell sides of the two substances in question may, with some confidence, be written as:

$$Li^6F:\ a_0 = 4{\cdot}0271\pm0{\cdot}0001\ \text{Å}$$
$$Li^7F:\ a_0 = 4{\cdot}0263\pm0{\cdot}0001\ \text{Å}\,.$$

According to Frohnmeyer & Glocker (1953), refraction effects themselves can be responsible for an uncertainty in the absolute value of the unit-cell side of about 0·0001 Å. In view of this, and the discussion above, it would seem very optimistic to hope to achieve any better accuracy than that claimed.

The author is indebted to Dr R. H. V. M. Dawton and Dr M. L. Smith for the provision of the samples and to Dr H. London for valuable discussions. He would also like to thank Messrs M. K. Hannon and A. R. Davey who, at different times, helped with the X-ray measurements.

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* The effect guarded against consists of an apparent displacement of the $K\alpha_1$ and $K\alpha_2$ reflexions from each other. The observed θ value for $K\alpha_1$ is thus too small and that for $K\alpha_2$ is too high.