Acta Cryst. (1955). 8, 32

The Geometrical Basis of Crystal Chemistry. Part 5

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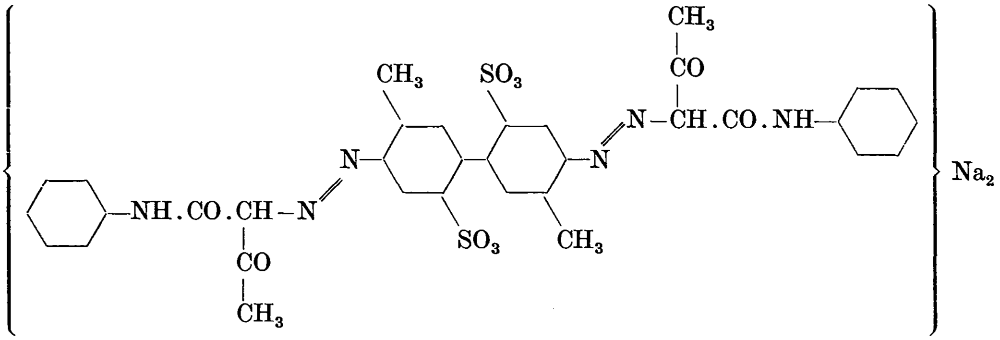
(*Received* 21 *May* 1954)

A preliminary X-ray study of the yellow wool dye Coomassie Yellow 7G is reported. The unusual diffraction effects from dry crystals and the very large unit cell of the wet crystals suggest a framework structure. Although the structures of the crystals are far too complex to analyse directly, some suggestions are made as to the possible nature of the framework.

A protein-like azo compound

It has been known for some time that certain complex dyes have unusual properties, for example, the formation of highly thixotropic aqueous pastes or very viscous aqueous solutions or gels. An X-ray study of the compound



(marketed as the wool dye Coomassie Yellow 7G) shows that certain of its crystalline forms exhibit quite novel X-ray diffraction effects, indicating that the crystals are of a type not hitherto encountered. The observations recorded here are of a very preliminary character; no systematic study has been made of either the physical chemistry of the compound or the X-ray diffraction effects. The results of this very incomplete study are presented in this form because no detailed work is contemplated in the immediate future and also because the structures of these crystals are probably examples of complex framework structures of the kind discussed in Part 4 and later in the present paper.

The compound is prepared by tetrazotizing *o*-tolidine-6:6′-disulphonic acid, coupling with two molecules of acetoacetanilide, and then precipitating the sodium salt of the dye by the addition of brine. The product, a yellow crystalline powder, is normally quite soluble in water (> 10% in boiling water), and if it is dissolved in hot water and the solution cooled a very viscous solution is obtained which sometimes does not crystallize over a period of days or even weeks. However, by controlled salting-out or the addition of ethyl alcohol beautifully crystalline materials can be obtained. Three characteristic developments are shown in Fig. 1(*a*)–(*c*).

This compound can also be obtained in a relatively insoluble form (< 1% in boiling water) but it has not been found possible to obtain crystals of this form large enough for single-crystal work. The X-ray powder photograph of the insoluble form is that of a normal microcrystalline powder (Fig. 2(*a*)), whereas those of the soluble forms of Fig. 1(*a*)–(*c*), after grinding lightly, show only a small number of very diffuse rings, resembling a photograph of a glass or liquid rather than a crystalline powder (Fig. 2(*b*)). Although they are apparently all quite normal crystals, readily obtainable with dimensions of the order of a millimetre or so, they give none of the sharp X-ray diffractions usually regarded as characteristic of crystals.

In an ion of the kind shown above the possibilities of tautomerism and stereo-isomerism are considerable, and polymorphism and different degrees of hydration are also possible. It is therefore not surprising that by varying the conditions of crystallization a number of different products can be obtained, and it is not possible to say anything about their intramolecular configurations. Chemical analyses have been made of various batches of crystals obtained by salting-out, filtering, and drying at room temperature. These analyses indicated considerable and variable degrees of hydration (up to 20 H_2O for 1 formula-weight of dye), but since the crystals were still losing weight at the time of analysis the initial water contents are not known.

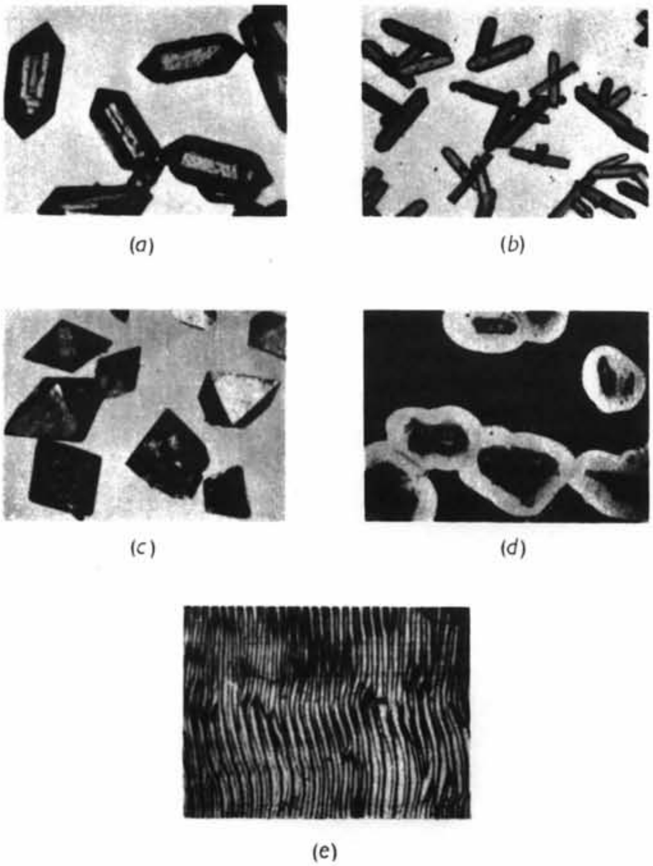


Fig. 1. (*a*), (*b*), (*c*) Photomicrographs of crystals (×18). (*d*) Crystals of type (*b*) dissolving in water (crossed Nicols, ×18). (*e*) Dried film of viscous solution on glass slide, showing fibrillar structure (crossed Nicols, ×27).

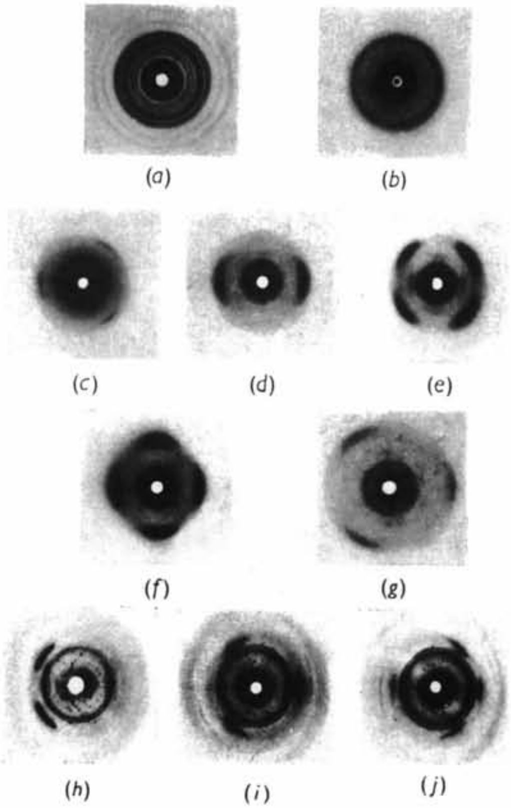


Fig. 2. (*a*), (*b*) X-ray powder photographs of insoluble and soluble forms. (*c*)-(*j*) 15° oscillation photographs: (*c*) dried crystals of Fig. 1(*b*); (*d*)-(*g*) dried crystals of Fig. 1(*c*); (*h*)-(*j*) wet crystal of Fig. 1(*a*).

The relation between the soluble and insoluble forms

The solubility/temperature curve of this compound might be expected to throw some light on the relation between the two forms. However, it is not possible to determine the solubility in the ordinary way of either the soluble or the insoluble form. The action of water on crystals of the soluble form is very extraordinary. The crystals break up but do not go into solution like a normal crystalline solid. They become coated with a gelatinous layer from which material slowly diffuses into the surrounding normal molecular solution. This phenomenon is clearly seen in the microscope with low magnification and crossed Nicols, the gelatinous layer appearing bright against the dark background of the normal solution (Fig. 1(*d*)). This apparent optical anomaly, that the gelatinous regions remain bright when rotated between crossed Nicols, is due to the presence of small volumes of oriented molecules which are not resolved under low magnification. These small birefringent regions corresponding to different molecular orientations can be distinguished under a high-power objective. When the viscous aqueous solution has been formed the soluble form of the dye does not crystallize out on cooling; crystallization may take days or weeks. The insoluble form also dissolves on heating to form a viscous solution, from which crystals of the soluble form separate after a long time.

The viscous solutions exhibit a greenish fluorescence, flow-birefringence, and characteristic striations. A film made by smearing the solution on a glass slide and allowing to dry is highly birefringent and often extinguishes perfectly between crossed Nicols (Fig. 1(*e*)). The striations and birefringence shown by these solutions disappear on heating to a temperature which depends on the concentration.

The morphology of the crystals of Fig. 1 (*a*)–(*c*)

Prisms of type (*a*)

These crystals are bounded by four prism faces and terminated at both ends by four pyramid faces. They are the form in which the compound is obtained when it separates comparatively rapidly from the viscous aqueous solutions. Interfacial angles measured on a number of well-developed crystals agreed with one another to within ½°. The faces can be indexed on an orthorhombic axial system,

$$a:b:c = 0{\cdot}6682:1:0{\cdot}8399\,,$$

as $\{110\}$ and $\{111\}$. Typical measurements are:

Prism zone: 112° 39′, 67° 36′, 112° 22′, 67° 23′
Prism : pyramid: 33° 32′, 33° 37′, 33° 34′, 33° 23′

$$\left.\begin{array}{l}(111):(1\bar{1}1) = 54^\circ\,54' \\ (\bar{1}11):(\bar{1}\bar{1}1) = 54^\circ\,31'\end{array}\right\}\ \text{(calculated,* } 55^\circ\,12'\text{)}$$

$$\left.\begin{array}{l}(1\bar{1}1):(\bar{1}\bar{1}1) = 87^\circ\,41' \\ (111):(\bar{1}11) = 87^\circ\,52'\end{array}\right\}\ \text{(calculated,* } 87^\circ\,48'\text{)}$$

These goniometric data are given to show that as regards planarity and parallelism of pairs of opposite faces these would be regarded as normal crystals. They are transparent and between crossed Nicols extinguish as normal orthorhombic crystals.

Prisms of type (*b*)

These are orthorhombic prisms $\{110\}$ terminated at both ends by $\{011\}$. The best observed values of the interfacial angles $(110):(1\bar{1}0) = 67^\circ\,30'$, and $(011):(0\bar{1}1) = 79^\circ\,16'$, give

$$a:b:c = 0{\cdot}6682:1:0{\cdot}8283\,.$$

The angles in the prism zones of crystals of types (*a*) and (*b*) are the same to within the experimental error, and it appears that these two types of prismatic crystal are referable to the same orthorhombic axial system.

Bipyramids of type (*c*)

These are orthorhombic bipyramids $\{111\}$. The faces were generally somewhat rough and gave rather poor reflexions on the optical goniometer. However, it was possible to determine the dimensions of the unit cell of these crystals, and the measured interfacial angles correspond approximately to the axial ratios obtained from the X-ray data, namely

$$a:b:c = 0{\cdot}823:1:0{\cdot}610\,.$$

$(111):(1\bar{1}1) = 52\tfrac{3}{4}^\circ$ (measured), 52° 08′ (calculated),
$(111):(\bar{1}11) = 66^\circ$ (measured), 64° 36′ (calculated).

X-ray diffraction effects

Dried crystals

Powdered crystals of types (*a*), (*b*) and (*c*) give the photograph of Fig. 2(*b*). The spacings of the very diffuse rings, of which only three are strong enough to be seen on the reproduction, are approximately 7·9, 4·8, 3·4, 2·0, and 1·7 Å.

In a Unicam 3 cm. cylindrical camera a single crystal of type (*a*) or (*b*), about 0·5 mm. in length, gives no crystalline diffraction pattern after an exposure of 60 mA. hr. A typical 15° oscillation photograph of a crystal of type (*b*) is shown in Fig. 2(*c*), exhibiting only very weak arcs and some low-angle scattering around the centre. With a fine lead-glass capillary sharper spots were obtained and up to eight weak spots were visible after an exposure of 120 mA. hr. The approximate dimensions of the orthorhombic unit cell are:

$$a = 39{\cdot}0,\quad b = 58{\cdot}8,\quad c = 48{\cdot}0\ \text{Å}\,,$$

which correspond to the axial ratios determined from the interfacial angles. The space group was not determined.

No discrete diffraction spots have been obtained from dry crystals of type (*a*), though it is possible that incompletely dried crystals might show such effects.

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* Based on the values $(110):(1\bar{1}0) = 67^\circ 30'$ and $(110):(111) = 33^\circ 30'$.

Typical 15° oscillation photographs of dry bipyramidal crystals of type (c) are shown in Fig. 2(*d*)–(*f*). The prominent diffuse arcs correspond to spacings of about 3·4 Å, and the sharp spots cut off rather suddenly at about 8 Å, that is, they lie within the strong inner ring of the powder photograph of Fig. 2(*b*). Fig. 2(*g*) shows a photograph taken with the fine lead-glass slit at a greater specimen–film distance. By rotating about the three axes of a bipyramid the cell dimensions were found to be:

$$a = 30{\cdot}8,\ b = 37{\cdot}4,\ c = 22{\cdot}8\ \text{Å}\,.$$

The absences indicate the space group *Pncn*(*Pnna*), though the total number of reflexions observed was rather small for an unambiguous determination. The observed density of the crystals (by flotation) is 1·380±0·005 g.cm.$^{-3}$. Assuming this to be the true density (see later), the unit cell would contain 24 ($C_{34}H_{30}N_6O_{10}S_2Na_2.6H_2O$).

From a complete set of oscillation photographs of the type of Fig. 2(*d*)–(*f*) the reciprocal lattice corresponding to the regions of diffuse scattering can be mapped out. For these dry bipyramidal crystals it consists of

I A complete spherical shell of radius ~0·2 (= 1·54/*d* (Å)).
II 12 volumes the centres of which lie on a sphere of radius 0·3.
III 6 volumes the centres of which lie on a sphere of radius 0·45.
IV A complete spherical shell of radius 0·75.
V 6 volumes the centres of which lie on a sphere of radius 0·9.

Of these, I, II and III are shown in Fig. 3(*a*). The volumes III give rise to the prominent diffuse reflexions on the photographs of Fig. 2(*d*)–(*f*), and correspond to smeared-out reflexions from sets of planes of spacing about 3·4 Å.

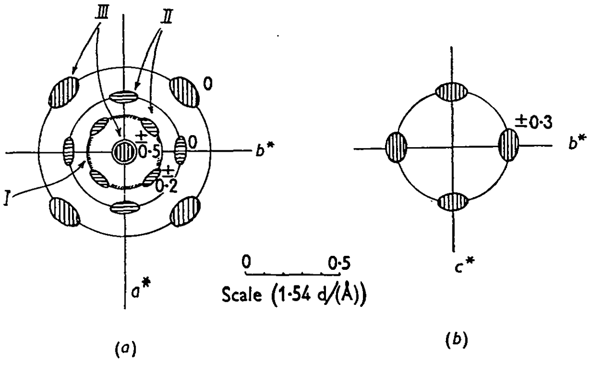


Fig. 3. Reciprocal lattices corresponding to (*a*) diffuse reflexions from dry bipyramidal crystal, and (*b*) groups of strong reflexions from wet crystal, as shown in Fig. 2, (*h*)–(*j*).

Wet crystals

X-ray photographs were then taken of prisms apparently of the type of Fig. 1(*a*) before removal from mother-liquor, the crystal being sealed up in a thin polythene tube with sufficient solution to keep it wet. Typical 15° oscillation photographs are shown in Fig. 2(*h*)–(*j*) on which the two strong powder rings are due to the polythene container. These photographs are comparable in complexity with those given by globular proteins and indicate a pseudo-rhombic cell with dimensions

$$a = 53{\cdot}5,\ b = 75{\cdot}2,\ c = 58{\cdot}1\ \text{Å}\,.$$

The symmetry of the wet crystals is almost certainly not higher than monoclinic, and their cell dimensions do not correspond to the angles measured on dry prismatic crystals. (The interfacial angles of the wet crystals have not been measured.) It seems likely that some structural changes accompany dehydration. In general the intensity of the reflexions falls off to very small values for planes of spacing $3\frac{1}{2}$ Å or less, except for groups of very intense reflexions which obviously correspond to the diffuse reflexions on the photographs of dried crystals. The volumes in which these groups of strong reflexions lie have been placed in the reciprocal lattice in Fig. 3(*b*).

These X-ray photographs suggest that the crystals have fairly rigid framework structures, the interstices in which are initially filled with water molecules, and possibly also ions of the dye. Removal of part or all of the water does not lead to collapse of the framework but does allow the molecules sufficient freedom of vibration to destroy most or all of the regular diffraction effects. It is possible that the molecules are bonded into a three-dimensional framework by N–H–O bonds, and since the NH and CO groups are near the ends of the molecules and close together compared with the length of the molecule (about 22 Å if fully extended) we may illustrate diagrammatically the structures of the wet and dried crystals by the two-dimensional analogy of Fig. 4.

The arrangement in the reciprocal lattice of the volumes corresponding to the diffuse reflexions from the dry crystals and to the groups of intense reflexions from the wet crystals (Fig. 3) suggests that the frame-

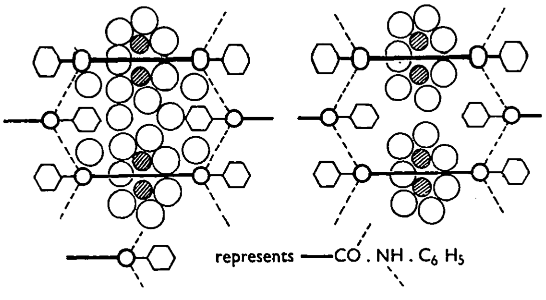


Fig. 4. Diagrammatic representation of wet and dry crystals. Shaded circles represent sodium ions, large open circles water molecules.

works of these crystals have some sort of polyhedral character. Crystals of NN′-diacetyl-*p*-phenylene diamine give one very strong reflexion of spacing about 3·4 Å from the plane of the layers; the reflexions 111 in Fig. 3(*a*) correspond to sets of planes with the same spacing parallel to the faces of a cube. The shaded volumes in Fig. 3(*b*) would arise from series of planes with the same 3·4 Å spacing arranged parallel to the faces of an octahedron. The systems of interpenetrating nets illustrated in Fig. 7 of Part 4 have no such polyhedral character; they are essentially uniaxial with series of tunnels (and therefore the walls of the tunnels) all parallel to one axis.

It appeared of interest, therefore, to consider nets containing small polygons (triangles, squares and hexagons) arranged with their planes parallel to cube and octahedron faces. For example, the 3-connected Net 9 (Figs. 6(*d*) and 11 of Part 1) arises by placing hexagons at the points of a cubic lattice with their planes all parallel; we require the related net with the planes of the hexagons parallel to all four {111} planes. Similarly, the net shown in Fig. 16 of Part 1 can be derived by placing squares at the points of a diamond net with their planes all parallel, giving a net with only tetragonal symmetry; we require the net in which the squares have their planes parallel to cubic {100} faces.

A further set of 3-connected nets with cubic symmetry

A 3-connected net containing *n*-gons results from replacing points in an appropriate *n*-connected net by *n*-gons. From the cubic configuration (with 8 points in the unit cell) of the simplest three-dimensional 3-connected net we obtain the net of Fig. 5 with 24 points in the cubic unit cell. (This is the net corresponding to the open packing 3_2 of Heesch & Laves—see Table 4 of Part 1.) Since the original net is a system of 10-gons the new net consists of 3-gons and 20-gons. Each corner of a triangle is connected to a corner of another triangle, and nets of the same kind are derivable from other 3-connected nets, in particular, the other 'uniform' nets mentioned in Part 1, with circuits of 8 and 12 points. These will give rise to nets consisting of 3-gons and respectively 16-gons or 24-gons. These nets are related to certain of the Archimedean semi-regular solids, namely, those resulting from truncation of the three regular solids having three edges meeting at an apex (tetrahedron, cube, and regular dodecahedron). Just as the uniform three-dimensional 3-connected nets continue the series of polytopes starting with the tetrahedron, cube, regular dodecahedron, and plane hexagonal net (Fig. 10 of Part 3) so the nets we are discussing form part of the series illustrated in Fig. 6.

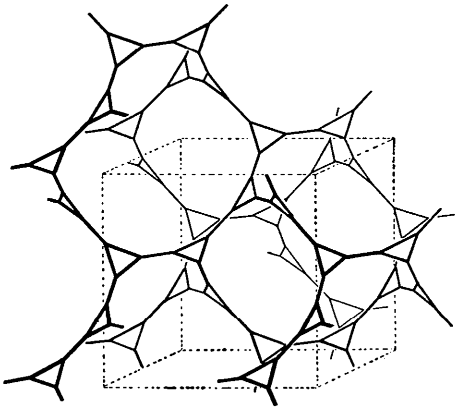


Fig. 5. Three-dimensional 3-connected net containing triangles having their planes parallel to tetrahedral planes.

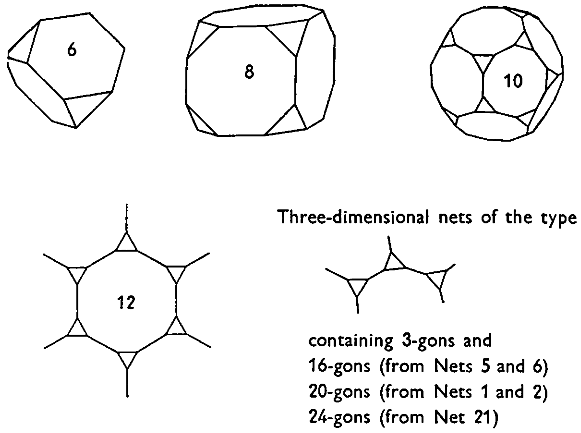


Fig. 6. The semi-regular solids and plane net related to the net of Fig. 5.

The net of Fig. 5 projects along [111] as shown in Fig. 7, and an indefinite number of identical nets can interpenetrate if they are related by successive small translations in this direction. The result is a structure consisting of a series of parallel tunnels in which the triangles *a*, *b*, *c*, and *d* in the projection of Fig. 7 represent stacks of triangles with their planes parallel in turn to the four faces of a tetrahedron. If these triangles represented rings of atoms joined by hydrogen bonds then, since these stacks form an essential part of the framework, they would remain in the dried crystal and might account for the octahedral distribution of the diffuse reflexions.

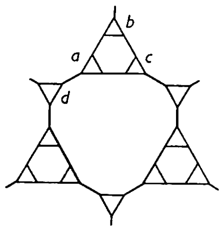


Fig. 7. Projection of the net of Fig. 5 along a cubic [111] axis.

The simplest 3-connected net containing squares with their planes parallel in turn to the three {100} 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.

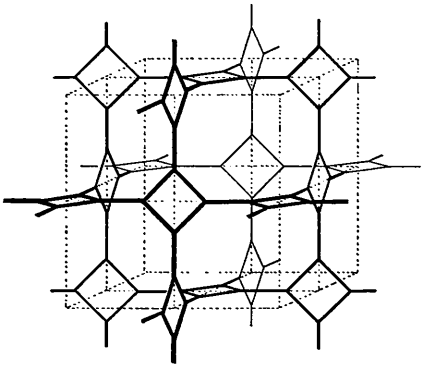
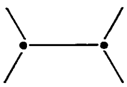


Fig. 8. Three-dimensional 3-connected net containing squares with their planes parallel to {100} planes.

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.

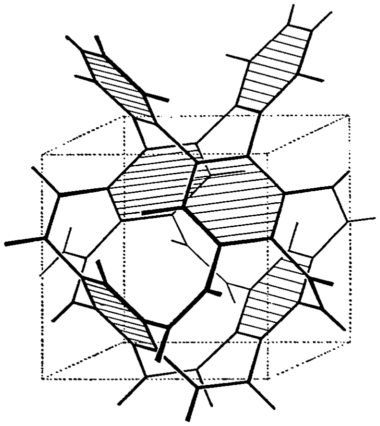


Fig. 9. Three-dimensional 3-connected net containing hexagons having their planes parallel to tetrahedral planes.

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)

Acta Cryst. (1955). 8, 36

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

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(*Received* 10 *November* 1954)

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