

$$M_{2m} = 1/(5\pi) (3\mu/2)^2 \sum_{kj} (3 \cos^2 \beta_{kj} + 1) r_{kj}^{-6}. \quad (5)$$

The atomic positions of the protons were not given by Hope & McCullough (1964), but a set of likely positions has been obtained by assuming that the carbon-hydrogen bond distance is 1.08 Å and the H-C-H angle is 109.5°. By means of these positions the second moment for the static case [equation (3)] and the fast oscillating case [equations (4) and (5)] have been calculated, and the results are given in Table 1.

Table 1. *Experimental and theoretical second moments for a static and flipping C<sub>4</sub>H<sub>8</sub>Se molecule*

Case	Theoretical second moment	Experimental second moment
Static	17.6 G <sup>2</sup>	19 ± 2 G <sup>2</sup>
Flipping	8.4	8.5 ± 1

The proton magnetic resonance spectra of C<sub>4</sub>H<sub>8</sub>Se · I<sub>2</sub> held at several temperatures from room temperature down to liquid nitrogen temperature were recorded on a Varian Asc. Dual Purpose Spectrometer operating at 60 Mc.sec.<sup>-1</sup>. The room temperature spectra were definitely narrower than the spectra obtained at liquid nitrogen temperature (Fig. 2). When the sample is cooled from room temperature the spectrum begins to broaden at about -70 °C, and the broadening is completed at about -140 °C. At these low temperatures the signal is easily saturated, indicating that the spin-lattice relaxation time gets longer as the temperature is decreased. To avoid saturating the signal we had to work at a low r.f. power level, resulting in a relatively poor signal to noise ratio. The spectrum also changes shape in the transition region from a simple bell shaped curve at room temperature to a broadened two-peak spectrum at low temperatures. For these two reasons we have not tried to evaluate an activation energy from the temperature dependence of the spectrum, as the accuracy using the standard procedure will be questionable. The second moments of a set of room temperature spectra and of a set of spectra obtained with the sample in liquid nitrogen have been evaluated, and the results are given in Table 1. The liquid nitrogen second moment is compared with the theoretical second moment calculated for a rigid molecule, and the room temperature second moment with the motionally averaged theoretical second moment.

All these observations give a consistent picture of the motion of the tetrahydroselenophene molecules in the solid iodine complex in accordance with the ideas of Hope &

McCullough (1964). The observed temperature dependence of the spectrum shows that the molecule is oscillating between two equivalent conformations with a thermally activated motion, which is slower than 10 kc.sec.<sup>-1</sup> below -140 °C and faster than this above -70 °C. The proton spin system is very likely relaxed by means of this oscillatory motion, explaining why the signal was easily saturated at low temperatures. The broadened two-peak spectrum obtained at low temperatures is due to the fact that the protons are grouped in pairs, methylene groups, in the molecule (Pake, 1948). The main contribution to the second moment, 11.6 G<sup>2</sup>, is given from this strong intra-pair interaction. When the molecule is oscillating fast, however, this interaction is greatly reduced, explaining the observed bell-shaped curve without any fine structure at high temperatures. Finally, the good agreement between the observed and calculated second moments given in Table 1 also more quantitatively supports the proposed model of the molecular motion.

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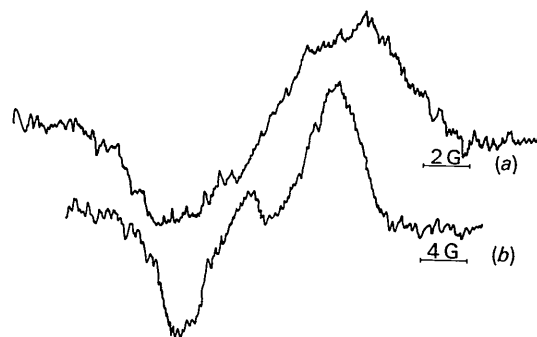


Fig. 2. The proton magnetic resonance spectra of C<sub>4</sub>H<sub>8</sub>Se · I<sub>2</sub> at (a) room temperature and (b) -200°C. Note the difference in scale.

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**Compound tessellations in crystal structures.** By HIROSHI TAKEDA\* and J. D. H. DONNAY, *Crystallographic Laboratory, The Johns Hopkins University, Baltimore, Maryland, U.S.A.*

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#### Introduction to tessellations

A *regular tessellation* (Coxeter, 1961, p. 61) is an assemblage of equal regular polygons that cover the plane without

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overlap or interstice. Schläfli proposed the symbol  $\{p, q\}$  to designate a tessellation of  $p$ -gons,  $q$  of which meet at each vertex. There are three regular tessellations. The vertices of  $\{4,4\}$  are the nodes of a primitive square net; those of  $\{3,6\}$  form a primitive hexagonal net. The vertices of  $\{6,3\}$ , on the other hand, do not make a net: they illustrate the structure

of a honeycomb. The dual of  $\{p,q\}$  being  $\{q,p\}$ , it is seen that  $\{4,4\}$  and its dual give a centered square net, while  $\{3,6\}$  and its dual  $\{6,3\}$  produce a hexagonal net, in which  $\{3,6\}$  defines the triple mesh and  $\{6,3\}$ , the corresponding  $H$ -centering nodes (Fig. 1).

Compound tessellations have been described by Coxeter (1948; 1961 to 1965) as follows. Start with the regular tessellation  $\{4,4\}$  and consider the vertex of coordinates  $(u,v)$ , say  $(2,1)$ . By applying rotations through one, two, and three right angles about the origin, we get four points in all:  $(u,v)$ ,  $(-v,u)$ ,  $(-u,-v)$ ,  $(v,-u)$ . The origin and these four points are the beginning of a new  $\{4,4\}$ , of edge  $\sqrt{u^2+v^2}$ , inscribed in the given  $\{4,4\}$ , of unit edge. By applying suitable translations we obtain a distribution of all the vertices of the original  $\{4,4\}$  among  $n=u^2+v^2$  such larger  $\{4,4\}$ 's. This set of  $n$   $\{4,4\}$ 's of edge  $\sqrt{u^2+v^2}$ , inscribed in a single  $\{4,4\}$  of unit edge, is called a compound tessellation and is denoted by

$$\{4,4\} [n\{4,4\}], \text{ with } n=u^2+v^2.$$

Here  $u$  and  $v$  may be any two non-negative integers, with  $u+v > 1$ .

Natural coordinates used by Coxeter in the study of the other tessellations are oblique coordinates, with interaxial angle equal to  $60^\circ$ . This system of coordinates will be convenient to handle problems in the hexagonal reciprocal lattice. In order to apply the concept of compound tessellations to crystal structures, however, it is better to choose the axes of coordinates according to crystallographic conventions: we use the Bravais axes, with  $a=b$  and interaxial angle  $\gamma=120^\circ$ . The vertices of a  $\{3,6\}$  of unit edge are all the points for which the coordinates  $u$  and  $v$  are integers. Consider a vertex  $(u,v)$ , say  $(2,1)$ . By applying rotations about the origin through multiples of  $60^\circ$ , we exhibit such a vertex  $(u,v)$  as belonging to a hexagon:  $(u,v)$ ,  $(u-v,u)$ ,  $(-v,u-v)$ ,  $(-u,-v)$ ,  $(v-u,-u)$ ,  $(v,v-u)$ . The origin and these six points constitute the beginning of a new  $\{3,6\}$ , of edge  $\sqrt{u^2-uv+v^2}$ , inscribed in the given  $\{3,6\}$ , of unit edge.

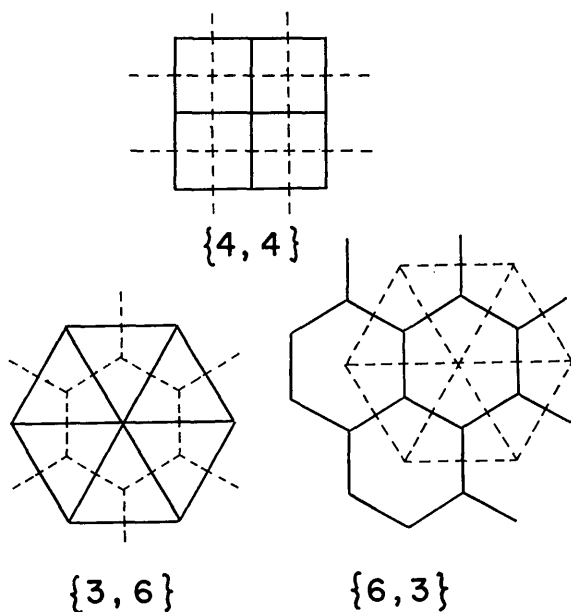


Fig. 1. The three regular tessellations (solid lines), each one with its dual (dashed lines). The vertices of the dual are inside the polygons of the original tessellation.

By applying suitable translations, we obtain a distribution of all the vertices of the latter among  $n=u^2-uv+v^2$  such larger  $\{3,6\}$ 's. This compound tessellation is denoted by

$$\{3,6\} [n\{3,6\}], \text{ with } n=u^2-uv+v^2,$$

where  $n$  is the multiplicity of the large cell. Examples of this compound tessellation (Fig. 2) are drawn for  $u=1$  and  $v$  ranging from 2 to 6; the corresponding multiplicities being 3, 7, 13, 21, and 31.

The concept of compound tessellations is useful to illustrate the relationships in two dimensions between: sub-net and net, net and supernet, crystal lattice and twin lattice. It can be applied to projections or to sections.

Iida (1957), although he did not mention the word tessellation, in a study of the layer structures found in magnetic oxides, described arrangements of points that are indeed compound tessellations of multiplicities 3 and 7. The latter has no physical representative.

The first compound tessellation recognized as such in crystallography was pointed out to us by Professor Coxeter, in 1963, in the structure of zinkenite (Sadanaga & Takeda, 1961). Other examples were then recognized in the structures of klockmannite, benstonite, and  $\text{CuAsSe}_2$  (Donnay & Takeda, 1963).

To classify crystal structures that contain closely packed ions, Loeb (1962, 1964) employed a subdivision of the hexagonal net into subarrays, which is nothing else than an hexagonal compound tessellation. Although he did not use the word tessellation either, he derived the multiplicity formula  $(h^2+hk+k^2)$ , which is the form\* that applies when the interaxial angle is equal to  $60^\circ$ . The examples given in his paper have multiplicities 3 (corundum), 4 (spinel and cuprite), and 12 (high-temperature quartz).

### Tessellations in crystallography

The regular tessellation  $\{4,4\}$ , crystallographically speaking, is a primitive square net. The compound tessellation  $\{4,4\} [n\{4,4\}]$ , with  $n=u^2+v^2$  and  $(u,v)=(1,1)$ , or  $\{4,4\} [2\{4,4\}]$ , is the supernet (double net) built on the double (centered) mesh.

The regular tessellation  $\{3,6\}$  is a hexagonal net. The compound tessellations are  $\{3,6\} [n\{3,6\}]$ , with  $n=u^2-uv+v^2$ .

\* Professor Coxeter (private communication) points out that the sequence of multiplicities may be represented equally well by the two forms  $h^2+hk+l^2$  and  $u^2-uv+v^2$  because of the identity  $(u-v)^2+(u-v)v+v^2=u^2-uv+v^2$ .

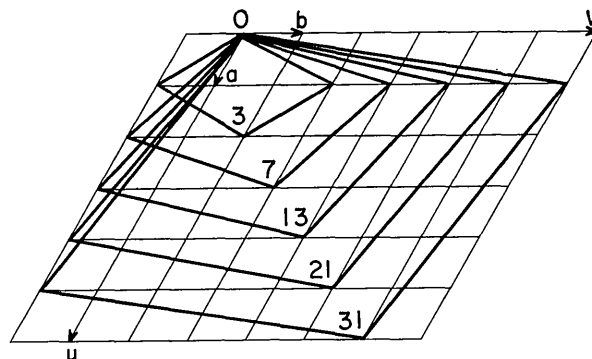


Fig. 2. Examples of compound tessellation  $\{3,6\} [n\{3,6\}]$ , where  $n=u^2-uv+v^2$  is the multiplicity of the large cell.

For  $(u,v)=(1,2)$  the compound tessellation is the  $H$  mode of the hexagonal net, and the multiplicity of the mesh is  $n=3$ .

For  $(u,v)=(1,3)$ ,  $n=7$ , no example is known.

For  $(u,v)=(1,4)$ ,  $n=13$ , an application is found in the twinning of klockmannite. Consider the projection on (001), given by Taylor & Underwood (1960, p. 362, Fig. 3). Starting with the net that has the smallest mesh, tessellation  $(u,v)=(4,1)$  defines the true net of crystal I, while tessellation  $(u,v)=(1,4)$  gives the net of crystal II. Likewise, starting from the true nets,  $(u,v)=(1,4)$  of crystal I and  $(u,v)=(4,1)$  of crystal II each gives the same supermesh. For all cells,  $c$  has the same value. The twin lattice may be defined either by the supercell or by the subcell of the true cell; the physical significance of the sublattice is obvious.

The same tessellation  $(u,v)=(1,4)$  also expresses the net, starting from a subnet, in  $\text{CuAsSe}_2$  (Sadanaga, 1962).

A third example is found in benstonite,  $\text{Ca}_7\text{Ba}_6(\text{CO}_3)_{13}$ , which was described by Lippmann (1962, p. 591, Fig. 1). This species is rhombohedral; its hexagonal cell has  $a=18.28$ ,  $c=8.67$  Å. The 'calcite subcell' of benstonite has  $a'=a/\sqrt{3}=5.07$ ,  $c'=2c=17.34$  Å (note that calcite has  $a=4.990$ ,  $c=17.06$  Å).

For  $(u,v)=(1,6)$ ,  $n=31$ , the compound tessellation expresses the net of zinkenite,  $\text{PbSb}_2\text{S}_4$ , from its subnet of metal atoms (Sadanaga & Takeda, 1961, 1964). The hexagonal subcell has  $a'=a/\sqrt{31}=3.98$ ,  $c'=c/2=2.16$  Å, with  $a=22.17$ ,  $c=4.33$  Å. The angle between the nearest  $a$  axes is  $8^\circ 57'$ . The concept of compound tessellation proved very helpful in deriving the structure of zinkenite.

The structure of koenenite,  $4\text{NaCl} \cdot 4(\text{Mg,Ca})\text{Cl}_2 \cdot 5\text{Mg}(\text{OH})_2 \cdot 4\text{Al}(\text{OH})_3$ , studied by Lohse, Allmann, Burzlaff & Hellner (1963), consists in an alternation of octahedral layers of two kinds: brucite-like OH double layers,  $[\text{Mg}_7\text{Al}_4(\text{OH})_{22}]^{4+}$ , and Cl double layers,  $[\text{Na}_4(\text{Ca,Mg})_2\text{Cl}_{12}]^{4-}$ . The Cl substructure is hexagonal —  $R$ :  $a_1=4.072$ ,  $c_1=3 \times 10.88=32.64$  Å, and the OH substructure is hexagonal —  $P$ :  $a_2=3.052$ ,  $c_2=10.88$  Å. The measured angle between  $a_1$  and  $a_2$  is  $28.3^\circ \pm 0.1^\circ$ . It can be explained by means of tessellations. As was pointed out by Allmann (1965), the compound tessellation  $(u,v)=(9,19)$ , with  $n=271$ , of the Cl layer, has a mesh with edge of  $4.072/\sqrt{271}=67.03$  Å, which can coincide with a block of  $22 \times 22$  meshes of the OH layer ( $3.052 \times 22=67.14$ ); and the predicted angle is  $28.26^\circ$ . Allmann also remarks that an angle of  $28.35^\circ$  can be predicted with the compound tessellation  $(u,v)=(19,40)$ ,  $n=1201$ , of the OH layer, in coincidence with a block of  $26 \times 26$  meshes of the Cl layer. The large mesh, in this case, would have an edge of  $105.67$  Å. A third possibility would be to consider a compound tessellation in each kind of layer, and let the meshes coincide.

The regular tessellation  $\{6,3\}$  is illustrated by the structure of a graphite sheet.

It is possible to extend the notion of tessellation to quasi-symmetrical cases. The twin lattice in cryolite,  $\text{Na}_3\text{AlF}_6$ , provides an example. The cell dimensions, determined by

Náray-Szabó & Sasvári (1938), are as follows:  $a=5.46$ ,  $b=5.61$ ,  $c=7.80$  kX,  $\beta=90^\circ 11'$ . The twinning is controlled by the pseudo-symmetry of a double cell, obtained by transformation  $110/110/001$ . This cell is a pseudo-cube, and in the (001) plane the compound tessellation  $\{4,4\} [2\{4,4\}]$  is approximated.

Galena-type substructures in freieslebenite and diaphorite, described by Hellner (1957, 1958), give other examples of this kind of approximate tessellation. Here the cells are orthorhombic, and their edges are multiples of the cell edge  $a'$  of the compound tessellation  $\{4,4\} [2\{4,4\}]$  of the galena-type substructure: for freieslebenite,  $a=2a'$ ,  $b=3a'$ ; for diaphorite,  $a=4a'$ ,  $b=8a'$ .

In pectolite  $\text{Ca}_2\text{NaHSi}_3\text{O}_9$  (Buerger, 1962) and miargyrite  $\text{AgSbS}_2$  (Hofmann, 1938), the subnets resemble  $\{3,6\}$ 's, but the meshes are parallelograms instead of  $120^\circ$  rhombs.

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**The structure of  $\text{AuMn}_3$ .** By P. GAUNT and A. EDEN, *Department of Physics, The University, Sheffield 10, England*

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Raub, Zwicker & Baur (1953) discovered two compounds in the Au–Mn phase diagram which gave very similar X-ray powder diffraction patterns. The structure of the compound

$\text{Au}_2\text{Mn}$  was determined by Herpin, Meriel & Meyer (1958) and Hall & Royan (1959). This compound has a spiral magnetic-spin structure and becomes ferromagnetic when a