their discontinuous bonding with the Tl atoms. The effect of this bonding is naturally less perceptible on O(9), O(10), O(11), O(12), O(18), O(19) and O(20) located in the (*xy*0) plane.

Discussion

The refinement suggests the formula $Tl_{7.7}Nb_{54.8}O_{146}$, which represents an electrical imbalance of about ten charges.

Since the difference syntheses do not show any excess of cations, we have carried out a refinement on the occupancy factor of O atoms with the highest temperature factors: O(2) and O(5). It shows that the O(2) site is occupied to 72% and O(5) to 81%, but the temperature factors do not drop and refinement does not improve. Thus no conclusions are possible.

To check whether or not fluoride impurities, always present with Nb, are the cause of the charge imbalance, a quantitative analysis for fluorine was made by fast γ-ray spectrometry (Borderie, Pinault & Barrandon, 1977) of the crystal studied and of the Nb_2O_5 used for the synthesis. It shows the atomic ratio $[F]/[O] = 0.028$ in Nb_2O_5 and ten times less in the crystal, consistent with the temperature of crystal formation. This small quantity of fluorine is not sufficient to lead to the charge imbalance. If this colourless, transparent oxide is electrically neutral, one can conclude that the charge imbalance is a combined effect of stacking faults of O atoms and an excess of cations, leading to the formula $Tl_{7.7}Nb_{54+x}O_{146-y}$.

The last problem is: why are the absorption coefficients given in *International Tables for X-ray Crystallography* (1974) almost twice as large as the observed values? It is possible that a systematic error occurred during the measurement of the intensities. We propose to continue the studies of absorption, with more favourable conditions, on another isotypic structure which should enable us to refine the model proposed here.

The non-stoichiometric tetragonal GTB niobates of monovalent ions, with $a \simeq 27.5$, $c \simeq 3.9$ Å, are built up from octahedra joined at corners which define tunnels with 4, 6 and 7 sides partially occupied by monovalent ions. This arrangement, first described by Gatehouse for a Rb niobate of unknown composition, is not observed in any other oxide. It seems to be stable enough to accommodate an excess of negative charge neutralized by a surplus of cations and probably by some vacancies of anions generating stacking faults.

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On the Stereochemistry of Valence Bonds and the Structures of XeO_3, XeF_4 and XeF_2

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Abstract

In the stereochemistry of valence bonds the difference in nucleus–lone pair and nucleus–bonding pair attraction is used to explain certain coordination geometry, and to predict the structures of simple molecules. The results are applied to the crystal structures of some Xe compounds.

In their theory of the stereochemistry of valence bonds, Sidgwick & Powell (1940) assumed that bonding pairs and lone pairs of electrons were of equal importance and distributed themselves to minimize interelectron repulsion. For example, three pairs are arranged to form a triangle, four a tetrahedron, five a trigonal prism and six an octahedron. The theory has proved successful, but could not account for the deviations from the tetrahedral angle that exist in NH_3 and H_2O.

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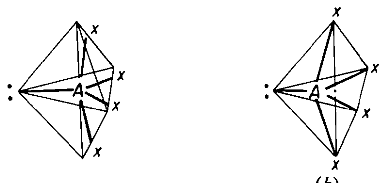
Also for the structure of the molecule ClF_3 it gave three different models.

Gillespie & Nyholm (1957) modified the theory by assuming that lone pairs are larger than bonding pairs, so that the repulsion between electron pairs decreases in the order: lone pair–lone pair > lone pair–bonding pair > bonding pair–bonding pair. This was used to explain the angles in NH_3 and H_2O, and a satisfactory model of ClF_3 could also be given: the lone pairs are in two equatorial positions in a trigonal bipyramid, as the repulsion between them is minimized.

The electron pairs are at the corners of a polyhedron with the nucleus at its centre. According to Gillespie & Nyholm the lone pair is so much bigger than a bonding pair that considerable distortions occur (Fig. 1*a*).

In our attempts to analyse and systematize structures of compounds with lone pairs, we used the space taken by a lone pair (and its cation) in a crystal to locate the centroid of its negative charge (Andersson & Åström, 1972; Galy, Meunier, Andersson & Åström, 1975). The volume of the lone pair was found to be of the same order as that of O^{2-} or F^-. Hence the lone pair was placed at the corner of a regular polyhedron such as the tetrahedron, trigonal bipyramid or octahedron. The lone pair–nucleus distance varies with the size of cations and anions, but is in the region of 1 Å. Sometimes, in compounds like $SbCl_3$ (Galy *et al.*, 1975), the lone-pair volume is small compared with the anion volume, and the tetrahedron is not regular. In this case the structure is best described as containing trigonal prisms of Cl^-, with the lone pair in the centre of the prism. This is also often the case for oxides or fluorides when the anion–cation ratio is high. Examples of this are SbF_3 and TeF_4, and the trigonal prisms are then distorted and enlarged.

The advantage of this approach is demonstrated in Fig. 1(*b*). The polyhedron is regular, and bond angles and bond distances are easily calculated for various ions (Galy *et al.*, 1975). There is no need to assume various magnitudes of repulsion between electron pairs. Instead we conclude that nucleus–electron pair attraction brings a lone pair closer to the nucleus than a bonding pair, since the bonding pairs are shared between two nuclei. The anions and the lone pair are roughly of the same size and *the cation must therefore be off-centre in the regular polyhedron* (Fig. 1*b*).



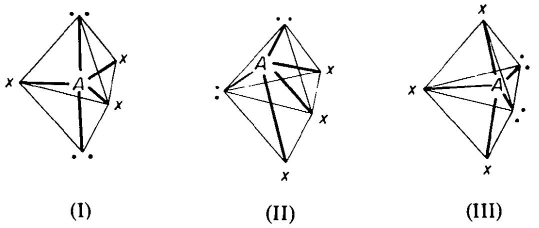
(*a*) (*b*)

Fig. 1. (*a*) Gillespie's repulsion model, with the lone pair at a corner and the cation at the centre of the polyhedron. (*b*) Our model. The lone pair–nucleus distance is determined by attraction. The lone pair and the anions are close packed. The lone pair + its cation form a corner of the polyhedron. The centre is empty.

Support for a short nucleus–lone pair distance is given by Verbaere, Marchand & Tournoux (1978). With an electrostatic model lone-pair positions were calculated for various Tl compounds. The Tl–*E* distances vary between 0·39 and 0·64 Å, close to the value (0·69 Å) obtained by Galy *et al.* (1975), and it will be interesting to follow their results with those for smaller cations.

The deviations from the tetrahedral angle observed in H_2O and NH_3 are a direct consequence of the shorter nucleus–lone pair distances. The three alternatives for ClF_3 are given in Fig. 2. The two lone pairs in axial positions in model (I), about 1 Å from the nucleus, would push out the F atoms far beyond bond distances; for steric reasons the structure is impossible. Model (II) is impossible with the two great differences in bond distances. Model (III) is the only one possible, and it represents the correct structure of the molecule ClF_3.

The structures of a large number of noble-gas compounds have been reported, and it is tempting to apply the ideas just described to explain the arrangement of molecules in crystals of some of these compounds. The models used to describe the bonding vary and cause confusion. Coulson (1964) states that two pictures are possible, *viz* a valence-bond resonance picture and a molecular-orbital picture. He also concluded that the hybridization model for xenon fluorides was inadequate. According to the Gillespie–Nyholm theory, XeF_2 should be a trigonal bipyramid with the three lone pairs in the equatorial plane and with sp^3d hybridization for the molecule (Gillespie, 1972). However X-ray data show that crystals of XeF_2 are tetragonal and that the linear molecules are aligned along the tetrad axes (Levy & Agron, 1963), which is inconsistent with a trigonal-bipyramidal arrangement of electron pairs. It is interesting that Lohr & Lipscomb (1963) showed from the MO model that the biggest binding energy in XeF_2 occurs when the molecule is linear and of symmetry $D_{\infty h}$. There is general agreement that these compounds are ionic. This means that structure and volume discussions should be useful for deriving centroids of lone pairs, as well as their geometrical shape and volume.



(I) (II) (III)

Fig. 2. Three alternatives for the structure of a molecule AX_3E_2.

XeO_3

XeO_3 is orthorhombic, $a = 6{\cdot}16$, $b = 8{\cdot}11$, $c = 5{\cdot}23$ Å, space group $P2_12_12_1$ (Templeton, Zalkin, Forrester & Williamson, 1963*b*). The volume divided by the number of oxygens + lone pairs is 16·35 $Å^3$; the corresponding figure for SbF_3 is 16·75 $Å^3$. The structure is shown in Fig. 3 and can be classified as an anti-Fe_3C type. In the cementite structure, described earlier as an example of chemical twinning in h.c.p., a C atom is situated in a two-capped trigonal prism of Fe atoms (Andersson & Hyde, 1974). In the XeO_3 structure the lone pair is at the centre of a somewhat distorted trigonal prism (Fig. 3). In $SbCl_3$ and $BiCl_3$ (Galy *et al.*, 1975) and SbF_3, all of anti-cementite type, the cations as well as the lone pairs are in the prisms. In the chlorides the trigonal prisms are of approximately the same shape as in cementite and, because of the large size of the anions, the prisms can accommodate the cations as well as the lone pairs. In SbF_3 the prism is smaller and has to become elongated to accommodate the lone pair as well as the cation. In the sequence $LaFeO_3$–LaF_3 a similar elongation of the trigonal prism was found, and shown to be due to an increase of the cation size, which leads to an increase in the coordination number of the cation (O'Keeffe & Hyde, 1977). In Xe^{6+} the distance between the nucleus and the lone-pair centroid has been calculated as 1·47 Å (1·09 Å for Sb^{3+}) (Galy *et al.*, 1975). This larger distance is obviously the reason why a trigonal prism of O^{2-} ions cannot accommodate a lone pair and Xe^{6+} at the same time. Consequently the cation is sitting in one of the capping square pyramids (Fig. 3).

XeO_3 is isostructural with HIO_3 (Templeton *et al.*, 1963*b*), while $NaIO_3$ is a normal anti-cementite. The distance I^{5+}—lone pair is calculated to be 1·23 Å, and I^{5+} is outside the trigonal prism in HIO_3, just like Xe in XeO_3. However, with Na in the normally empty octahedron in the cementite structure, there is considerable expansion of the crystal dimensions for $NaIO_3$ compared with HIO_3, and the trigonal prism in the crystal structure of $NaIO_3$ is big enough to accommodate I^{5+} and its lone pair.

XeF_4

XeF_4 is monoclinic, $a = 5{\cdot}05$, $b = 5{\cdot}92$, $c = 5{\cdot}77$ Å, $\beta = 99{\cdot}6°$ (Templeton, Zalkin, Forrester & Williamson, 1963*a*). The volume per fluorine and lone pair is rather low, 14·2 $Å^3$, which indicates that the two lone pairs could be closer to their nuclei than the lone pair is in Xe^{6+}. In the crystal, Xe^{4+} is surrounded by four F^- ions in a plane to form a XeF_4 molecule. The rhombic prism is a suitable building unit for cations which prefer square-planar coordination (Nyman, 1976) and in Fig. 4 it is shown how such units form the structure, and also how the lone pairs are organized in the centres of the trigonal prisms. These prisms are reasonably regular, again indicating that each of these double pairs is smaller than a single pair. The Xe—*E* distance is estimated to be 0·9–1·1 Å. In the ClF_3 molecule (Levy & Agron, 1963) the nucleus—lone pair distance must also be rather short, about 1·1 Å. Each of these double pairs belonging to Cl^{3+} is thus smaller than a single pair attached to Cl^{5+} would be; this is also in agreement with volume calculations on the crystal dimensions of solid ClF_3. The volume per anion and lone pair is 12·1 $Å^3$. The distance lone pair—fluorine in ClF_3 is about 2·25 Å, which is close to the corresponding distance in XeF_4.

With nucleus–lone pair attraction, a square-planar arrangement of anions is the only one possible for a close-packed molecule AX_4E_2.

The structure of XeF_4 is topologically the same as the structure of $CoGa_3$, with Co situated in the rhombic prisms by analogy with the lone-pair positions in XeF_4. Also, the XeF_4 structure is related to the CaF_2 structure type. The F atoms are arranged in a distorted primitive cubic structure, with the Xe atoms centring cube faces.

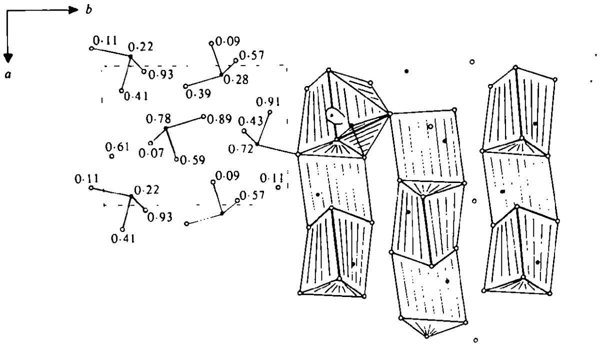


Fig. 3. The structure of XeO_3. Small circles are Xe^{6+}, situated in the capping square pyramids. The lone pairs are at the centres of trigonal prisms.

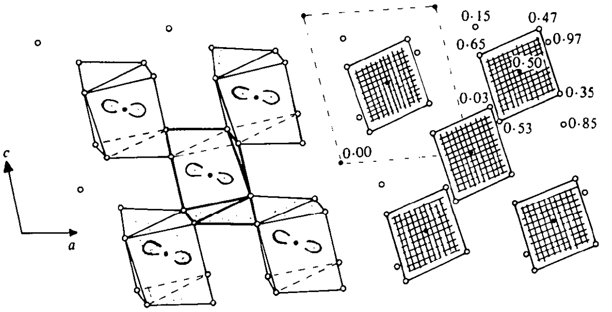


Fig. 4. The structure of XeF_4. Small circles are Xe^{4+}.

XeF_2

XeF_2 is tetragonal, $a = 4{\cdot}315$, $c = 6{\cdot}990$ Å, space group *I*4/*mmm* (Levy & Agron, 1963). Symmetric linear molecules are aligned in the tetrad axes with Xe—F = 1·98 Å. Volume calculations show that the three lone pairs on each Xe^{2+} take up a relatively small space; the volume per fluorine and lone pair is 13·0 $Å^3$. On the other hand the volume per fluorine is 32·5 $Å^3$ and, as the tetragonal symmetry excludes a trigonal-bipyramidal symmetry of the molecule XeF_2E_3, it is of considerable interest to find the shape of the space occupied by three lone pairs. If spheres of F^- ions of the normal radius 1·33 Å are packed with ions of Xe^{2+}, the remaining space is a ring around each Xe^{2+} (Fig. 5). It is surprising how well these rings and spheres fill space in this tetragonal structure. We cannot describe the electronic structure of the molecule but it is indeed tempting to call the ring a vortex, as if the three pairs are revolving around the nucleus.

The trigonal-bipyramidal structure contradicts the lone pair–nucleus attraction theory: the lone pairs would keep the F atoms too far away from the nucleus. However, with a vortex structure, the lone pairs are smeared out in a ring, and the F atoms can pack at a suitable distance from the nucleus.

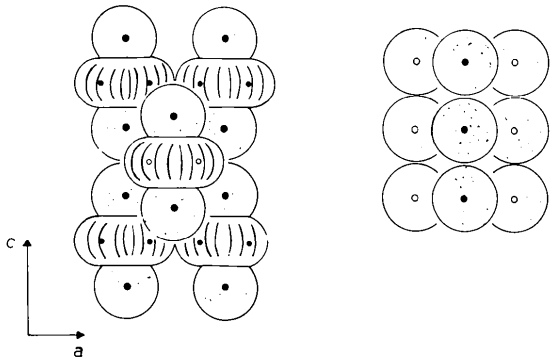


Fig. 5. The structure of XeF_2. To the right the anions are as in CaF_2. Large circles are anions, with the smaller circles marking their centres. Smallest circles mark the central circle of the vortex, its centroid. Xe atoms are omitted, but are situated in between the anions in the centre of the vortex.

The XeF_2 structure is related to the CaF_2 structure type. Xe^{2+} is situated in the middle of an edge of a cube of F atoms, and the transformation to obtain the fluorite structure is obvious. Perhaps high pressure could force the lone pairs into spherical symmetry around the Xe^{2+} nucleus, and cause XeF_2 to take the CaF_2 structure.

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Die Kristallstruktur von Bariumgermanat-hydrat $BaO.GeO_2.5H_2O$

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Abstract

The barium germanate hydrate $BaO.GeO_2.5H_2O$ crystallizes in space group *C*2/*c* with the unit-cell dimensions $a = 15{\cdot}677\,(5)$, $b = 8{\cdot}404\,(1)$, $c = 11{\cdot}368\,(2)$ Å, $\beta = 97{\cdot}60\,(2)°$ and $Z = 8$, $D_x = 3{\cdot}114$ Mg m^{-3}. The atomic positions, except for those of the H atoms, were determined by the X-ray method and refined to an *R* value of 0·081. The structure, which is

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