Crystal Structure and Lattice Energy of Thallium(I) Fluoride: Inert-pair Distortions

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The crystal structure of TlF has been redetermined from *X*-ray single-crystal (*R* 0·101 ; 105 observed reflections) and neutron powder data. Crystals are orthorhombic with $a = 5{\cdot}1848(2)$, $b = 6{\cdot}0980(3)$, $c = 5{\cdot}4916(2)$ Å, $Z = 4$, space group *Pm2a*. Two independent thallium ions have similar environments, surrounded by octahedra of fluoride ions, with two close approaches (Tl · · · F 2·25—2·62 Å), two intermediate distances, and two (*cis*) long approaches (Tl · · · F 3·07—3·90 Å). The lattice energy is recalculated as $-781{\cdot}9$ kJ mol^{-1}, but it is concluded that the presence of an aspherical thallium ion probably means that the model used for the calculation is inadequate.

THALLIUM(I) fluoride was originally examined crystallographically by Ketelaar;[1] the structure was reported to be a distortion of the sodium chloride type. It appeared to be an example of an inert-pair distortion, in which a metal ion with a formal s^2 configuration shows a substantial departure from a sphere, as judged by the distances to neighbouring anions. Dunitz and Orgel[2] pointed out that the reported structure must be incorrect as it gave the thallium atom a centrosymmetric environment, while inert-pair distortions are required theoretically to be non-centrosymmetric.

Because of the theoretical interest of these distortions, the structure was re-examined. Single-crystal *X*-ray techniques showed that Ketelaar's lattice assignment was incorrect and enabled the thallium atoms to be located precisely; a preliminary report was published.[3] The fluorine atom positions had rather high errors and these were therefore refined from neutron powder diffraction data. An independent examination[4] has confirmed the reassignment of the lattice, although proposing a different space group.

EXPERIMENTAL

Following Ketelaar,[1] thallium(I) fluoride was prepared by dissolving thallium(I) carbonate in 40% hydrofluoric acid in a platinum crucible; the solution was then evaporated to dryness and fused. On cooling, long prismatic crystals were formed, but single crystals could not be isolated. The solid was therefore dissolved in slightly more than the minimum quantity of water and eight times the volume of ethanol was added. This gave a slow precipitate of very thin flakes. In other preparations, when solutions of TlF in ethanol–water were allowed to evaporate, some chunky hexagonal plates were formed. These are probably identical to those reported by Barlow and Meredith.[4] They have been identified as Tl_3FCO_3 and their structure determined.[5]

The thin plates of TlF were very fragile and distorted readily, but a crystal was found which gave *X*-ray photographs of reasonable quality. For neutron powder studies, to reduce preferred orientation, a sample was fused and then ground to a powder.

Crystal Data.—Orthorhombic, $a = 5{\cdot}1848(2)$, $b = 6{\cdot}0980(3)$, $c = 5{\cdot}4916(2)$ Å, $U = 173{\cdot}63$ Å^3, $D_c = 8{\cdot}54$, $Z = 4$, $D_m = 8{\cdot}48$ (ref. 1). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 1747 cm^{-1}.

Unit-cell dimensions and standard deviations were determined by least-squares fit to the neutron powder pattern. Crystals were very thin flakes with *b* perpendicular to the flakes. Layers $l = 0$—4 were collected by the Weissenberg technique with Cu-K_α radiation. Intensities were estimated visually and Lorentz, polarization, and absorption corrections were applied, giving 105 observed reflections. The photographs were not of very high quality and the intense reflections in particular were suspected of being inaccurate.

Space Group.—The photographs showed a very marked pseudo-face-centering and this explains the F-lattice proposed by Ketelaar, whose oscillation photographs would not be expected to show very weak reflections. In fact, the lattice is primitive and the only systematic absence is $hk0$, $h \neq 2n$. A Patterson synthesis showed peaks at $0,\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},0$ of almost equal height, corresponding to a face-centred array of thallium atoms as would be expected from the pseudo-centering in the intensity pattern; on packing considerations, the fluorine atoms must also be approximately face-centred.

Of the reflections $h0l$ with $l \neq 2n$, only 201 is observable. This class of reflection is also very weak in the neutron data. Of the pseudo-face-centering conditions, $h + l \approx 2n$ is the most marked. Three space groups are consistent with the observed absence: $P2_1ma$ (No. 26, $Pmc2_1$ in standard setting), *Pm2a* (No. 28, *Pma2*), and *Pmma* (No. 51). Barlow and Meredith[4] failed to observe the reflection 201 and so reported space groups *Pmca* (No. 57, *Pbcm*) or $P2_1ca$ (No. 29, $Pca2_1$) (referred to our axes). The possible space groups can be reduced by considering ways of placing four TlF molecules in a nearly face-centred arrangement. All the space groups contain mirror planes, but face-centering is not consistent with atoms related by mirror planes, and so only the special positions lying in the mirror planes need be considered. In $P2_1ma$ this requires one Tl in *b* ($x_1,\frac{1}{2},z_1$; $\frac{1}{2} + x_1,\frac{1}{2},-z_1$) and one in *a* ($x_2,0,z_2$; $\frac{1}{2} + x_2,0,-z_2$) with $x_1 = 0$ (arbitrary), $x_2 \approx 0$, $z_1 \approx \frac{1}{4}$, $z_2 \approx \frac{3}{4}$. However, if these two atoms have nearly identical temperature factors, this placing of one atom in *b* and one in *a* gives a further extinction condition $0k0$, $k = 2n$, at variance with the observed reflections 050 and 070. In space group *Pmma*, positions *a*, *b*, *c*, *d* (symmetry $2/m$) produce vectors in the Patterson synthesis of type

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[1] J. A. A. Ketelaar, *Z. Krist.*, 1935, **92**, 30.

[2] J. D. Dunitz and L. E. Orgel, *Adv. Inorg. Chem. Radiochem.*, 1960, **2**, 42.

[3] N. W. Alcock, *Acta Cryst.*, 1969, **A27**, *S*101.

[4] M. Barlow and C. C. Meredith, *Z. Krist.*, 1969, **130**, 304.

[5] N. W. Alcock, *Acta Cryst.*, 1973, **B29**, 498.

$\frac{1}{2}$,0,0: one atom in *e* and one in *f* (*mm*) can be discarded for the same reason as *a* and *b* in $P2_1ma$, and *i*, *j* and *k* (*m*) produce vectors of type 0,2*y*,0.

In space group *Pm*2*a*, two independent Tl atoms must be placed in *c* ($\frac{1}{4},y,z$; $\frac{3}{4},y,-z$) with $y_1 = 0$ (arbitrary), $z_1 \approx \frac{1}{4}$; $y_2 \approx \frac{1}{2}$, $z_2 \approx \frac{3}{4}$. The two fluorine atoms (also in *c*) will then have $y_1 \approx \frac{1}{2}$, $z_1 \approx \frac{1}{4}$; $y_2 \approx 1$, $z_2 \approx \frac{3}{4}$ and this imposes no unacceptable conditions on the reflections. Barlow and Meredith showed that (with an origin shift) the space group $P2_1ca$ allows the same approximate structure (with one Tl and one F in position 4*a*) but imposes an extra relationship $z_2 = -z_1$; they quoted ideal co-ordinates for the face-centred arrangement in this space group, but did not attempt refinement. Position *d* in *Pmca* again does not allow a face-centred arrangement, producing vectors of type 0,$\frac{1}{2}$,0.

The positions of the two thallium atoms were refined in space group *Pm*2*a* to *R* 0·19. A difference-Fourier synthesis showed two peaks at possible fluorine positions, and on insertion of these, refinement gave *R* 0·162. Because the thickness of the crystal was very uncertain, a series of refinements were done, varying the assumed thickness, applying an absorption correction, and refining by least squares. This gave a minimum at *t* 0·0006 cm, *R* 0·101. All these calculations were done with the '*X*-RAY '63' system on the SRC ATLAS computer.[6a] Scattering factors were from ref. 6*b*.

At this stage, the errors in the fluoride ion co-ordinates were too great to give much information about the co-ordination. Neutron powder data were therefore collected on the high-resolution Petten powder diffractometer. The beam was collimated by 15′ Soller slits, monochromated by reflection from Cu (111 plane, $\lambda = 2{\cdot}5702$ Å), diffracted from the sample contained in a 15 mm vanadium can and passed through a further set of 15′ Soller slits to the counter. The pattern was collected from 10·8—144° (2θ). Refinement, starting from the *X*-ray co-ordinates, converged to *R* 0·075, (based on I), using the profile-fitting program.[7,8]

A second run with 30′ Soller slits gave noticeably worse resolution, and was not used. A substantial correction for preferred orientation had to be applied, as could be expected from the nature of the crystals. The peak halfwidth (in dmc units, 10^4 dmc = 360°) was given by: $H^2_\theta = 607 \,.\, \tan^2\theta - 774 \tan\theta + 358$, with the three numerical parameters refined; no asymmetry parameter was needed. Temperature factors were varied for each atom type. The scattering lengths used were: Tl 0·890, F 0·574. Standard deviations were obtained from the diagonal elements of the inverse matrix.

Final atomic parameters are in Table 1. *X*-Ray and neutron results agree well, with the exception of Tl(2) *Z* for which the discrepancy may indicate that the *X*-ray standard deviations are rather underestimated. Observed and calculated *X*-ray and neutron structure factors and the point-by-point observed and calculated neutron powder pattern are listed in Supplementary Publication No. SUP 21051 (10 pp. 1 microfiche).*

The final neutron parameters have been used in all further calculations. Because $P2_1ca$ could not be conclusively excluded by the single inconsistent reflection, refinement was attempted with the *X*-ray data in this space group, starting with the best thallium atom position obtainable from a mean of Tl(1) and Tl(2). A fluorine atom peak appeared on a difference synthesis, but refinement terminated at *R* 0·16. Final confirmation that this space group is not satisfactory came from a refinement of the neutron data in space group $P2_1ca$; this could not be continued below *R* 0·17.

TABLE 1

Final atomic and thermal parameters, with standard deviations in parentheses. Values from the *X*-ray refinement are listed first, with those from the neutron refinement second

Atom	*X*	*Y*	*Z*	B/Å^2
Tl(1)	0·25	0·0	0·2425(15)	1·5(2)
		0·0	0·2400(16)	1·39(8)
Tl(2)	0·25	0·4877(16)	0·7348(18)	2·2(3)
		0·4869(9)	0·7450(15)	1·39
F(1)	0·25	0·52(4)	0·20(3)	4(4)
		0·5719(24)	0·1943(19)	2·41(11)
F(2)	0·25	0·86(1)	0·67(2)	0(1)
		0·8500(26)	0·6713(19)	2·41

DISCUSSION

Structural Results.—The crystals of TlF are built up of F^- and distorted Tl^+ ions with no indications of directed interactions. The structure shows a general relationship to the sodium chloride type, but the atomic positions, particularly of the fluoride ions depart substantially from the ideal values. The most striking feature is that the two independent thallium ions have different environments (Table 2) although they show the same pattern. Each is surrounded by a distorted octahedron of fluoride ions of which two (*cis*) are much more distant than the others (Figure). This can be seen as the result of an aspherical thallium ion, in which the s^2 lone pair has been distorted, probably by mixing with a *p* orbital, producing a bulge on one side towards the distant fluoride ions (Tl · · · F 3·07—3·91 Å), and a reduction in size on the other towards the nearest fluoride ions (Tl · · · F 2·25—2·62 Å). The difference between the two thallium environments may indicate that the bulge and contraction are either pointed almost directly towards two fluorine atoms [Tl(2)] or more nearly midway between two pairs [Tl(1)]. Alternatively, there may be a real difference in degree of distortion between the two atoms; this is certainly not impossible, because the change from TlF to TlCl leads to the complete disappearance of any distortion.[9] The difference between the two environments presumably arises as a result of packing effects.

The only compound to which TlF can be directly compared is Tl_3FCO_3 (ref. 5), because no other highly ionic salt of Tl^+ has been examined in detail. In

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[6] (*a*) '*X*-Ray '63,' program system, Report TR 64 6, University of Maryland; (*b*) 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[7] H. M. Rietveld, *Acta Cryst.*, 1967, **22**, 151.

[8] H. M. Rietveld, RCN Report 104, Petten, 1969; *J. Appl. Cryst.*, 1969, **2**, 65.

[9] R. W. G. Wyckoff, 'Crystal Structures,' vol. 1, 2nd edn., Interscience, New York, 1963.

Tl_3FCO_3 the thallium ions are again very distorted. They have seven neighbours, rather than the six in TlF, in monocapped octahedral geometry. Three atoms (*cis*) are distant (Tl $\cdots$ O 3·06—3·19 Å) corresponding to the bulge of the Tl^+ ion, three are intermediate (Tl $\cdots$ O and Tl $\cdots$ F 2·74—2·89 Å), and one opposite the bulge is short (Tl $\cdots$ O 2·61 Å). This then corresponds closely to the geometry in TlF, although in the present compound the distortion is rather more marked, with the longest Tl $\cdots$ F 3·07—3·91 and the shortest 2·25—2·62 Å.

TABLE 2

Interatomic distances and angles with standard deviations in parentheses

(*a*) Distances (Å)

Tl(1) $\cdots$ F(2^{I})	2·539(14)	Tl(2) $\cdots$ F(2)	2·251(17)
Tl(1) $\cdots$ F(1^{I})	2·623(14)	Tl(2) $\cdots$ F(1^{V})	2·521(13)
Tl(1) $\cdots$ F(2^{II})	2·792(6)	Tl(2) $\cdots$ F(1^{VI})	2·665(3)
Tl(1) $\cdots$ F(2^{III})	2·792(6)	Tl(2) $\cdots$ F(1^{VII})	2·665(3)
Tl(1) $\cdots$ F(2^{IV})	3·254(14)	Tl(2) $\cdots$ F(1)	3·069(13)
Tl(1) $\cdots$ F(1)	3·496(14)	Tl(2) $\cdots$ F(2^{I})	3·905(17)

(*b*) Angles (°)

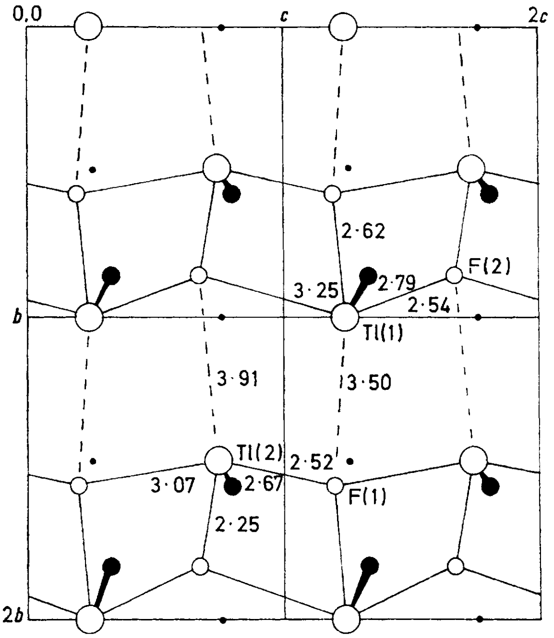
F(2^{I}) $\cdots$ Tl(1) $\cdots$ F(1^{I})	74·4(4)
F(2^{I}) $\cdots$ Tl(1) $\cdots$ F(2^{II})	73·7(3)
F(2^{I}) $\cdots$ Tl(1) $\cdots$ F(2^{III})	73·7(3)
F(2^{I}) $\cdots$ Tl(1) $\cdots$ F(2^{IV})	142·6(5)
F(2^{I}) $\cdots$ Tl(1) $\cdots$ F(1)	115·2(4)
F(1^{I}) $\cdots$ Tl(1) $\cdots$ F(2^{II})	72·0(3)
F(1^{I}) $\cdots$ Tl(1) $\cdots$ F(2^{III})	72·0(3)
F(1^{I}) $\cdots$ Tl(1) $\cdots$ F(2^{IV})	68·2(4)
F(1^{I}) $\cdots$ Tl(1) $\cdots$ F(1)	170·4(4)
F(2^{II}) $\cdots$ Tl(1) $\cdots$ F(2^{III})	136·4(4)
F(2^{II}) $\cdots$ Tl(1) $\cdots$ F(2^{IV})	94·3(3)
F(2^{II}) $\cdots$ Tl(1) $\cdots$ F(1)	109·8(3)
F(2^{III}) $\cdots$ Tl(1) $\cdots$ F(2^{IV})	94·3(3)
F(2^{III}) $\cdots$ Tl(1) $\cdots$ F(1)	109·8(3)
F(2^{IV}) $\cdots$ Tl(1) $\cdots$ F(1)	102·2(4)
F(2) $\cdots$ Tl(2) $\cdots$ F(1^{V})	88·5(5)
F(2) $\cdots$ Tl(2) $\cdots$ F(1^{VI})	80·3(3)
F(2) $\cdots$ Tl(2) $\cdots$ F(1^{VII})	80·3(3)
F(2) $\cdots$ Tl(2) $\cdots$ F(1)	70·0(4)
F(2) $\cdots$ Tl(2) $\cdots$ F(2^{I})	163·7(5)
F(1^{V}) $\cdots$ Tl(2) $\cdots$ F(1^{VI})	80·7(3)
F(1^{V}) $\cdots$ Tl(2) $\cdots$ F(1^{VII})	80·7(3)
F(1^{V}) $\cdots$ Tl(2) $\cdots$ F(1)	158·4(5)
F(1^{V}) $\cdots$ Tl(2) $\cdots$ F(2^{I})	107·8(4)
F(1^{VI}) $\cdots$ Tl(2) $\cdots$ F(1^{VII})	153·3(5)
F(1^{VI}) $\cdots$ Tl(2) $\cdots$ F(1)	95·2(3)
F(1^{VI}) $\cdots$ Tl(2) $\cdots$ F(2^{I})	101·9(3)
F(1^{VII}) $\cdots$ Tl(2) $\cdots$ F(1)	95·2(3)
F(1^{VII}) $\cdots$ Tl(2) $\cdots$ F(2^{I})	101·9(3)
F(1) $\cdots$ Tl(2) $\cdots$ F(2^{I})	93·8(4)

Roman numeral superscripts denote the following equivalent positions, relative to the reference molecule at x, y, z:

I $x, y - 1, z$
II $1 - x, y - 1, 1 - z$
III $-x, y - 1, 1 - z$
IV $x, y - 1, z - 1$
V $x, y, 1 + z$
VI $1 - x, y, 1 - z$
VII $-x, y, 1 - z$

There is a clear empirical correlation (Table 3; further considered later) for the elements with stable s^2 ions, Tl^+, Sn^{2+}, and Pb^{2+}, where a small anion gives a distorted structure and a large one a regular structure. Also, the smaller the cation, the larger is the anion needed to produce a regular structure.

Packing.—The Figure shows the dominant feature of the packing of TlF, that the thallium ions are in layers held together by close Tl $\cdots$ F interactions, but that in the *b* direction there are only long Tl $\cdots$ F interactions between the layers. This corresponds to the extreme platy habit of the crystals.



The structure of TlF shown in projection down *a*. Large circles are thallium at $x = 0·25$, small circles fluorine: open, at $x = 0·25$, and solid, at $x = 0·75$ and $-0·25$. Dashed lines indicate long interactions in the *b* direction. Thallium atoms at $x = 0·75$ (whose interactions are not shown) are indicated by dots. For clarity, Tl(1) and F(1) are shown in the cell ($y + 1$, $z + 1$), Tl(2) is shown in the cell ($y + 1$), and F(2) is shown in the cell ($z + 1$)

Lattice Energy (*By N. W. Alcock and H. D. B. Jenkins*).—Calculations of the lattice energy of TlF have been made, in the hope that these might throw light on the cause of the distortion. A preliminary calculation, based on the *X*-ray co-ordinates,[3] was criticised by Ladd and Lee[10] who gave alternative, apparently self-consistent figures. However, examination has shown that their results are entirely meaningless. They claim to have used the structure determination of Barlow and Meredith,[4] but as has been noted, the latter did not determine a refined structure, but proposed a space

TABLE 3

Distorted and undistorted MX structures (Anion size increased from left to right)

Distorted	Undistorted
TlF	TlCl, TlBr
SnO, SnS, SnSe	SnSe, SnTe
PbO	PbS, PbSe, PbTe

Data from ref. 9, except for SnSe (undistorted) from A. Nishiyama and T. Okada, *Mem. Fac. Sci. Kyushu Univ.*, 1960, **B3**, 3; *Chem. Abs.*, 1961, **55**, 14004*h*.

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[10] M. F. C. Ladd and W. H. Lee, *Trans. Faraday Soc.*, 1970, **66**, 2767.

group, together with an idealised set of co-ordinates satisfying the face-centred condition exactly from which refinement could begin.*

A further calculation by Ladd and Lee[10] with the original co-ordinates of Ketelaar led them to discard this structure because the crystal energy was improbably large, a surprising result in view of the fact that this and the Barlow and Meredith[4] structures are identical, apart from an origin shift. Their suggestion from this calculation that Ketelaar's sample was likely to be impure, seems to ignore both the likely location of error in such work, in the co-ordinates, and the good agreement in cell constants between Ketelaar,[1] Barlow and Meredith,[4] and Alcock.[3]

By use of the refined co-ordinates from the neutron powder data, a recalculation of the lattice energy gives $U(R)$ $-781{\cdot}9$ kJ mol^{-1}. This is close to the value of -770 kJ mol^{-1} obtained in a refined calculation based on the original *X*-ray data.[10] †

The lattice-energy calculated from a Born–Haber cycle, ΔU_c, is -837 kJ mol^{-1} (ref. 10). Ladd and Lee commented in relation to the original value, that the difference of 67 kJ mol^{-1}, implying a covalent contribution of this magnitude, was difficult to reconcile with the high solubility of TlF in water, and this comment is still valid for the revised lattice energy. We believe that this difference may be due to deficiences in the calculation because of the presence of non-spherical ions, rather than to covalency, and it does not then follow that it should result in low solubility. The energy of solution will mainly depend on the difference in lattice energy and ion hydration energy. In water, the thallium ion will almost certainly also have an asymmetric environment, probably with six water molecules arranged similarly to the fluoride ions in the crystal. Because of the chemical similarity between H_2O and F^-, it is reasonable to suppose that the non-spherical effects on the lattice energy are offset by non-spherical effects on the hydration energy.

A further argument suggests that the discrepancy between the calculated and the 'gross' lattice energy (*i.e.* the energy to convert crystal into gaseous distorted ions) is even greater than the values given would indicate. No account has been taken of the energy needed to distort the thallium ion, which is spherical in its s^2 ground-state. The distortion can be considered to take place by partial mixing of the *p* orbital with the *s* orbital, with the electron pair being in an orbital of *sp* type. In the limiting case, this would correspond to the promotion of one electron to the *p* orbital, requiring 589 kJ mol^{-1} followed by hybridization.[11] In reality, the hybrid orbital is not likely to contain as much as 50% *p* character, but it is clear that considerable energy will be needed to distort the thallium ion, and this energy, as well as the 'observed difference,' must be counter-balanced by an extra bonding energy of the crystal.

The calculation of lattice energy for TlF, although made by the best available method, is still likely to be inaccurate for the following reasons. The Tl^+ ions in TlF are very far from spherical, with apparent radii ranging from 0·93 to 2·59 Å in different directions [assuming 1·32 Å for the radius of F^- (ref. 12)]. This distortion must be accompanied by some shift in the position of the positive charge, towards the 'bulge,' and the calculation of electrostatic energy will therefore be inaccurate. There is a further effect on the repulsion energy, because the presence of fluoride ions as close to the thallium ions as 2·25 and 2·53 Å will not lead to the same repulsion as would be expected with a spherical thallium ion.

The reason for distortion occurring in TlF, PbO, *etc.* and not in TlCl or PbS can possibly be understood from consideration of the lattice energy. It is a thermodynamic necessity that the net lattice-energy of the distorted form exceeds that of the undistorted form. This net lattice-energy will be the difference between the gross lattice-energy arising from interaction between the already distorted ions, and the energy needed to distort the cation; the gross lattice-energy must therefore exceed the lattice-energy of the undistorted salt. The source of this increased gross lattice-energy may lie in electrostatic effects, when it would be greater for a small anion (giving short cation–anion distances, which are reduced proportionately more by a distortion in the cation shape). Only for these salts would the increase in gross lattice-energy be sufficient to compensate for the distortion-energy of the cation. Similarly, a small cation (*e.g.* Sn) in place of a large one (*e.g.* Pb) would allow distortion to occur with a larger anion. Even if this electrostatic source is not correct, it is likely that the change in gross lattice-energy on distortion is approximately proportional to the initial lattice-energy, while the cation distortion-energy should not be affected by a change in anion.

A rigorous test of this proposal would require a comparison of the electrostatic energies for both distorted and undistorted forms of the same salt. These values are not accessible, and even those electrostatic energies which can be calculated are suspect, for the reasons discussed. However, an estimate of the lattice-energy, excluding covalent contributions, of an undistorted TlF can be obtained from the approximate formula:

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* Recalculation has shown that these ideal co-ordinates were in fact used. Some further errors in the published results of Ladd and Lee should be noted because of the difficulties that are imposed on attempts to check the calculations. The most significant is that *R*, the minimum interionic separation is given as 2·90 Å, instead of 2·595 Å, and this value has been used in the calculation of *A*, the Madelung constant, which is therefore given as 1·8329, instead of 1·6407. It seems, however, that for most of their calculation the correct values of *R* and *A* were used, and that the numerical values of *C* and *D* are correct, as printed. It should also be noted that the units of β are correctly 10^6 bar^{-1}, and of *D* are 10^{76} erg cm^8 ion-pair^{-1}.

† The preliminary value[3] was -724 kJ mol^{-1} but for this a very crude model was used for the repulsion energy. All previously published values have been converted from kilocalories to kilojoules (1 calorie = 4·184 joules).

[11] C. E. Moore, 'Atomic Energy Levels,' National Bureau of Standards, Circular 467, 1958.

[12] T. C. Waddington, *Trans. Faraday Soc.*, 1966, **62**, 1482.

$U(R) = -K/R\,.\,(1 - 0{\cdot}345/R)$. With values of R and $U(R)$ from ref. 10, K is 626·1 for TlCl, 625·0 for TlBr, and 629·7 for TlI. Then taking $R_{\mathrm{TlF}} = R_{\mathrm{TlCl}} - (r_{\mathrm{Cl^-}} - r_{\mathrm{F^-}}) = 2{\cdot}82$ Å (with $r_{\mathrm{Cl^-}}$ and $r_{\mathrm{F^-}}$ from ref. 12) and $K = 625{\cdot}5$ gives $U(R) = -814{\cdot}6$ kJ mol^{-1}. The true (non-covalent) lattice-energy of distorted TlF is probably close to the -837 kJ mol^{-1} given by a Born–Haber cycle calculation, *i.e.* the specifically covalent contribution is small. This difference between *ca.* 837 and *ca.* 815 kJ mol^{-1} gives the driving force for distortion, and is sufficiently small to make it plausible that when the lattice-energy of the undistorted form is considerably lower (*e.g.* -707 kJ mol^{-1} for TlCl) the gross gain on distortion is not sufficiently large to compensate for the energy needed to distort the Tl^+ ion.

CALCULATIONS

A term-by-term lattice-energy calculation (Table 4) for thallium(I) fluoride was performed with the refined neutron co-ordinates (Table 1), by use of the equation:[13] $U = U_M + U_R + U_D + U_Z$.

TABLE 4

Values obtained for parameters in the term-by-term calculation for thallium(I) fluoride

M	1·318461
L/Å	2·2509
U_M/kJ mol^{-1}	−813·8
c'_{++}	1·25
c'_{--}	0·75
c'_{+-}	1·00
$10^{12}b$/ergs ion pair^{-1}	1·00
$10^3\sum\exp(-R_{++}/\rho)$	0·13809
$10^3\sum\exp(-R_{--}/\rho)$	0·50740
$10^3\sum\exp(-R_{+-}/\rho)$	1·87761
U_R/kJ mol^{-1}	147·7
$I(\mathrm{Tl^+} \longrightarrow \mathrm{Tl^{2+}})$/eV	20·42
$10^{12}\,\varepsilon_+$/ergs ion pair^{-1}	24·52
$10^{12}\,\varepsilon_-$/ergs ion pair^{-1}	19·00
$10^{24}\,\alpha_+$/cm^3	5·2
$10^{24}\,\alpha_-$/cm^3	0·64
$10^{60}\,c_{++}$/ergs cm^6	497·6
$10^{60}\,c_{--}$/ergs cm^6	5·8
$10^{60}\,c_{+-}$/ergs cm^6	53·4
$10^3\sum_6^{++}$/Å^{-6}	3·87975
$10^3\sum_6^{--}$/Å^{-6}	6·38169
$10^3\sum_6^{+-}$/Å^{-6}	13·76947
$10^{60}\,C$/ergs cm^6	223·6
U_{dd}/kJ mol^{-1}	−103·3
$10^{76}\,d_{++}$/ergs cm^8	1115·0
$10^{76}\,d_{--}$/ergs cm^8	5·4
$10^{76}\,d_{+-}$/ergs cm^8	84·6
$10^3\sum_8^{++}$/Å^{-8}	0·22415
$10^3\sum_8^{--}$/Å^{-8}	0·53241
$10^3\sum_8^{+-}$/Å^{-8}	1·73711
$10^{76}\,D$/ergs cm^8	180·1
U_{qd}/kJ mol^{-1}	−16·3
U_D/kJ mol^{-1}	−119·6
U_Z/kJ mol^{-1}	3·76
U/kJ mol^{-1}	−781·9

The Madelung constant, M, was evaluated by the method of Bertaut[14] and is quoted based on the shortest distance, L, in the crystal. The electrostatic component of the lattice-energy, U_M, was evaluated by use of the conversion factor 1 e^2 Å^{-1} = 1389·3 kJ mol^{-1}. The repulsion term U_R was calculated by Huggins' method[15] with $\rho = 0{\cdot}345$ Å, taking the 'basic radii' $\bar{r}_+$ and $\bar{r}_-$ for Tl^+ and F^- to be 1·32 and 1·10 Å respectively (Tl^+ and Rb^+ have the same Goldschmidt radii and were assumed to have equal 'basic radii').

$$\begin{aligned} U_R &= U_R{}^{+-} + U_R{}^{++} + U_R{}^{--} \\ &= b\Big[c'_{+-}\exp\Big(\frac{\bar{r}_+ + \bar{r}_-}{\rho}\Big)\sum\exp\Big(-\frac{R_{+-}}{\rho}\Big) \\ &\quad + \tfrac{1}{2}\Big\{c'_{++}\exp\Big(\frac{2\bar{r}_+}{\rho}\Big)\sum\exp\Big(-\frac{R_{++}}{\rho}\Big) \\ &\quad + c'_{--}\exp\Big(\frac{2\bar{r}_-}{\rho}\Big)\sum\exp\Big(-\frac{R_{--}}{\rho}\Big)\Big\}\Big] \end{aligned}$$

The exponential sums required were performed exhaustively.

For U_D, the method of Meyer was used.[16] The most recent polarisability values[17] were employed.

$$\begin{aligned} U_D &= U_{dd} + U_{qd} \\ U_{dd} &= c_{+-}\textstyle\sum_6^{+} + \tfrac{1}{2}(c_{++}\sum_6^{++} + c_{--}\sum_6^{--}) \\ U_{qd} &= d_{+-}\textstyle\sum_8^{+-} + \tfrac{1}{2}(d_{++}\sum_8^{++} + d_{--}\sum_8^{--}) \end{aligned}$$

where

$$\sum\nolimits_n^{ij} = \sum_{\substack{i\\ i \neq j}}\sum_{j}(1/R_{ij})^n$$

The $\sum_n^{ij}$ summations were performed exhaustively.

The oscillator energy, ε_+, was taken[16] as 0·75 of the second ionisation potential (I) of Tl^+ (ref. 11) with ε_- taken from ref. 18. The electron numbers (p_+ and p_-) were computed following Meyer,[16,18] by use of the Herzfeld and Wolf[19] formula to calculate p_+ and p_-, and then for F^-, replacing the calculated p_- value by the geometric mean of this value and 8 (the expected value).

For the zero-point energy, the Debye frequency was estimated to be 140 cm^{-1}, the maximum of the broad i.r. absorption band (examined on an FS 720 i.r. interferometer). The final result is U $-781{\cdot}9$ kJ mol^{-1}.

As a check, the summation has also been performed by use of the equation of Ladd and Lee[10] which avoids direct calculation of U_R, with constants (other than those in Table IV) from their paper. This gave ρ/L 0·096 and U $-779{\cdot}4$ kJ mol^{-1}.

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