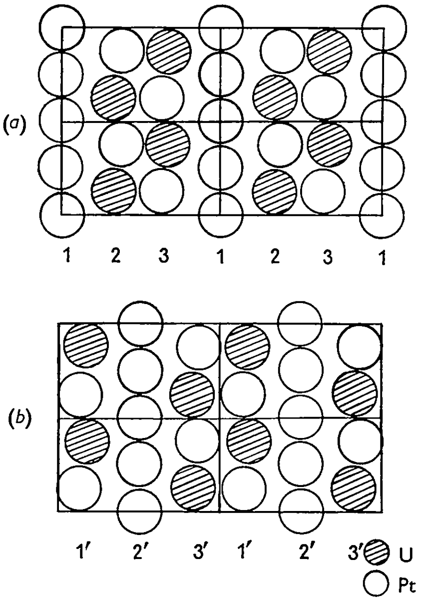

Fig. 2. UPt_2 atoms on planes $z = 0$ and $z = \frac{1}{2}$.

to c as shown in Figs. 1(*a*) and (*b*). The atoms in UPt_2 are also arranged on two planes perpendicular to c as shown in Figs. 2(*a*) and (*b*).

UPt_3 can be converted to UPt_2 by removing the rows of atoms 3 from Fig. 1(*a*) thus allowing rows 2 and 4 to move closer together to give the packing of Fig. 2(*a*). Similarly by removing rows 2′ from Fig. 1(*b*) rows 3′ and 1′ move closer together. If these two planes are then moved $\mathbf{b}/6$ relative to each other, the UPt_2 packing sequence is obtained. These changes remove 4 Pt atoms from the UPt_3 orthohexagonal cell leaving 4 uranium and 8 platinum atoms as required for the UPt_2 structure.

The similarity between the two structures suggests that nucleation of UPt_2 on UPt_3 and of the rearrangement from UPt_3 to UPt_2 by diffusion will be comparatively easy, and therefore the reaction to equilibrium should be correspondingly rapid.

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The Lattice Energies of Alkaline Earth Fluorides

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The lattice energies U_0 of the alkaline earth fluorides CaF_2, SrF_2, and BaF_2 have been derived by term-by-term theoretical calculation. The results have been compared with 'experimental lattice energies' U obtained from thermodynamic data using the Born-Haber cycle. The values of U_0 and U are respectively for CaF_2 610, 617, for SrF_2 582, 584, and for BaF_2 550, 549 kcal/mole at 0 °K. The small discrepancies in the case of CaF_2 and SrF_2 have been attributed to some deformation and interpenetration of the ions in the crystals.

1. Introduction

This communication reports calculations of lattice energies of the alkaline earth fluorides CaF_2, SrF_2, and BaF_2. Theoretical values for the lattice energies have been computed on the basis that the compounds are ionic crystals with a van der Waals potential. The underlying theory is that of Born & Mayer (1932), and the method used is similar to that employed by Morris (1958) for alkali monosulphides. The results are presumably more accurate than those previously obtained, using approximation equations, by Sherman (1932), Yatsimirskii (1951), Morris (1957), and others.

The theoretically calculated lattice energies have been compared with 'experimental' values derived from thermodynamic data by means of the Born–Haber cycle.

2. Theoretical calculation of lattice energies

The lattice energy per mole at 0 °K. of an ionic crystal is given by the following expression (Born & Mayer, 1932; Huggins, 1937):

$$U_0 = U_E - U_R + U_W - U_Z\,, \qquad (1)$$

where U_E is the Coulomb or electrostatic energy of attraction between the ions, U_R is the repulsion energy, U_W the van der Waals energy, and U_Z the zero-point energy. The terms U_E, U_R, U_W and U_Z for alkaline-earth fluorides can be calculated individually by means of the following equations:

$$U_E = e^2NA/r_0 \qquad (2)$$

$$\begin{aligned} U_R = bN[&nc_{+-}\exp\{(r_+ + r_- - r_0)/\varrho\} \\ &+ \tfrac{1}{2}n'c_{++}\exp\{(2r_+ - k_1r_0)/\varrho\} \\ &+ n''c_{--}\exp\{(2r_- - k_2r_0)/\varrho\}] \end{aligned} \qquad (3)$$

$$U_W = N(C/r_0^6 + D/r_0^8) \qquad (4)$$

$$U_Z = \tfrac{27}{8}.Nh\nu_{\text{max.}}\,. \qquad (5)$$

The symbols in these equations have the following significance:

N = Avogadro number;
e = electronic charge;
A = Madelung constant, referred to r_0, for the fluorite lattice;
r_0 = shortest equilibrium distance between anion and cation;
b = a repulsion constant obtainable from the condition
$$(dU_0/dr)_{r=r_0} = 0;$$
n = the number of nearest unlike neighbours of a cation;
n', n'' = the number of nearest like neighbours of a cation and an anion, respectively;
r_+, r_- = basic radii of cation and anion respectively;
c_{+-}, c_{++}, c_{--} = factors introduced by Pauling (1928) for the dependence of the repulsion of two ions on their charges and the number of electrons in their outermost shells;
ϱ = a constant obtainable from compressibility data;
k_1 = ratio of the shortest cation–cation distance to r_0;
k_2 = ratio of the shortest anion–anion distance to r_0;
C, D = van der Waals constants, calculated as described below;
h = Planck's constant;
$\nu_{\text{max.}}$ = characteristic Debye frequency for the solid fluoride.

The van der Waals constants C and D refer to dipole–dipole and quadrupole–dipole attraction respectively, and may be evaluated using the following relations:

$$C = S_6'd_{+-} + \tfrac{1}{2}S_6''d_{++} + \tfrac{1}{2}S_6'''d_{--} \qquad (6)$$

$$D = S_8'q_{+-} + \tfrac{1}{2}S_8''q_{++} + \tfrac{1}{2}S_8'''q_{--} \qquad (7)$$

$$d_{1,2} = \tfrac{3}{2}\alpha_1\alpha_2\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\,; \quad q_{1,2} = \frac{9d_{1,2}}{4e^2}\left\{\frac{\alpha_1\varepsilon_1}{p_1} + \frac{\alpha_2\varepsilon_2}{p_2}\right\}, \qquad (8)$$

where α refers to the polarizability of an ion, ε refers to an energy characteristic of the oscillators in an ion, and p refers to the 'effective number' of outer electrons (Mayer, 1933). S_6', S_6'', S_6''', S_8', S_8'' and S_8''' are sums of l^{-6} and l^{-8} over the unlike and like points of the lattice, if l is the distance between the lattice points. The sums depend on the lattice type and on the choice of r, which is here taken as the distance between unlike neighbouring ions.

The experimental lattice constants used in the present calculations are those listed in the compilation of Wyckoff (1951). The constant ϱ has been taken as $\frac{1}{3}\times10^{-8}$ cm. (Huggins, 1937). The basic radii of the cations are from Huggins & Sakamoto (1957) and the value for the fluoride ion from Huggins (1937). The frequencies of the anions have been estimated following a consideration of the magnitudes used by Mayer (1933) in his work on alkali halides. Polarizabilities are from the data of Tessman, Kahn & Shockley (1953).

The choice of values of some of the quantities used

Table 1. *Theoretical calculation of the lattice energies of alkaline earth fluorides*

	CaF^2	SrF^2	BaF^2
1. Crystal type	Fluorite	Fluorite	Fluorite
2. r_0 (Å)	2·360	2·505	2·679
3. $10^{-23}N$	6·023	6·023	6·023
4. $10^{-10}e$ (e.s.u.)	4·802	4·802	4·802
5. A	5·03878	5·03878	5·03878
6. $10^{12}b$ (ergs.mol.)	1·21	1·13	1·10
7. n	8	8	8
8. n'	12	12	12
9. n''	6	6	6
10. k_1	1·633	1·633	1·633
11. k_2	1·154	1·154	1·154
12. r_+ (Å)	1·17	1·31	1·46
13. r_- (Å)	1·05	1·05	1·05
14. c_{+-}	1·125	1·125	1·125
15. c_{++}	1·5	1·5	1·5
16. c_{--}	0·75	0·75	0·75
17. $10^8\varrho$ (cm.)	0·3333	0·3333	0·3333
18. $10^{60}C$ (erg.cm.^{6})	207	268	392
19. $10^{76}D$ (erg.cm.^{8})	286	394	654
20. $10^{24}\alpha_+$ (cm.^{3})	0·99	1·4	2·2
21. $10^{24}\alpha_-$ (cm.^{3})	0·759	0·759	0·759
22. $10^{12}\varepsilon_+$ (ergs./ion)	61·5	52·4	44·4
23. $10^{12}\varepsilon_-$ (ergs./ion)	26·3	24·3	22·2
24. S_6'	8·709	8·709	8·709
25. S_6''	0·762	0·762	0·762
26. S_6'''	1·524	1·524	1·524
27. S_8'	8·208	8·208	8·208
28. S_8''	0·253	0·253	0·253
29. S_8'''	0·506	0·506	0·506
30. $10^{60}d_{+-}$ (ergs.cm.^{6})	20·8	26·5	37·1
31. $10^{60}d_{++}$ (ergs.cm.^{6})	45·2	77	161
32. $10^{60}d_{--}$ (ergs.cm.^{6})	11·4	10·5	9·6
33. $10^{76}q_{+-}$ (ergs.cm.^{8})	33	45	72
34. $10^{76}q_{++}$ (ergs.cm.^{8})	85	169	452
35. $10^{76}q_{--}$ (ergs.cm.^{8})	14·8	12·6	10·5
36. $10^{-12}\nu_{\text{max.}}$ (S^{-1})	9·69	7·38	6·99
37. U_E (kcal./mole)	708·7	667·9	624·4
38. $-U_R$ (kcal./mole)	−116·8	−103.2	−91·1
39. U_W (kcal./mole)	21·5	19·3	18·8
40. $-U_z$ (kcal./mole)	−3·1	−2·4	−2·3
41. U_0 (kcal./mole)	610	582	550

in calculating the van der Waals energy is subject to some uncertainty. However, by using an empirical repulsive potential, determined from the attractive potential and the constants of the crystal, the magnitude of error introduced into the computation of lattice energy by an error in the values of C and D is less than that introduced into the van der Waals energy.

Data and results of theoretical calculations are shown in Table 1.

3. Thermodynamic derivation of lattice energies

The lattice energies of alkaline earth fluorides may also be derived from thermodynamic data by means of the Born–Haber cycle relationship:

$$U = -\Delta H + D + L_0 + I - 2E \qquad (9)$$

where

ΔH = heat of formation of the solid fluoride;
D = heat of atomization of fluorine;
L_0 = heat of atomization of the metal constituent;
I = first plus second ionization potential of the metal;
E = electron affinity of atomic fluorine.

The results obtained for these experimental lattice energies U, and relevant thermodynamic data from which they are calculated, are shown in Table 2. Values of heats of formation ΔH at 298·16 °K. have been taken from Rossini *et al.* (1952). The heat of dissociation of fluorine at 298·16 °K. is the value due to Stamper & Barrow (1958), and the heats of atomization of the metals at 0 °K. are those adopted by Baughan (1954). The ionization potentials at 0 °K. have been taken from Moore (1949). The value of Bailey (1958) has been adopted for the electron affinity of atomic fluorine at 0 °K.; this value, obtained from mass spectrometric work, agrees closely with the value accepted by Pritchard (1953) and the result of Stamper & Barrow (1958).

The values of U refer to 0 °K. and where necessary thermodynamic data have been corrected to 0 °K. The small energy changes between 0 and 298·16 °K. have been estimated and included in the calculation of the lattice energies, although they are not given explicitly in Table 2.

Table 2. *Calculation of the experimental lattice energies*
(Values in kcal./mole)

	$-\Delta H$	D	L_0	I	$-2E$	U
CaF_2	290·3	37·72	42	414·4	−164·2	617
SrF_2	290·3	37·72	39	384·2	−164·2	584
BaF_2	286·9	37·72	42	349·4	−164·2	549

4. Discussion

The differences Δ between the experimental lattice energies U and the theoretical values U_0 are 7, 2, and −1 Kcal. for the calcium, strontium and barium fluorides respectively. These discrepancies may be due in part to uncertainties in some of the data used in the calculations. However, it is considered that the values of Δ for CaF_2 and SrF_2 may be correlated with some deformation and interpenetration of the electron clouds of the constituent ions in the crystals. Fajans's rules and ionization potential data (Morris & Ahrens, 1956) suggest that among the alkaline-earth fluorides such polarization phenomena would be most extensive in CaF_2 and least extensive in BaF_2.

The electron-density distribution in crystalline CaF_2 has been investigated, and the minimum electron density between Ca^{2+} and F^- ions is not zero, as between Na^+ and Cl^- ions in NaCl, for example (Weiss, Witte & Wölfel, 1957).

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