ELECTROSTATIC ENERGY OF KHF$_2$

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Abstract — Electrostatic lattice energies are calculated in KHF$_2$. Fractional charges occurring in the complex anions are treated with a general procedure and the results are compared to a specialized approach reported earlier. Interstitial potentials are calculated to obtain the electrostatic field through which a migrating proton must pass. The influence of cooperative movement of up to ten protons on the electrostatic potential distribution is studied. The results are not in favour of any fast proton migration.

1. INTRODUCTION

THE LIMITATIONS of the value of electrostatic calculations in crystal lattices have been studied by several authors[1–3]. It has been recognized that these limits are wider than might be expected from a superficial evaluation due to the compensating influence of some neglected effects[4–6]. Another aspect is that even when certain complex anions or cations (complexions) have an important intracovalent bonding, the interaction between the complexions and the other ions of the lattice might be predominantly electrostatic. These arguments suggest that it is important to have a general method for calculating the electrostatic effects in these materials.

KHF$_2$ is an interesting example for this situation. Recent calculations using semi empirical and *ab initio* LCAO–MO–SCF methods show important covalent contributions to the bonding in the (FHF)$^-$-ion[7–9]. However, the interaction between the (FHF)$^-$-ions and with K^+ is predominantly electrostatic. In this paper we want to evaluate the electrostatic contribution to the lattice energy. We certainly do not pretend to give total energy considerations.

The interesting aspect of the calculations is that in the situation sketched above effective fractional charges occur in the ions. These fractional charges pose special problems in the numerical calculations. Waddington reported some time ago the calculation of the electrostatic energy in this situation[10]. He made use of specially developed interaction formulas. Furthermore some of the assumptions made by Waddington are not directly obvious. We summarize Waddington's approach in Section 2, whereas in Section 3 the results are obtained and analyzed

1. M. P. Tosi, *Solid St. Phys.* **16**, 1 (1964).
2. M. F. C. Ladd and W. H. Lee, *Prog. Solid St. Chem.* **1**, 37 (1964); **3**, 265 (1967).
3. T. C. Waddington, *Adv. inorg. Radiochem.* **1**, 157 (1959).
4. A. E. van Arkel, *Moleculen en kristallen*. W. F. van Stockum, Gravenhage (1961).
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10. T. C. Waddington, *Trans. Faraday Soc.* **54**, 25 (1958).

following a general procedure. This analysis shows that the general methods presently used to calculate lattice (self-) potentials and energies, can be used to obtain the results for fractional charges. No special procedures are required for interactions of this type. The numerical results are summarized in Section 4.

Another problem of interest is the possibility of cooperative movement of protons in KHF_2 as an explanation for its relatively high conductivity[11]. We studied the electrostatic aspects of such a migration (Section 5).

2. APPROXIMATE ELECTROSTATIC CALCULATIONS IN KHF_2

The low temperature phase of KHF_2 is tetragonal, space group D_{4h}^{18} (I 4/mcm) with K^+ at $(0, 0, \frac{1}{4})$, $(0, 0, \frac{3}{4})$, B.C.[12]. The hydrogen atoms of the symmetrical $(FHF)^-$ anion are at $(0, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, 0)$, B.C. The directions of the linear anions are $(1\ 1\ 0)$ and $(1\ \bar{1}\ 0)$ in the $(h, k, 0)$ and $(h, k, \frac{1}{2})$ planes in such a way that neighbouring anions point into different directions (Fig. 1). The fluorine ions in $(FHF)^-$ are 2·258 Å apart. When the anion is described as a single negative charge at the H-position, a smaller unit cell can be used. This cell is indicated in Fig. 1a and is presented in Fig. 1b. Obviously, when the fluorine atoms are taken into account,
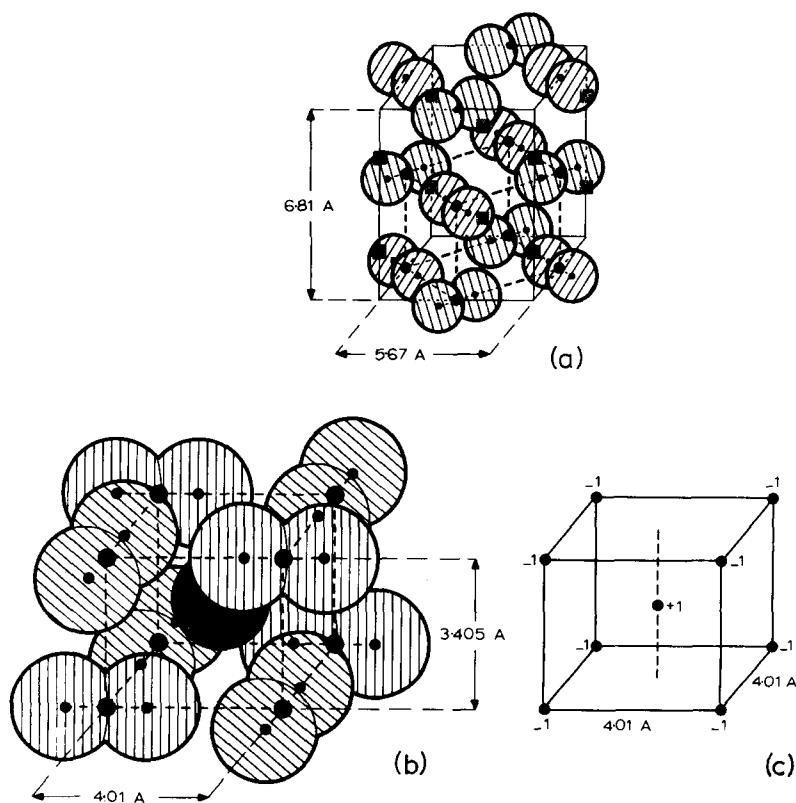

Fig. 1. Tetragonal structure of KHF_2. (a) Unit cell; (b) and (c) subcell used in calculations.

11. J. Bruinink and G. H. J. Broers, *J. phys. chem. Solids*. To be published.
12. R. W. G. Wyckoff, *Crystal Structures*, Vol. II. Wiley, New York (1965).

the cell in Fig. 1b is not a unit cell. Fig. 1c gives the most simple approach to the electrostatic description of KHF$_2$.

In the earlier calculations of Waddington the CsCl-type charge distribution of Fig. 1c is the starting point of the calculation. Note that this calculation uses a charge of -1 at the H-positions and a zero charge at the F-positions. This model is corrected for an effective charge distribution in the F–H–F anion with $q_F = -0.781$, $q_H = 1.562$. This is a quadrupole in the sense of $[-0.781; (+0.781, +0.781); -0.781]$. Formulas are developed for the quadrupole-quadrupole interaction and the quadrupole-ion (H$^-$, K$^+$) interaction. Together with corrections for van der Waals–London interaction, zero-point energy and Born repulsion, the electrostatic energy change for the reaction:

$$(F^{-0.781} H^{+0.562} F^{-0.781})_g + K^+ \rightarrow (K^+ F^{-0.781} H^{+0.562} F^{-0.781})_s \qquad (1)$$
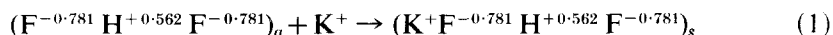
is obtained.

With a Born–Haber cycle the enthalpy change $\Delta H(2)$ of the process

$$(HF)_g + F^- \rightarrow (FHF)_g^- \qquad (2)$$

is established to be -60.4 kcal.

3. EXACT ELECTROSTATIC CALCULATIONS IN KHF$_2$

With a computer program based upon the Ewald procedure, it is possible to calculate the total electrostatic energy of any point charge distribution in a crystalline lattice[13]. The use of fractional charges does not give problems. The calculated potentials and energies are summarized in Table 1.

The following remarks can be made about the results. The charge distribution 3 is the sum of the distribution 1 and 2. Thus the potentials are additive but the energies are not[14]. Note that the charge distribution 2 can be obtained by subtracting the quadrupole lattice 1 from the point lattice 3. The same situation 2 is obtained by adding the quadrupole lattice 5 to the point lattice 4. The last addition

Table 1. Potential and energy calculations in KHF$_2$ [$a = b = 5.67$ Å; $c = 6.81$ Å]

Charge distribution			Potential (e.u. A^{-1})			Electrostatic energy (kcal/mole)
K-site	H-site	F-site	K-site	H-site	F-site	
1 0	+0.438	−0.219	−0.02021	−0.40642	0.27998	49.88
2 +1	+0.562	−0.781	−0.59562	−0.92585	0.64023	351.08
3 +1	+1	−1	−0.61583	−1.33228	0.92020	628.58
4 +1	−1	0	−0.52354	0.52354	−0.35822	173.73
5 0	+1.562	−0.781	−0.07208	−1.44939	0.99845	634.39*

*Charges in distribution 5 are 3.566210 times the charges of distribution 1. By consequence, the potentials at corresponding sites have the same ratio, whereas the energy of 5 is (3.566210)^2 times the energy of 1.

13. W. van Gool and A. Piken, *J. Mat. Sci.* **4**, 95, 105 (1969).
14. W. van Gool, *J. inorg. nucl. Chem.* **34**, 3585 (1972).

is actually the procedure followed by Waddington as described in Section 2. Waddington calculated 168·1 kcal for the situation **4**. Based upon a large number of calculations of electrostatic energies in other lattices we believe that our value (173·73 kcal/mole) is correct within 0·05 kcal. The quadrupole-quadrupole interaction energy (Section 2) can be obtained from the results of situation **5**. The electrostatic calculation does include the electrostatic energy of the individual quadrupoles.

This is for N quadrupoles $N(2q_Hq_F/r_{HF} + q_F^2/2r_{HF})$(see Fig. 2). With r in Å ($r_{HF} = 1·129$ Å); q in electron charges we get

$$E_{quad} = -331·84 \times [-7q_F^2/(2r_{HF})] = 627·47 \text{ kcal/mole.} \qquad (3)$$

Thus the quadrupole–quadrupole interaction energy is

$$E_{quad-quad} = 634·39 - 627·47 = 6·92 \text{ kcal/mole.}$$

This value must be compared to the value of 9·2 kcal/mole, following from the approximate calculation according to Waddington.
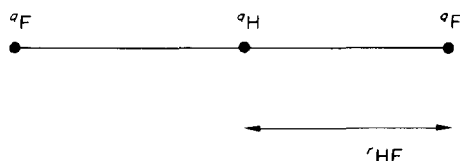
$$q_F \quad\quad\quad\quad\quad q_H \quad\quad\quad\quad\quad q_F$$

$$\bullet\text{————————}\bullet\text{————————}\bullet$$

$$\overleftarrow{}\overrightarrow{}$$

$$r_{HF}$$

Fig. 2. Distances and charges in $(FHF)^-$-ion.

The quadrupole–ion interaction (Section 2) is obtained by placing the quadrupole at one F–H–F position in a lattice existing of H^{-1} and K^{+1} ions. The H^{-1}–ion is removed from that special position. When the lattice self-potential calculated in charge distribution **4** at the H-position is $V_H^{(4)}$ and the (interstitial) potential at the F-position is $V_F^{(4)}$, then

$$E_{quad-ion} = -331·84 [V_H^{(4)}q_{quad, H} + 2(V_F^{(4)} + 1/r_{HF})q_{quad, F}] = 2·056 \text{ kcal/mole.} \quad (4)$$

Here $V_H^{(4)}$, $V_F^{(4)}$ are the values reported in Table 1 for charge distribution **4**. The correction of $2/r_{HF}$ on the $V_F^{(4)}$ is necessary since the (interstitial) potential V_F is calculated with a charge -1 on the H-position. With the quadrupole present this -1 charge has been removed. This result compares favourably with the value 2·1 kcal/mole obtained by Waddington by approximative formulas.

As has been demonstrated elsewhere[14], the energy $E_{ion-quad}$ obtained by placing the K^{+1} and H^{-1} ions in a lattice of (F–H–F) quadrupoles only, must be equal to $E_{ion-quad}$. $E_{ion-quad}$ is obtained by using $q_K = +1$ in the K-positions and $q_H = -1$ in the H-positions of the quadrupole charge distribution **5**. Let $V_K^{(5)}$, $V_H^{(5)}$ represent here the corresponding potentials in charge distribution **5**. $V_H^{(5)}$ includes the contribution from the two neighbouring F^- ions. This influence must be corrected, since in the reference point $(FHF)^-$ is replaced with H^{-1}.

Thus

$$E_{\text{ion-quad}} = -331 \cdot 84 \left[q_k V^{(5)}_{\text{K,quad}} + q_\text{H} \left\{ V^{(5)}_{\text{H,quad}} + 2 \frac{q_{\text{F,quad}}}{(r_{\text{HF}})} \right\} \right] = 2 \cdot 056 \,\text{kcal/mole.} \quad (5)$$

Note that the potentials used in the calculation of $E_{\text{quad-ion}}$ and $E_{\text{ion-quad}}$ originate from two complete different charge distributions 4 and 5, Table 1. The results (4) and (5) demonstrate the numerical consistency of the different approaches.

Other calculations can be made according to the methods described. For example, the electrostatic energy of the charge distribution 3 can be corrected for the energy of the quadrupoles $(-1, +2, -1)$, giving the change of the electrostatic energy for the reaction

$$(\text{F}^{-1}\text{H}^{+1}\text{F}^{-1})_g + (\text{K}^+)_g \rightarrow [\text{K}^{+1}\text{H}^{+1}(\text{F}^{-1})_2]_s. \quad (6)$$
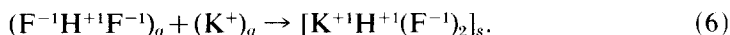
The results of the calculations are summarized and discussed in the next section. Theoretical aspects, such as the annihilation of charges by joining a quadrupole lattice to a point charge lattice, and the meaning of the reference level when fractional charges are used have been discussed elsewhere [14].

4. NUMERICAL RESULTS

In Figure 3 the more important results of the calculations have been summarized. The following indications have been used:
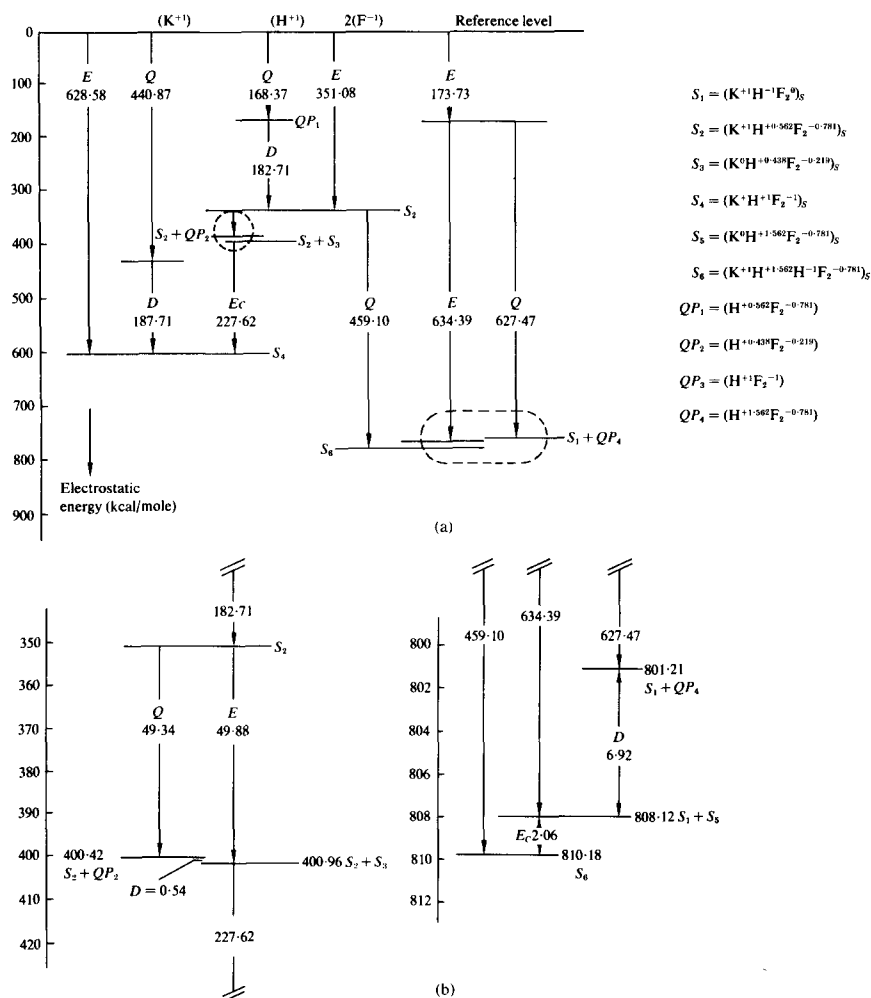
E: electrostatic calculations with computer program

Ec: potentials and self-potentials of computer program have been used to calculate corrections according to Equations (4) and (5)

Q: electrostatic energy of N isolated quadrupoles according to Equation (3)

D: difference between calculated values

$(\;)_\infty$: electrostatically isolated ions

$(\text{K})_S$: solid with charges indicated in figures

(QP): N isolated quadrupoles.

The following explanations might be helpful for the interpretation of Fig. 3.

The reference level describes a situation where the total *charge* of mole (N) of K^{+1}-ions and H^{+1}-ions and 2 mole (2N) of F^{-1}-ions are present without interaction (infinite distances).

A simple process is represented by the upper-left cycle, characterized by $E = 628 \cdot 58$, $Q = 440 \cdot 87$. The formation of $(\text{K}^{+1}\text{H}^{+1}\text{F}_2^{-1})_s$ $(= S_4)$ is described in two ways: first all charges are used to form the lattice directly ($E = 628 \cdot 58$ kcal/mole), next N seperated quadrupoles $(\text{F}^{-1}\text{H}^{+1}\text{F}^{-1})_g$ $(= QP_3)$ are formed ($Q = 440 \cdot 87$) and the N quadrupoles are combined with N K^{+1}-ions to form $(\text{K}^{+1}\text{H}^{+1}\text{F}_2^{-1})_S$ $(D = 187 \cdot 71)$.

A corresponding process is the cycle in the middle-upper part, characterized by $Q = 168 \cdot 37$, etc. Here only a fraction of the charges is used to form $(\text{K}^{+1}\text{H}^{+0.562} \text{F}_2^{-0.781})_s$ $(= S_2)$. The electrostatic energy $D = 182 \cdot 71$ kcal/mole is the electrostatic energy involved in reaction (1). Note that the values $D = 187 \cdot 71$ and $D = 182 \cdot 71$ of the two cycles discussed differ only $5 \cdot 00$ kcal although the total electrostatic energies involved in the two cycles differ largely. This illustrates the fact that the total charge of the quadrupole ion (which is -1 in both situations) gives the

$S_1 = (K^{+1}H^{-1}F_2^0)_S$

$S_2 = (K^{+1}H^{+0.562}F_2^{-0.781})_S$

$S_3 = (K^0H^{+0.438}F_2^{-0.219})_S$

$S_4 = (K^+H^{+1}F_2^{-1})_S$

$S_5 = (K^0H^{+1.562}F_2^{-0.781})_S$

$S_6 = (K^{+1}H^{+1.562}H^{-1}F_2^{-0.781})_S$

$QP_1 = (H^{+0.562}F_2^{-0.781})$

$QP_2 = (H^{+0.438}F_2^{-0.219})$

$QP_3 = (H^{+1}F_2^{-1})$

$QP_4 = (H^{+1.562}F_2^{-0.781})$

Fig. 3. Electrostatic energies calculated for KHF_2. For explanation see text.

important contribution to the condensation reaction, rather than the contribution due to the charge distribution in the quadrupole.

Interesting, but conceptually more difficult is the connection between the two discussed cycles through the situation $S_2 + S_3$ (see Fig. 3b, left side). Here the charges left behind in the reference level during the formation of $(K^{+1}H^{+0.562}$ $F_2^{-0.701})_s$ $(= S_2)$ are used to form another quadrupole lattice $(K^0H^{+0.438}F_2^{-0.219})_s$ $(= S_3)$. Note that we have created temporarily more matter, since we have 1 mole $S_2 + 1$ mole S_3. This is due to the consequent attaching of charges to chemical symbols. The formation of S_3 gives 49·88 kcal/mole (see Table 1, charge distribution 1). Forming N quadrupoles $(H^{+0.438}F_2^{-0.219})_g$ $(= QP_2)$ gives 49·34 kcal/mole and thus condensing these isolated quadrupoles QP_2 to the quadrupole lattice S_3 gives only $49·88 - 49·34 = 0·54$ kcal/mole. The lattices S_2 and S_3 can be joined. The electrostatic energy of this addition can be calculated, either by placing a quadrupole $(H^{+0.438}F_2^{-0.219})$ in S_2 or by placing the ions K^{+1},

$H^{+0.562}$, $2F^{-0.781}$ in QP_2. Both procedures give the same end situation $(K^{+1}H^{+1}$ $F_2^{-1})_s$ $(= S_4)$ and deliver 227·62 kcal/mole. During the addition formal relations of the type $H^{+0.562} + H^{+0.438} = H^{+1}$ are used and the temporarily used additional matter disappears. The total energy according to this procedure is in exact agreement with the direct calculation of situation $S_4(351·08 + 49·88 + 227·62 = 628·58)$.

The use of the addition procedure needs some amplification. The problem is that a real addition of the lattices S_2 and S_3 should give infinite large energies, since charges (for example of hydrogen) are added at the same site. The correctness can best be demonstrated by the cycle on the right side of Fig. 3a $(E = 173·73,$ etc.) and its connection to the middle-cycle $(E = 351·08,$ etc.).

The electrostatic energy $E = 173·73$ kcal/mole is obtained when the CsCl-type lattice $(K^{+1}H^{-1}F_2^{0})_s$ $(= S_1)$ is formed. By using -1 in connection with the H-position, an additional charge of $+1$ has been created in the reference level. The sum of the charges of this remainder and S_1 gives the original amount of charge. From the remainder a fraction is used to form the quadrupole lattice $(K^0H^{+1.562}F_2^{-0.781})_s$ $(= S_5)$ with $E = 634·39$ kcal/mole. (Table 1, charge distribution 5).

This leaves behind in the reference level $N(H^{+0.438} + 2F^{-0.219})$. This is exactly the amount that was left behind during the formation of S_2 (middle cycle) and the importance of this observation is that later on, after "adding" $S_1 + S_5$ (see below) the situation S_2 plus the corresponding amount in the reference level is obtained. First we note that S_5 can also be obtained by forming N quadrupoles $(H^{+1.562}$ $F_2^{-0.781})_g (= QP_4)$ with $Q = 627·47$, followed by condensation of the quadrupoles Q_5 to the lattice S_5. This was used already in section 3 to calculate $E_{quad-quad} = 6·92$ kcal/mole (Fig. 3b). Next, the quadrupole–ion or the ion–quadrupole interaction is calculated (Section 3), leading to $E_c = 2·06$ kcal/mole. This leads to the artificial situation $(K^{+1}H^{+1.562}H^{-1}F_2^{-0.781})_s$ $(= S_6)$. The artificial aspect is that both H-charges are present at the same site, but their interaction has been left out. Note that the amount of matter corresponds to $(KH_2F_2)_s$. In order to come to the situation $(K^{+1}H^{+0.562}F_2^{-0.781})_s$ $(= S_2)$ the symbolic addition $H^{+1.562} + H^{-1} = H^{+0.562}$ has to be made. This means that some of the quadrupole energy changes, all other interactions depending upon the effective charge at the sites only. The disappearing energy is that of a charge -1 at the H-position with the two neighbouring charges -0.781 of F (Note: the F–F interaction is unchanged). This leads to 459·10 kcal/mole for $S_2 \rightarrow S_6$. An exact derivation is given in Appendix 1.

We finally want to compare our results with those of Waddington. In his approach the situation S_1 (ref. $\rightarrow S_1: 173·73$) is corrected with $D = 6·92$ $(S_1 + QP_4 \rightarrow S_1 + S_5)$ and with $E_c = 2·06$ $(S_1 + S_5 \rightarrow S_6)$ giving $173·73 + 6·92 + 2·06 = 182·71$ (all values in kcal/mole). This value is equal to the energy of the transition $QP_1 \rightarrow S_2$ (for a general proof see Appendix II). Waddington's values are in the same sequence: $168·1 + 9·2 + 2·1 = 179·4$. Using the same corrections as Waddington for van der Waals interaction, zero point energy and Born repulsion (total 26·0 kcal) we find $-156·71$ for U_{MHF_2} $(W = -153·4)$ and $\Delta H = -57·09$ $(W = -60·4)$ for the reaction (2). More important than the rather small differences in the final answers are the following two aspects. First our method is quite general and can be applied directly to all other crystals containing complexions.

Secondly, very large total energies are involved and the essential assumption made in the calculation is left obscure in the original paper[10]. This assumption involves the constancy of the fractional charges in the $(FHF)^-$ ion when this ion is being coordinated with K^+ to a crystalline lattice. From $D = 187 \cdot 71$ $(QP_3 \rightarrow S_4)$ it is obvious that the electrostatic lattice energy for the process (6) is rather insensitive to the charge distribution in the complexion, as was shown already. A change of the fractional charges during the formation of the solid phase produces larger deviations than the small discrepancies between the different computations. There is however, no evidence enough to decide upon charge values in the complex ions in the two different situations[15]. Note that the use of charges $q_F = -1$, $q_H = +1$ lead to $\Delta H = -52 \cdot 09$ for reaction (2) using the other corrections as before. This value also falls in a range acceptable with respect to other data[15]. The conclusion is that ΔH of Equation (2) is rather insensitive to the charge distribution in the anion, but that a change of the charges in the anion during the condensation process will influence ΔH of reactions (1) and (2) considerably.

In a more recent approach Jenkins and Waddington[16–17] make use of formulas advanced by Bertaut[18] for the electrostatic energy calculations. Essentially the method used by Jenkins and Waddington is equal to the one presented here. The same assumption about the constancy of the charge distribution in the gas and the solid phase is implicitedly used for a number of complexions. Our formulation shows that such an assumption is not required for the calculations of the electrostatic energy of crystalline solids.

5. COOPERATIVE MOVEMENT OF PROTONS

KHF_2 is known to be an ionic conductor. Usually this conductivity is interpreted in terms of H^+-migration[19]. Recent experiments by one of the authors [11] demonstrate that a definite proof for the H^+-migration has not yet been given.

Some electrostatic calculations were performed to gain some insight about activation energy involved in proton migration when a pure electrostatic model is used. Using a vacancy model, interstitial potentials were calculated analogously to the method used in β-Al_2O_3[13]. Curve (1) in Fig. 4 gives this potential in the (0 0 1) direction, curve 3 in the (1 1 0) direction. In both cases the origin of the figure is at a H-position. Activation energies according to these calculations will be as high as $0 \cdot 35 \times 14 \cdot 4$ eV ≈ 5 eV ≈ 115 kcal/mole in contradiction to experimental values.

Since present discussions of fast migration of ions concentrate upon cooperative phenomena, we calculated the influence of the cooperative displacement of n protons. The potential $V(x, i)$ at the site x of proton i due to the displacement of $n - 1$ other protons is

$$V(x, i) = V^0(x) + \left\{ \sum_{j=1}^{n} {}' \frac{1}{(j-i)} - \sum_{j=0}^{n} \frac{1}{(j-i+x)} \right\} \frac{1}{a}. \qquad (7)$$

15. D. G. Tuck, *Prog. inorg. Chem.* **9**, 161 (1968).
16. H. D. B. Jenkins and T. C. Waddington, *Nature phys. Sci.* **232**, 5 (1971).
17. H. D. B. Jenkins, *Chem. phys. Lett.* **9**, 473 (1971).
18. E. F. Bertaut, *J. phys. Rad.* **13**, 499 (1952).
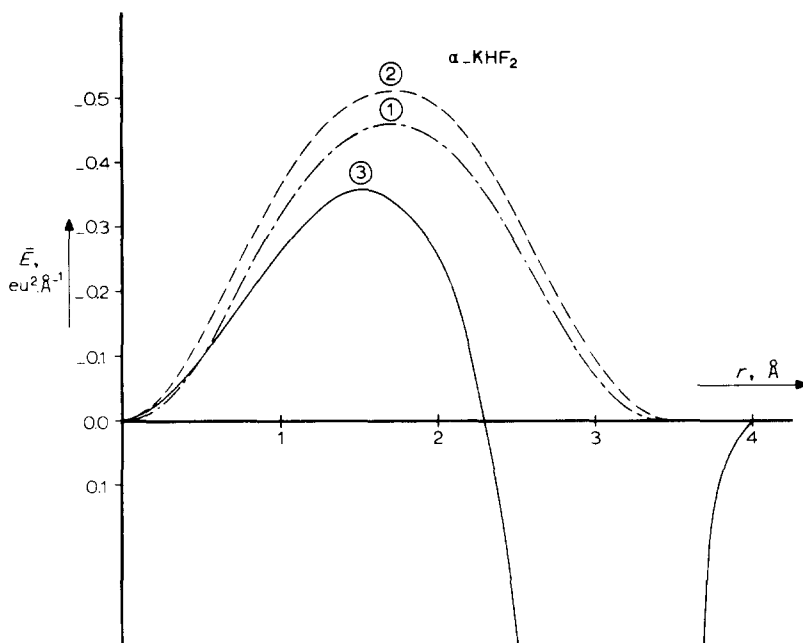19. J. Bruinink, *J. appl. electrochem.* To be published.

Fig. 4. Potential distributions in KHF$_2$. 1. Two empty proton sites, other ions at normal positions, (0 0 1) direction. 2. Two empty proton sites, from other ions 8 protons in (0 0 1) direction adjacent to the two empty sites have been displaced over the distance x (see Fig. 5). 3. Two empty proton sites, other ions at normal positions, (1 1 0) direction.
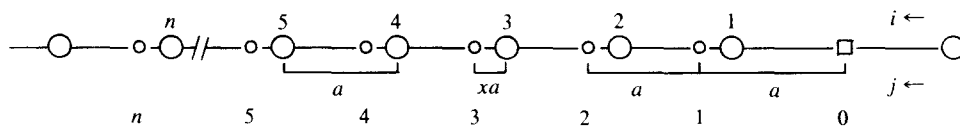

Fig. 5. Model used for cooperative displacement of n protons on a line (j indicates original positions of the protons, $i = 1, n$ are displaced protons).

Here $V^0(x)$ is the (interstitial) potential at point x (see Fig. 5) for the undisturbed lattice, $\sum\limits_{j=1}^{n}{}'$ gives the contribution of the displaced protons leaving out the proton at i ($j \neq i$) and $j = 0$ (vacancy), $\sum\limits_{j=0}^{n}$ gives the change of the potential due to the removal of the protons from their original positions (now including $j = 0$ in order to create the vacancy), a is the distance between two proton positions.

For the evaluation of the possibility of a concerted move of the n protons, the average energy $\bar{E}(x, n)$ is of importance:

$$\bar{E}(x, n) = -\frac{1}{n} \sum_{i=1}^{n} [V(x, i) - V(0, i)]. \tag{8}$$

Note that

$$V(0, i) = V^0(0) - 1/(ia) \tag{9}$$

where $V^0(0)$ is the lattice self-potential at the proton position and the term $1/(ia)$ represents the influence of the vacancy.

The calculations according to (7) and (8) were performed with an additional computer program. The results for $n = 10$ are represented for the $(0\ 0\ 1)$ direction as curve 2 in Fig. 4. This shows that the cooperative movement does not improve the value of the activation energy for migration. The present results show that fast proton migration is not directly obvious from the electrostatic description.

APPENDIX I

Electrostatic energy for transition $S_2 \rightarrow S_6$

The electrostatic energy for the transition $S_2 \rightarrow S_6$ can be found by comparing the contributions composing the electrostatic energy of S_2 and S_6. This is done by using formulas such as

$$E = -\left(\sum_i \nu_i q_i \sum_j q_j/r_{ij} \right)/2z$$

$$E(\text{kcal/mole}) = -331 \cdot 84 \left(\sum_i \nu_i q_i \sum_j q_j/r_{ij} \right)/2z \tag{A1-1}$$

where ν_i is the frequency of symmetrically different sites i in the unit cell, q_i the charge at these sites, q_j charges on other symmetry sites, r_{ij} the distance between i and j, z the number of molecules per unit cell. With q in electron charges, r in A, the factor $331 \cdot 84$ gives the energy in kcal/mole. In the following formulas we use $z = 1$ and choose ν_i correspondingly. When i and j refer to the same set, $\sum_j '$ will be used to exclude the situation $j = i$ with $r_{ij} = 0$. In some situations the summation Σ'' occurs, which refers to one of the ions in $(FHF)^-$ and which excludes the other ions in the complexion from the summation. Writing

$$-E' = -(E.2z)/(331 \cdot 84) = \sum_i \nu_i q_i \sum_j q_j/r_{ij} \tag{A1-2}$$

simplifies the notation of the equations to be used. We consider the following energies, summation of which leads to S_6 (compare Fig. 3).

$E = 173 \cdot 73$

$$E' = q_H^{(-1)}\left[\sum_K q_K/r_{HK} + \sum_H' q_H^{(-1)}/r_{HH} \right] + q_K\left[\sum_H q_H^{(-1)}/r_{HK} + \sum_K' q_K/r_{KK} \right]$$

$E = 634 \cdot 39$

$$E' = q_H^{(1 \cdot 562)}\left[\sum_F q_F/r_{HF} + \sum_H' q_H^{(1 \cdot 562)}/r_{HH} \right] + 2q_F\left[\sum_H q_H^{(1 \cdot 562)}/r_{HF} + \sum_F' q_F/r_{FF} \right]$$

$E = 2 \cdot 06$

$$E' = q_H^{(1 \cdot 562)}\left[\sum_H' q_H^{(-1)}/r_{HH} + \sum_K q_K/r_{HK} \right] + 2q_F\left[\sum_K q_K/r_{FK} + \sum_H'' q_H^{(-1)}/r_{HF} \right]$$

$$+ q_K\left[\sum_F q_F/r_{FK} + \sum_H q_H^{(1 \cdot 562)}/r_{HK} \right] + q_H^{(-1)}\left[\sum_H' q_H^{(1 \cdot 562)}/r_{HH} + \sum_F'' q_F/r_{HF} \right].$$

Here all interactions are counted twice. For $E = 2 \cdot 06$ this is done by using the energy of the quadrupole placed in the ionic lattice and the ions K^{+1} and H^{-1} placed in the quadrupole lattice. For the charges of K^{+1} and $F^{-0 \cdot 781}$ the symbols q_K and q_F are used. For H the different values are indicated: $q_H^{(-1)} = -1$ e.u., $q_H^{(1 \cdot 562)} = 1 \cdot 562$ e.u., etc. The sum of these energies can be split into sums $\Sigma(1)$ to $\Sigma(6)$, containing all sumations over one set of distances r_{HH}, r_{HK} etc. The result is:

$$\Sigma(1) = q_H^{(-1)} \sum_K q_K/r_{HK} + q_K \sum_H q_H^{(-1)}/r_{HK} + q_H^{(1 \cdot 562)} \sum_K q_K/r_{HK} + q_K \sum_H q_H^{(1 \cdot 562)}/r_{HK}.$$

$$\sum(2) = q_H^{(-1)} \sum_H{}' q_H^{(-1)}/r_{HH} + q_H^{(1\cdot562)} \sum_H{}' q_H^{(1\cdot562)}/r_{HH} + q_H^{(1\cdot562)} \sum_H{}' q_H{}^{-1}/r_{HH} + q_H^{(-1)} \sum_H{}' q_H^{(1\cdot562)}/r_{HH}.$$

$$\sum(3) = q_K \sum_K{}' q_K/r_{KK}.$$

$$\sum(4) = q_H^{(1\cdot562)} \sum_F q_F/r_{HF} + 2q_F \sum_H q_H^{(1\cdot562)}/r_{HF} + 2q_F \sum_H{}'' q_H^{(-1)}/ r_{HF} + q_H^{(-1)} \sum_F{}'' q_F/r_{HF}.$$

$$\sum(5) = 2q_F \sum_F{}' q_F/r_{FF}.$$

$$\sum(6) = 2q_F \sum_K q_K/r_{FK} + q_K \sum_F q_F/r_{FK}.$$

Next the energy of S_2 is decomposed correspondingly:

$E = 351\cdot08$

$$E' = q_K\Big[\sum_K{}' q_K/r_{KK} + \sum_F q_F/r_{FK} + \sum_H q_H^{(0\cdot562)}/r_{HK}\Big] + q_H^{(0\cdot562)}\Big[\sum_K q_K/r_{HK} + \sum_H{}' q_H^{(0\cdot562)}/r_{HH}$$

$$+ \sum_F q_F/r_{HF}\Big] + 2q_F\Big[\sum_K q_K/r_{FK} + \sum_H q_H^{(0\cdot562)}/r_{HF} + \sum_F{}' q_F/r_{FF}\Big].$$

This leads to:

$$\sum{}'(1) = q_K \sum_H q_H^{(0\cdot562)}/r_{HK} + q_H^{(0\cdot562)} \sum_K q_K/r_{HK}.$$

$$\sum{}'(2) = q_H^{(0\cdot562)} \sum_H{}' q_H^{(0\cdot562)}/r_{HH}.$$

$$\sum{}'(3) = q_K \sum_K{}' q_K/r_{KK}.$$

$$\sum{}'(4) = q_H^{(0\cdot562)} \sum_F q_F/r_{HF} + 2q_F \sum_H q_H^{(0\cdot562)}/r_{HF}.$$

$$\sum{}'(5) = 2q_F \sum_F{}' q_F/r_{FF}.$$

$$\sum{}'(6) = q_K \sum_F q_F/r_{FK} + 2q_F \sum_K q_K/r_{FK}.$$

Inspection and some rearrangement of terms shows that the corresponding terms $\Sigma(1)$, $\Sigma(2)$, $\Sigma(3)$, $\Sigma(5)$ and $\Sigma(6)$ are equal. In $\Sigma(4)$ some terms cancel and using the relationships

$$2q_F \sum_H{}'' q_H^{(-1)}/r_{HF} = 2q_F \sum_H q_H^{(-1)}/r_{HF} - 2q_F q_H^{(-1)}/r_{HF}$$

$$q_H^{(-1)} \sum_F{}'' q_F/r_{HF} = q_H^{(-1)} \sum_F q_F/r_{HF} - 2q_H^{(-1)}q_F/r_{HF}$$

the result is

$$\sum(4) - \sum{}'(4) = -4q_H^{(-1)}q_F/r_{HF}$$

which leads to an energy difference

$$E(\text{kcal/mole}) = 331\cdot84\ 2q_H^{(-1)}q_F/r_{HF} = 459\cdot10$$

which was used in Fig. 3 to relate S_2 and S_6.

APPENDIX II

Proof of equivalence of Waddington's energy with D

We want to demonstrate that Waddington's procedure using $E_{CsCl} + E_{ion-quad} + E_{quad-quad}$, gives the value $D = S_2 - QP_1 = 182\cdot71$. This proof can be given by collecting energy terms analogously to the method used in Appendix I.

However, symbolic notations are sometimes easier to use in these energy calculations than the summations. Therefore we represent this proof by means of such a symbolic notation, presented in Fig. 6.

The following procedure is used. The electrostatic energy is calculated from the potential a "refer-

Reference points   Special points   Infinite lattice

(a) $\quad 2S_2 = \left.\begin{array}{l} K^{+1} \\ H^{+0\cdot562} \\ 2F^{-0\cdot781} \end{array}\right\} \longleftarrow \boxed{K^{+1}, H^{+0\cdot562}, 2F^{-0\cdot781}}$

(b) $\quad 2S_2 = \left.\begin{array}{l} K^{+1} \\ H^{-1} \\ H^{+1\cdot562} \\ 2F^{-0\cdot781} \end{array}\right\} \longleftrightarrow \left.\begin{array}{l} H^{+0\cdot562} \\ 2F^{-0\cdot781} \end{array}\right]_n + \boxed{K^{+1}, H^{+1\cdot562}, H^{-1}, 2F^{-0\cdot781}}_{nn}$

(c) $\quad 2S_2 = \left\{ \begin{array}{l} \left.\begin{array}{l} K^{+1} \\ H^{-1} \end{array}\right\} \xleftarrow{2''\text{CsCl}''} \boxed{K^{+1}, H^{-1}} \\[2pt] + \\ \left.\begin{array}{l} K^{+1} \\ H^{-1} \end{array}\right\} \xleftarrow{\text{ion-quad}} \boxed{H^{+1\cdot562}\,2F^{-0\cdot781}}_{nn} \\[2pt] + \\ \left.\begin{array}{l} H^{+1\cdot562} \\ 2F^{-0\cdot781} \end{array}\right\} \xleftarrow{\text{quad-ion}} \boxed{K^{+1}, H^{-1}}_{nn} \\[2pt] + \\ \left.\begin{array}{l} H^{+1\cdot562} \\ 2F^{-0\cdot781} \end{array}\right\} \xleftarrow{2(\text{quad-quad})} \boxed{\begin{array}{l} H^{+1\cdot562} \\ 2F^{-0\cdot781} \end{array}}_{nn} \\[2pt] + \\ \left. H^{-1} \quad\longleftrightarrow\; 2F^{-0\cdot781}\right]_n \\ + \\ \left. H^{+1\cdot562} \quad\longleftrightarrow\; 2F^{-0\cdot781}\right]_n \quad\Big\} \quad = 2QP_1 \\ + \\ \left. 2F^{-0\cdot781} \quad\longleftrightarrow\; H^{+0\cdot562}\right]_n \end{array}\right.$

(d) $\quad S_2 = E_{\text{CsCl}} + E_{\text{ion-quad}} + E_{\text{quad-quad}} + QP_1.$
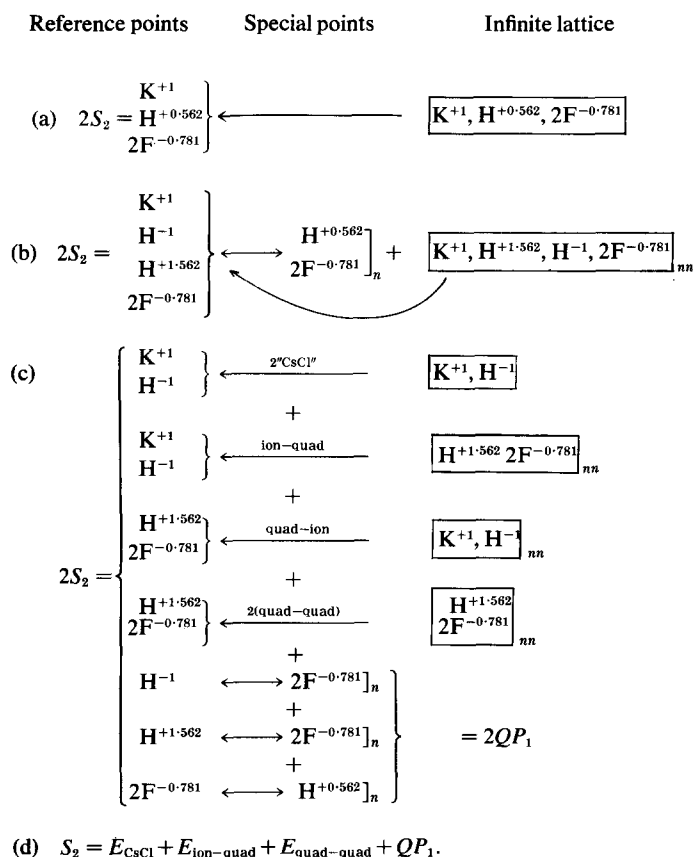
Fig. 6. Symbolic derivation of energy relationship.

ence points". A single-headed arrow indicates that the reference points are placed in the infinite lattice indicated by boxes.

Line (a) represents twice the electrostatic energy of situation S_2 (all interactions are counted twice). Going to line (b) the following changes have been made:

(1) Charges of hydrogen both in the reference point and in the infinite lattice are replaced by the sum of two other charges. This does not change the energy [14].

(2) Special points are seperated, viz. the two neighbouring fluorines of the complexion when H is reference point and vice versa. The neighbouring special points are indicated by "n", the non-neighbouring remaining lattice be "$n\,n$". The interaction between reference point and special points is indicated by a two-headed arrow.

In (c) the interactions are rearranged in order to give the desired terms. Note that the energy of "ion-quad" is equal to that of "quad-ion" [14] and that the last three lines added together represents twice the formation energy of N quadrupole $(H^{(0\cdot562)}F_2^{-0\cdot781})_g$. The energies mentioned in (c) lead to (d) which was to be proved.