

c axis in the case of asymmetrical tilt boundaries, nor the real nature of interactions between the two types of dislocations is known. Therefore, it is difficult to describe exactly the formation of irregularly shaped rings.

(vi) All the above cases of ring-formations have been discussed for the common CdI_2 polytype *4H* excepting the upper part of crystal No. 3 which is a mixture of types *4H* and *48R*. In addition, rings have also been observed on Laue photographs of other polytypes (photographs not reproduced).

Density of dislocations

The density of dislocations inside the boundaries can be calculated from the X-ray photographs as outlined in part I.

Conclusion

The most significant conclusions emerging from the experimental findings are (i) the occurrence of triple nodes of dislocations, created by simultaneous slip along the directions of close packing and (ii) the constancy of their spacing in most cases. The latter points to the generation of dislocations at equal intervals during crystal growth. It is noteworthy that the ring-formations have mostly been observed in the lower parts of the crystals, the upper parts usually show-

ing either single spots or only a small amount of arcing. This is to be expected because the conditions are favourable for the formation of a large number of dislocations in the initial stages when the saturation is high and the rate of growth is rapid. The phenomenon of ring formation shows that under certain suitable circumstances these dislocations can arrange themselves into highly symmetrical threefold boundaries. Apart from the X-ray methods used by us, electron microscopy can also be profitably employed to reveal the arrangements of dislocations inside the crystals. However, Forty (1960) has observed that CdI_2 crystals decompose under the action of the electron beam.

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Direct Summation of Madelung Energies

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A computerized procedure based on the Evjen method for the direct summation of Madelung energies of centrosymmetric structures is described. The values obtained are strictly according to the definition of the Madelung function and the accuracy depends only on the number of terms taken into consideration. Madelung energies for a variety of structures calculated by this method are compared with values obtained by various other methods.

Introduction

Madelung constants of most simple ionic salts are known accurately, but analyses of the electrostatic interactions in numerous ionic and ion-dipole complexes still have to be made. Methods for the rapid evaluation of the Madelung energies of complicated structures are thus highly desirable and it was surprising to find that almost negligible use has been made of the most obvious methods, *viz.* direct evaluation of lattice sums using computers. Indirect methods which

often involve mathematical expressions and correction factors which are much more complicated than the basic equation ($U = -(ze)^2\alpha/r$) which defines the Madelung function, are usually employed. The most popular procedure uses the method of Bertaut (1952) with correction factors given by Templeton, 1955 (see also Jones & Templeton, 1956). Evjen (1931) cells are used occasionally together with various devices (Verwey & Heilmann, 1947) to compensate for surface dipoles (de Boer, 1948; Verwey, de Boer & van Santen, 1948). Wood (1959) suggested a method for eliminating

surface dipoles by summation over 'neutral molecules' and applied the method to three simple salts. The actual procedure is described extremely vaguely and the results are confused. The computer time of 8 hr which was used per calculation also appears to be unreasonable. Frank (1950) added fictitious charges at various points in the structure to ensure convergence. It will be shown that most of the problems are not real and that the Madelung energy for any centrosymmetric structure can be computed directly in a matter of minutes.

Procedure

The electrostatic or Madelung energy of an ionic crystal is given by the sum of an infinite series with terms corresponding to all pairwise interactions between ions considered as point charges. The series converges and is evidently well suited for summation by digital methods. The obvious sum to evaluate is

$$U = - \frac{N}{2D} \sum_{h=-n}^n \sum_{k=-n}^n \sum_{l=-n}^n \sum_{i=1}^c \sum_{j=1}^f \frac{q_i q_j}{r_{ij}}$$

where:

- r_{ij} = distance between ions i and j ,
- $q_{i,j}$ = electrostatic charges on the ions,
- f = number of ions in one formula unit (reference ions),
- c = number of ions in one unit cell,
- N = Avogadro number,
- D = dimensional constant,
- n = integer large enough to ensure convergence,
- h, k, l = denote unit cells in the three crystallographic directions. The i atoms are taken in the cell defined by the current values of h, k and l while the j atoms are always taken in the zero cell.

In words: all the interactions between the ions of one formula unit in the centre of a block consisting of

$(2n+1)^3$ unit cells, and all the ions in that block are calculated successively and the sum of the interactions is accumulated as the calculation proceeds. The input parameters are the cell constants, the fractional coordinates of all c ions with the f ions first in the parameter list, suitable charge numbers for each ion and a definition of the extent of the calculation – the number n . To assess the rate of convergence it is convenient to have the sub-totals corresponding to the interactions of the chosen formula unit with all the ions in the blocks defined by $h, k, l = 0, -1$ to $1, -2$ to 2 , etc. as output. These blocks contain 1, 27, 125, etc. unit cells.

The input parameters and the results (Table 1) obtained for the NaCl structure are given as an illustration: $n = 10, a_0 = 5.64, c = 8, f = 2$.

x	y	z	q
0	0	0	1
0	0	0.5	-1
0	0.5	0	-1
0.5	0	0	-1
0.5	0.5	0.5	-1
0	0.5	0.5	1
0.5	0	0.5	1
0.5	0.5	0	1

The convergence is satisfactory and the complete calculation over the 9261 cells took less than 5 minutes of IBM 360/40 computer time.

An analogous summation for the CsCl structure gave convergence of $-U$ to -5.602 kcal.mole⁻¹. The method breaks down because of the large surface dipole created by this method of generating the volume included in the calculation. This dipole does not occur in the NaCl structure since the calculation is terminated in a surface containing a regular alternation of positive and negative charges and hence no surface dipoles. A similar surface can be arranged in the CsCl structure by

Table 1. U (kcal.mole⁻¹)

Block	Direct	Transformed cell			Evjen cells		Evjen surface
	NaCl	ZnS	CaF ₂	CsCl	CsCl	Cu ₂ O	Cu ₂ O
1	171.057	832.925	561.647	131.519	64.212	315.582	493.211
2	205.246	927.838	706.205	163.035	164.097	797.610	400.990
3	205.299	926.959	705.584	163.474	163.664	796.083	393.811
4	205.305	926.779	705.596	163.549	163.668	796.073	391.839
5	205.306	926.711		163.578	163.668	796.063	391.027
6	205.306	926.678		163.592	163.668	796.046	390.607
7	205.306			163.600		796.038	390.370
8	205.306			163.605		796.039	390.229
9	205.306			163.609		796.050	390.146
10	205.306			163.611		796.064	390.094
11	205.306			163.612		796.083	796.122
a_0	5.64	5.409	5.463	4.12	4.12	4.27	4.27
α	1.74755	1.3878	5.0379	1.7631	1.7626	4.4425	4.4427
Johnson & Templeton (1961)	1.74756	1.3881	5.0388		1.76268		4.4425

Table 2. Direct summation results

Compound	Structure	$-U$ (kcal.mole ⁻¹)	α	Literature	Reference	Remarks
Rutile (TiO ₂)	<i>P4₂/mnm</i> , Ti- <i>a</i> ; O- <i>f</i> :0.3053; <i>a</i> =4.59373, <i>c</i> =2.95812	3248.933	4.7713	(19.0803)/4 =4.7701	Johnson & Templeton (1961)	<i>n</i> =10
Spinel (MgAl ₂ O ₄)	<i>Fd3m</i> ; Mg- <i>a</i> ; Al- <i>d</i> ; O- <i>e</i> :0.262; <i>a</i> =8.08	5440.394	7.8712	(31.475)/4 =7.869	Johnson & Templeton (1961)	Origin at centre ($\bar{3}m$) <i>n</i> =4
AlCl ₃	<i>C2/m</i> ; Al- <i>g</i> :0.167; Cl- <i>i</i> :0.226; 0.219; Cl- <i>j</i> :0.25, 0.175, 0.781, <i>a</i> =5.93, <i>b</i> =10.24, <i>c</i> =6.17, β =108	1199.108	8.3072	8.303	Johnson & Templeton (1961)	<i>n</i> =5
Cs ₂ CuCl ₄	<i>Pnma</i> ; Cs- <i>c</i> :0.1317, 0.1018; Cs- <i>c</i> :0.0065, -0.3268; Cu- <i>c</i> :0.232, 0.4178; Cl- <i>c</i> :0.334, 0.5745; Cl- <i>c</i> :0.003, 0.3935; Cl- <i>d</i> :0.2940, 0.0, 0.35; <i>a</i> =9.719, <i>b</i> =7.658, <i>c</i> =12.358	342.357	3.5524	348.4 kcal.mole ⁻¹	Blake & Cotton (1963)	Cu ²⁺ , Cl- <i>n</i> =5
K ₂ SO ₄	<i>Pnma</i> ; K- <i>c</i> :0.6768, 0.4182; K- <i>c</i> : -0.0115, -0.2954; S- <i>c</i> :0.2358, 0.4155; O- <i>c</i> :0.0315, 0.4032; O- <i>c</i> :0.297, 0.5579; O- <i>c</i> :0.2997, 0.041, 0.3484; <i>a</i> =7.483, <i>b</i> =5.772, <i>c</i> =10.072	458.735 474.849	3.6811 4.7300	455.8 kcal.mole ⁻¹ 480.4 kcal.mole ⁻¹	Wood (1959) Wood (1959)	S ²⁺ , O ⁻ , <i>n</i> =5 S ²⁻ , O ⁰ , <i>n</i> =10 (Some assumptions had to be made in calculating the liter- ature values from the listed constants.)
TiNO ₃ .4(thiourea)	<i>P4/mcc</i> ; Ti- <i>a</i> ; (NO ₃) ⁻ <i>d</i> ; S- <i>m</i> :0.2614, 0.0411; N- <i>n</i> :0.168, 0.367, 0.147; <i>a</i> =10.34, <i>c</i> =8.29	200.903	18.0279	201 kcal.mole ⁻¹	Boeyens & Gafner (1968)	<i>q_s</i> = -0.66e <i>q_N</i> = 0.33e <i>n</i> =5
Cs ₂ CoCl ₄	<i>Pnma</i> ; Cs- <i>c</i> :0.36, 0.1009; Cs- <i>c</i> :0.0208, -0.1762; Co- <i>c</i> :0.2668, 0.4227; Cl- <i>c</i> :0.497, 0.402; Cl- <i>c</i> :0.1893, -0.4133; Cl- <i>d</i> :0.1775, 0.0016, 0.3466; <i>a</i> =9.737, <i>b</i> =7.392, <i>c</i> =12.972	338.409	3.5039	342.5 kcal.mole ⁻¹	Blake & Cotton (1963)	Co ²⁺ , Cl- <i>n</i> =5

transformation to a distorted NaCl structure using the matrix (111/111/111). For this transformed structure the input parameters are: $n=10$, $a_0=b_0=c_0=7.137 \text{ \AA}$; $\alpha=\beta=\gamma=109^\circ 26'$; x, y, z, q as for NaCl, and the output values as shown in Table 1. This method applies only to structures which can be transformed to cells bounded by neutral faces, e.g. zinc blende and fluorite. The transformation matrices are the same as for CsCl and the results are summarized in Table 1. For structures like rutile and cuprite, however, such neutral faces do not exist and this method can therefore not be applied (Boeyens & Gafner, 1968).

Another way of eliminating the surface dipoles is by using Evjen cells instead of the conventional crystallographic unit cells. In an Evjen cell any ion shared by more than one unit cell is placed, properly scaled, at all equivalent positions in the unit cell. Thus ions lying at the corners, on the edges or in the faces of the unit cell will appear 8, 4 or 2 times and the charges will be scaled by factors of $\frac{1}{8}$, $\frac{1}{4}$ and $\frac{1}{2}$. By generating a block of unit cells as described before, all these fractional charges will add up to unit charges in the body of the block and will appear as fractions only on the surface where the summation is terminated. Whenever one of the reference ions occupies such a position, a multiplier of 8, 4 or 2 must be introduced to get its contributions calculated on the right scale. Care should also be taken not to calculate the interaction of a reference ion with an equivalent fraction with which it coincides after translation (i.e. $r_{ij}=0$). Typical results obtained by this method are also shown in Table 1.

To optimize the program efficiency the block needed for convergence can be generated from conventional unit cells and then corrected for the constant surface error by enveloping this volume in an Evjen surface. Correction for surface dipoles is thus not applied continuously and is included only when the outermost shell is considered. As shown in Table 1 for Cu_2O the correction is contained only in the last entry (block 11) and hence the course of the convergence is not as striking as before, but obviously the correct answer is again obtained.

The Madelung energies of ionic salts containing complex ions are often of importance. (Blake & Cotton, 1963). In such ions the charges can be situated as fractions at various centres on the ion. The same is true for fractional charges on a dipole in ion-dipole complexes (Boeyens & Gafner, 1968). Obviously the electrostatic interactions between such charge centres on the same ion or dipole do not contribute to the Madelung energies and can easily be excluded in a computer summation.

Results

Table 2 shows the results obtained by direct summation for a variety of structures. These results are all exact and higher accuracy can easily be obtained by increasing the extent of the calculations. Even in the large structures the time factor is not too important. The calculations were all done in a matter of minutes on the IBM 360/40H. The slight discrepancies occurring in Table 1 are all due to rounding-off errors and disappear if double precision (64 bit) arithmetic is used. The corresponding values obtained by previous workers using other techniques are also given. All the Madelung constants (α) listed are based on the closest interionic approach and the smallest charge in the structure. In several cases this quantity is not really meaningful and since authors often do not give a precise definition of their Madelung constants, it is suggested that for complicated structures the Madelung energy should always be given in either kcal.mole^{-1} or eV.

The program described here can handle any symmetry but its applicability to structures without a centre of symmetry at the origin is doubtful. If the CsCl structure is described in terms of the unit cell with origin at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ from the centre of symmetry, a Madelung energy of $-5.6 \text{ kcal.mole}^{-1}$ would be calculated.

As seen from the two calculations for CsCl in Table 1, convergence is faster for Evjen cells than for suitably transformed cells and since the introduction of an Evjen surface speeds up the calculation this last procedure is recommended for general use.

A Fortran listing of this program and a companion transformation program which can also be used to prepare the input data for the Madelung program can be obtained from the authors.

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