

The Calculation of Crystal Energies as an Aid in Structural Chemistry. I. A Semi-empirical Potential-Field Model with Atomic Constants as Parameters*

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A computer program has been written to calculate crystal energies as sums of Coulomb, van der Waals, repulsion and covalent bonding interactions. In this paper the general theory that leads to the energy expression is explained. It is shown that the choice of parameters and the inclusion of anisotropic thermal motion leads to the successful calculation of actual minimum energies for existing structures both for ionic and non-ionic compounds. The lattice-dynamical aspects of the model are discussed and the model is shown to be applicable to the analysis of lattice vibrations as used in the refinement of X-ray structure determinations. In further papers there will be a discussion of structural chemistry of different classes of compounds in terms of crystal energy.

1. Introduction

The interpretation of the crystalline state of matter in terms of interatomic or intermolecular forces has always been of interest in crystallography, although there has been no fundamental improvement of the energy expressions used since Born & Mayer (1932). This field of crystallographic investigation has been approached in two different ways depending on the substances treated. One, using the Born–Mayer potential, deals only with ionic crystals; the other, using more or less empirically evaluated expressions, deals only with organic molecules (Kitaigorodski, 1961). Although somewhat crude in its assumptions the latter model gave good results for the packing of organic molecules. As shown by Mirsky (1975) the quality of the results obtained from simple force-field calculations depends only on the choice of a suitable parameter set. For ionic crystals the problem is much more complicated. Busing (1970) has shown that the use of the Born–Mayer potential fails to predict structures that are influenced by strong electronic interactions. On the other hand the need for extensive computer time for solving relatively simple structural problems decreases the interest in treating crystallographic problems by lattice-energy calculations. So it is not surprising that there exists no general energy expression that can be used for calculations of ionic as well as non-ionic crystal structures. Skorczyk (1975) investigated the possibility of an approach to a general field theory applicable to all types of compounds and crystal structures. The only restriction on this theory is that it fails in cases where the structures are determined solely by electronic effects, as in metals, or in substances where spin orientation has to be taken into account.

2. The potential field

The crystal structure of a compound is determined mainly by two interdependent influences that are responsible for the formation of the observed lattice and the topology of each lattice point. These are the energy gained by forming a more or less close packing of the atoms involved, mainly determined by Coulomb, van der Waals and repulsion forces and the energy gained by forming as many covalent bonds as possible to each atom, determined by the most favourable electron distribution with respect to the neighbours (this be correlated with the heat of formation of complexes for example and with all types of electronic calculations for isolated molecules).

The first part can be called the Born–Mayer part (BMPCE) and the second the covalent bonding part of the crystal energy (CBPCE). The mathematical problem is then to evaluate the two parts independently and to optimize the energy as a sum of them with respect to the geometry of the crystal.

The requirement of spending as little computer time as possible demands that all potentials should be evaluated without the use of quantum mechanics. This choice of a classical description leads to the use of parameters to be varied independently but their number must be restricted because it is well known from theoretical chemistry that it is possible to describe any phenomenon if there are enough variable parameters.

2.1. Definition of the crystal energy

Because of the narrow definition of lattice energy which is only useful for ionic crystals, it is convenient to define a 'crystal energy' as follows: The crystal energy is the work done in bringing the atoms in the state they have in the crystal, including any partial charge as actually observed in the crystal, from infinity to their places in the lattice. For pure ionic crystals this defini-

* Part of the thesis of Reinhard Skorczyk.

tion is in accordance with the definition of lattice energy. More generally the lattice energy is the energy obtained by subtracting the bonding energy from the crystal energy.

2.2. The choice of parameters

The set of parameters is subdivided into atomic and structural parameters. In each group there is only one parameter that can be varied independently. The others are all calculated from atomic constants or well-known structural features. The atomic constants are taken from standard compilations. This restriction on the

choice of parameters is made because the calculations must be done easily and not depend on measurements to be carried out in advance.

2.3. The atomic parameters

All atomic parameters are listed in Table 1 with their symbols as used in the energy expressions. The so-called Pauling radii b_{ij} (Table 2) are atomic increments with the dimension of a length that are needed to compute incremental force constants from Badger's (1934) equation. The parameter $\rho_{r_{ij}}$ (Table 3) (percentage covalent character) is given as an atomic param-

Table 1. *The atomic constants of atom i , ordering number Z_i , electronegativity E_i , ionic radius (of charge) $R_i(Q_i)$, covalent radius c_i*

Atom _{<i>i</i>}	Z_i	E_i	$R_i(Q_i)$	c_i	Atom _{<i>i</i>}	Z_i	E_i	$R_i(Q_i)$	c_i
H	1	2.1	2.08 (-1)	0.37	Ru	44	2.2	0.69 (+3)	—
Li	3	1.0	0.60 (+1)	1.34				0.64 (+4)	—
Be	4	1.5	0.31 (+2)	0.90	Rh	45	2.2	0.86 (+2)	—
B	5	2.0	0.20 (+3)	0.82	Pd	46	2.2	0.50 (+2)	—
C	6	2.5	2.60 (-4)	0.77	Ag	47	1.9	1.26 (+1)	1.53
			0.15 (+4)		Cd	48	1.7	0.97 (+2)	1.48
N	7	3.0	1.71 (-3)	0.75	In	49	1.7	0.81 (+3)	1.44
			0.11 (+5)		Sn	50	1.8	1.12 (+2)	1.41
O	8	3.5	1.40 (-2)	0.73				0.71 (+4)	
F	9	4.0	1.36 (-1)	0.72	Sb	51	1.9	2.45 (-3)	1.38
Na	11	0.9	0.95 (+1)	1.54				0.62 (+5)	
Mg	12	1.2	0.65 (+2)	1.30	Te	52	2.1	2.21 (-2)	1.35
Al	13	1.5	0.50 (+3)	1.18				0.56 (+6)	
Si	14	1.8	2.71 (-1)	1.11	I	53	2.5	2.16 (-1)	1.33
			0.41 (+4)					0.50 (+7)	
P	15	2.1	2.12 (-3)	1.06	Cs	55	0.7	1.69 (+1)	2.25
			0.34 (+5)		Ba	56	0.9	1.35 (+2)	1.98
S	16	2.5	1.84 (-2)	1.02	La	57	1.1	1.15 (+3)	1.69
			0.29 (+6)		Ce	58	1.1	1.01 (+4)	1.65
Cl	17	3.0	1.81 (-1)	0.99	Pr	59	1.1	1.09 (+3)	1.65
			0.26 (+7)		Nd	60	1.2	1.08 (+3)	1.64
K	19	0.8	1.33 (+1)	1.96	Sm	62	1.2	1.04 (+3)	1.66
Ca	20	1.0	0.99 (+2)	1.74	Eu	63	(1.2)	1.12 (+2)	1.85
Sc	21	1.3	0.81 (+3)	1.44	Gd	64	1.1	1.02 (+3)	1.61
Ti	22	1.5	0.68 (+4)	1.36	Tb	65	1.2	1.00 (+3)	1.59
V	23	1.6	0.59 (+5)	—	Dy	66	(1.2)	0.99 (+3)	1.59
Cr	24	1.6	0.52 (+6)	—	Ho	67	1.2	0.97 (+3)	1.58
Mn	25	1.5	0.46 (+7)	—	Er	68	1.2	0.96 (+3)	1.57
Fe	26	1.8	0.76 (+2)	—	Tm	69	1.2	0.95 (+3)	1.56
			0.64 (+3)		Yb	70	1.1	1.13 (+2)	1.70
Co	27	1.8	0.78 (+2)	—	Lu	71	1.2	0.93 (+3)	1.56
			0.63 (+3)		Hf	72	1.3	0.81 (+4)	—
Ni	28	1.8	0.78 (+2)	—	Ta	73	1.5	0.73 (+5)	—
			0.62 (+3)		W	74	1.7	0.68 (+6)	—
Cu	29	1.9	0.96 (+1)	1.38	Re	75	1.9	—	—
			0.69 (+2)		Os	76	2.2	0.67 (+4)	—
Zn	30	1.6	0.74 (+2)	1.31	Ir	77	2.2	0.66 (+4)	—
Ga	31	1.6	0.62 (+3)	1.26	Pt	78	2.2	0.52 (+2)	—
Ge	32	1.8	0.53 (+4)	1.22	Au	79	2.4	1.37 (+1)	1.50
As	33	2.0	2.22 (-3)	1.19	Hg	80	1.9	1.10 (+2)	1.49
			0.47 (+5)		Tl	81	1.8	0.95 (+3)	1.48
Se	34	2.4	1.98 (-2)	1.16	Pb	82	1.8	1.20 (+2)	1.47
			0.42 (+6)					0.84 (+4)	
Br	35	2.8	1.95 (-1)	1.14	Bi	83	1.9	1.20 (+3)	1.46
			0.39 (+7)					0.74 (+5)	
Rb	37	0.8	1.48 (+1)	2.11	Fr	87	0.7	1.76 (+1)	—
Sr	38	1.0	1.13 (+2)	1.92	Ra	88	0.9	1.40 (+2)	—
Y	39	1.3	0.93 (+3)	1.62	Ac	89	1.1	1.18 (+3)	—
					Th	90	1.3	1.14 (+3)	1.65
Zr	40	1.4	0.80 (+4)	1.48	Pa	91	1.5	1.12 (+3)	—
Nb	41	1.6	0.70 (+5)	—	U	92	1.7	1.11 (+3)	1.42
Mo	42	1.8	0.62 (+6)	—				0.89 (+4)	

eter because its value depends on the difference in electronegativity between bonded atoms and it is needed to calculate the effective charge on each atom. In addition it belongs to the CBPCE which is assumed atom specific. Its numerical values are listed in Table 3. All atomic parameters which cannot be obtained from compilations directly are explained in the next sections.

Table 2. Constants for calculation of force constants from Badger's equation

Element	a_{ij}	b_{ij} (in Å)
H ₂	2.32	0.025
Cl ₂	2.04	1.25
Br ₂	1.98	1.48
I ₂	2.04	1.76
Li, Be, C	2.89	1.13
Na, Mg, Al, Si	3.10	1.73
K, Ca, Ti, V, Ge	2.06	1.46
Cr, Fe, Co, Ni, Cu	13.30	2.31
Rb, Sr, Zr, Nb, Mo, Sn	2.32	1.86
Ru, Rh, Pd, Ag	4.12	2.10
Ba, Ta, W	2.03	1.80
Ce, Ir, Pt, Au, Tl	2.96	1.99

Table 3. The parameter Pr_{ij} (percent ionic character) and its dependence on the difference of electronegativity

$(E_i - E_j) \times 10$	% Ionic character	Pr_{ij}	$(E_i - E_j) \times 10$	% Ionic character	Pr_{ij}
1	0.5	0.995	17	51	0.49
2	1	0.99	18	55	0.45
3	2	0.98	19	59	0.41
4	4	0.96	20	63	0.37
5	6	0.94	21	67	0.33
6	9	0.91	22	70	0.30
7	12	0.88	23	74	0.26
8	15	0.85	24	76	0.24
9	19	0.81	25	79	0.21
10	22	0.78	26	82	0.18
11	26	0.74	27	84	0.16
12	30	0.70	28	86	0.14
13	34	0.66	29	88	0.12
14	39	0.61	30	89	0.11
15	43	0.57	31	91	0.09
16	47	0.53	32	92	0.08

2.3.1. The effective charge

For the calculation of the effective charge the following expression is used:

$$Q_i(\text{eff}) = Q_i + \sum_j^N Pr_{ij}^2 \text{sign}(E_i - E_j), \quad (1)$$

(N = number of atoms j bonded to atom i).

As only the effective charge is used in calculations, the index (eff) will be omitted. The partial charges obtained in this way are in good agreement with those obtained from quantum-mechanical calculations by semi-empirical methods (Skorczyk, 1972). The quadratic form of the Pr_{ij} comes from the fact that a power-series expansion was used and it was found that agreement is sufficient when only the quadratic term is used.

2.3.2. The polarizability

From quantum mechanics (Schäfer, 1965) it is known that the polarizability is proportional to the third power of the radius of the electron shell. Because the value of P_i depends directly on the strength of the electron attraction by the nucleus, the proportionality constant can be approximated by an expression using the ratio of electronic charge to charge of the nucleus (atomic number) and the electronegativity,

$$P_i = \frac{(4\pi/3)R_i^3}{E_i} \exp(-Q_i/Z_i). \quad (2)$$

If one thinks of the polarizability in a more classical fashion, as in the Clausius-Mosotti equation, the validity of (2) may be doubted, especially for heavy atoms. A better interpretation is to think of the cube root of (2) as the root mean amplitude of the Cartesian components of the zero-point vibration.

2.3.3. The hardness parameters

The hardness parameters are defined as a measure of the compressibility of an isolated atom in a bond direction. In the work of Born & Mayer (1932) they are not incremented but taken as an average factor specific to the class of compound involved. Because this procedure is valid only for binary systems, Gilbert (1968) generalized the concept by splitting this factor into individual atomic parameters. As Gilbert's way of obtaining the hardness parameters from SCF calculations and from the vibrational spectra of diatomic molecules is too complicated, an empirical expression is used which calculates the parameters from the atomic number, the electronic charge and the ionic radius only. For computing the expression uses only relative values of the hardness parameters. Their absolute values are somewhat structure dependent and are adjusted by a scale factor explained in § 2.3.4. The formula is based on the fact that the hardness increases with the number of electrons in a given volume and decreases with that volume because of less hindrance of the electrons. The second influence taken into account is the electron attraction by the net charge of the atom. The expression is (note that a small numerical value means great hardness and *vice versa*, because the dimension is a length)

$$h_i = \frac{R_i}{Z_i - Q_i} \exp(Q_i). \quad (3)$$

2.3.4. The scale factor of the hardness parameters

This factor scales the values of the hardness parameters in pairs of all possible interactions, *e.g.* for NaCl these pairs are Na-Na, Na-Cl and Cl-Cl. It is an overall factor that is adjusted according to certain minimum conditions for the crystal energy obtained from the second derivatives of the repulsion potential and the difference between overall potential and repulsion. Its numerical value can be interpreted as the percentage contribution of the repulsion in the crystalline state

compared with that in the isolated molecule. One condition for its calculation is the fact that in an existing structure the positions of all atoms belong to a local energy minimum corresponding to the equilibrium position of each atom. From this the conditions for the second derivatives are

$$\left(\frac{\partial^2 R}{\partial r_{ij}^2}\right)_{r=r_0} = a \leq 0 \leq \left(\frac{\partial^2(W-R)}{\partial r_{ij}^2}\right)_{r=r_0} = b \quad (4)$$

and

$$|a| = |b|, \quad (4a)$$

(W = overall potential = crystal energy, R = repulsion). The above conditions mean that at equilibrium the repulsive force must increase at the same rate as the attractive force with respect to interatomic distances.

2.4. The structural parameters

The common structural parameters are the lattice constants and the atomic parameters. In addition, the tensor of the thermal motion represented by a probability density function of the atoms is treated as a structural parameter in crystallography. From the lattice constants and the atomic parameters a set of equilibrium distances for a given structure can be evaluated. This set of r_0 's uses, for the calculation of the other structural parameters, the so-called soft-sphere radii (Gilbert, 1968) which correspond to the thermal vibrations of the atoms. The calculation of the soft-sphere radii from the thermal ellipsoids leads to the successful calculation of energy minima for non-spherical structures as will be shown in part III of this series.

2.5. The soft-sphere radii

The calculation of the soft-sphere radii is separated into two steps. The first is the analysis of the possible vibrations of each atom with respect to nearest-neighbour interactions and the determination of the orientation and the relative length of the axes of the thermal ellipsoids. The second step is the determination of the absolute volume of the ellipsoids with respect to the crystal energy.

2.5.1. The analysis of atomic vibrations

The possible directions of vibration for an atom in a neighbourhood of given symmetry are determined by two influences. One is the strength of the bonds and the other the stretching-force constant for these bonds. For the calculation of the crystal energy only components in bond directions are taken into account; force constants for torsional oscillation can be omitted. To calculate the relative elongation from the harmonic oscillators, reduced values for energy and force constant are used. They are defined as

$$E_{ij} = E(r=r_{ij})/E(r=r_0) \quad (5)$$

$$f_{ij} = (f_i + f_j)_{r_{ij}} / (f_i + f_j)_{r=r_0} \quad (5a)$$

(Note that r_0 is not the equilibrium distance but an arbitrarily chosen distance which in normal cases is set

to 1 Å by the program.) The force-constant increments are obtained from Badger's equation (Badger, 1935; Pauling, 1968):

$$f_{ij}^{-1/3} = a_{ij}(r_{ij} - b_{ij}) \quad (6)$$

The increments are obtained from the assumption

$$f_{ij} = \frac{1}{2}(f_{ii} + f_{jj}) \quad (6a)$$

This might appear to be a rather rough assumption, but as one needs only relative values the agreement of calculated and observed temperature factors with this approximation is very good (Table 4). With this term a displacement vector is calculated to each neighbouring atom j from atom i after the harmonic oscillator

$$\bar{u}_i^j = (E_{ij}/f_{ij})^{1/2} \quad (7)$$

To this star of vectors an ellipsoid is now fitted minimizing the quadratic deviation of the endpoints of these vectors from the ellipsoid surface. From this the lattice-dependent orientation and relative length of the axes are obtained.

Table 4. Observed and calculated Debye-Waller factors for different structures

Compound	Atom	B_{calc} (Å ²)	B_{obs} (Å ²)	$B_{\text{calc}} - B_{\text{obs}}$	$\left[\frac{B_{\text{calc}} - B_{\text{obs}}}{B_{\text{obs}}}\right] \times 100$ (%)
MgCl ₂ <i>R3m</i>	Mg	0.68			
	Cl	2.17			
CaCl ₂ <i>Pnmm</i>	Ca	0.37			
	Cl	0.85			
SrCl ₂ <i>Fm3m</i>	Sr	0.19			
	Cl	0.69			
BaCl ₂ <i>Pbnm</i>	Ba	1.43			
	Cl(1)	1.52			
	Cl(2)	1.79			
EuCl ₂ <i>Pbnm</i>	Eu	1.13	1.04	0.09	8.6
	Cl(1)	1.17	1.09	0.06	5.5
	Cl(2)	1.31	1.25	0.06	4.8
EuBr ₂ <i>P4/n</i>	Eu(1)	1.60	1.52	0.08	5.3
	Eu(2)	1.48	1.39	0.09	6.5
	Br(1)	2.16	2.02	0.14	6.9
	Br(2)	1.67	1.59	0.08	5.0
	Br(3)	1.43	1.38	0.05	3.6
EuI ₂ <i>P2₁/c</i>	Eu	1.51	1.5	0.01	0.7
	J(1)	2.10	2.04	0.06	2.9
	J(2)	1.51	1.5	0.01	0.7
	Eu	1.4	1.37	0.03	2.2
EuI ₂ <i>Pbca</i>	J(1)	2.2	2.15	0.05	2.3
	J(2)	1.6	1.57	0.03	1.9
	Eu	1.4	1.37	0.03	2.2
(C ₆ H ₆) ₂ Cr	Cr	0.37	0.36	0.01	2.8
	C(1)	0.77	0.9	0.13	14.4
	C(2)	0.72	0.8	0.08	10.0
	H(1)*	(0.95)	(1.0)	0.05	(5.0)
	H(2)*	(1.2)	(1.0)	0.2	(20.0)

* Not significant.

The expression used to calculate the E_{ij} is the same (with isotropic soft-sphere radii for the repulsion) as for the total crystal energy. As recently shown by Killean & Lisher (1975*a, b, c, d*) and Mair, Mathieson & Killean (1975) simple potentials give good results for calculated Debye–Waller factors.

2.5.2. The absolute thermal ellipsoids

The tensor u^{ij} of the thermal ellipsoids is absolutely determined by the following conditions:

$$dW(u^{ij})=0, \quad (8)$$

$$d(W-R)/du^{ij} = -dR(u^{ij}). \quad (8a)$$

The ellipsoids are fitted to those conditions by varying their volume. These values can be compared directly with those obtained from X-ray determinations. Table 4 shows that the agreement is within experimental error.

The so-called soft-sphere radii are now defined as the vector components \bar{u}_i^j of u^{ij} in direction $i-j$. For a pure *ab initio* calculation of the crystal structure of a compound they might be used in a different way, because there is no lattice known for vibrational analysis. In this case one can take them to imply the deviation of the electron shell from spherical symmetry depending on the influence of a non-spherical Fermi surface. The author doubts that there is much purpose in such calculations. In part II it will be shown that a partial *ab initio* calculation is a useful aid in structural chemistry.

2.6. The crystal energy

2.6.1. The BMPCE

The BMPCE consists of three terms which are modifications of that used in Busing's (1970) work to calculate the lattice energy. The expression used here is

$$L = \sum_i \sum_j \frac{Q_i Q_j e^2}{r_{ij}} \exp(R_i + R_j - r_{ij}) - v_s^{-3} K_v \frac{Z_i \sqrt{p_i} Z_j \sqrt{p_j}}{r_{ij}^6} + S_h(h_i + h_j) \exp\left(\frac{U_{ij} - r_{ij}}{S_h(h_i + h_j)}\right). \quad (9)$$

The sound velocity v_s in the van der Waals term is the second free parameter. If it is not known, it is determined from the condition $W_{\text{obs}} - W_{\text{calc}} = \min$. The inner summation goes over all atoms in one unit cell, while the outer summation goes over all atoms in a sphere which contains enough atoms to take all interactions sufficiently into account. There are 27 cells* from $-a$ to $2a$, $-b$ to $2b$ and $-c$ to $2c$ (a , b and c are cell parameters). This sphere must always follow Pauling's principle of electroneutrality.

The van der Waals term is derived from the London model of perturbed coupled oscillators. As it is often difficult to evaluate the frequencies needed, the am-

plitudes of the oscillation are calculated from the polarizability with the relation $1/\nu_i \sim Z_i/p_i$. With this the constant K_v is determined as $(3e^4 h)/(64\pi^4 m_e^2)$, m_e being the mass of the electron. The consequence of the modification of the London model to a model of mechanical interaction of the electron shells is the introduction of the sound velocity into the van der Waals term.

The Born distance U_{ij} in the repulsion potential is calculated as the sum of the ionic radii and the soft-sphere radii,

$$U_{ij} = R_i + R_j + \bar{u}_i^j + \bar{u}_j^i. \quad (9a)$$

The exponential factor in the Coulomb potential is used as a modification function to improve convergence, because all summations are carried out in direct space. On the other hand, it can be used to calculate permanent dipole moments by varying the ionic radii with respect to the energy minimum, which gives the components of the polarization tensor. The results obtained from this potential cannot be compared with those from MAPLE calculations (Hoppe & Stewner, 1971) except for cubic structures because the atoms are not taken as point charges. For the 'classical' compounds treated with lattice-energy calculations (Born, 1918*a, b*; Landé, 1918; Ewald, 1921; Born & Mayer, 1932; Bertaut, 1952) the calculation of the BMPCE is sufficient, because the CBPCE gives only small corrections to the results. Simple MAPLE calculations (Hoppe & Stewner, 1971) are not as useful in structural chemistry, as emphasized by Hoppe himself.

2.6.2. The CBPCE

It is known from quantum-mechanical calculations that the influence of covalent bonding is always present, even in LiF or NaCl. Thus it is obvious that its contribution to the crystal energy cannot be neglected.

The treatment of the problem is separated into a radial and an angular part according to the classical treatment of wave functions. The radial part is taken as a simple energy distribution with respect to ideal bond lengths weighted by the percentage of covalent character of the bond treated:

$$C = - \sum_i \sum_j \text{Pr}_{ij} E_{ij}^d \left\{ 1 - \exp \left[- \left(\frac{r_{ij}}{r_{ij} - (c_i + c_j)} \right)^2 \right] \right\}. \quad (10)$$

The energy of dissociation E_{ij}^d can be taken from compilations or from quantum-mechanical calculations. The angular part of the CBPCE calculates the angular strain of the coordination polyhedra coming from the deviation from ideal hybridization of the central atom. By ideal hybridization is meant that electron distribution which depends only on the electron configuration of the atom in the bond state. This potential is also weighted by the percentage covalent character:

$$\Phi = \sum_i \sum_j \text{Pr}_{ij} E_{ij}^d \sum_k \sin^2 \Delta\varphi_{ijk}. \quad (11)$$

The index k runs over all bonded neighbours.

* This value is set by the program.

2.6.3. The total energy

The total energy, the crystal energy itself, is the sum of all potentials presented:

$$W = L + C + \Phi. \quad (12)$$

Fig. 1 shows a representation of all contributing potentials with respect to distance.

The five-potential expression not only provides a more detailed description of existing structures with respect to lattice, topology and dynamics but also predicts stable phases by comparing possible structures (see part II of this series).

3. Program LATTICE

A computer program *LATTICE* has been written in Fortran for crystal-energy calculations with the potential-field model presented (Skorczyk & Tigges, 1975). The program is available for computers of the Univac 1100 series in two versions, one with 27 K words of core used and one for large molecules with 60 K words of core used. The small version is dimensioned as follows (large version given in brackets): 5 (99) atoms in asymmetric unit, 30 (792) in unit-cell and 540 (2500) atoms overall. Each atom may have six different neighbours and a maximum coordination of 12. The versions can readily be adopted for other computers with a minimum word length of 36 bit. A version for IBM 370 computers is in preparation (Skorczyk & Stegemann, 1975).

For minimization the program uses a simplex procedure written by the author. This simplex has the advantage of a very high speed, as does the whole program. On the Univac 1106/II of the Rechenzentrum Freiburg it takes 11 s CPU time to minimize the energy of $MgCl_2$ in its hexagonal cell and the calculation of all thermal ellipsoids of bis(benzene)chromium with 100 atoms in the unit cell and 1600 atoms overall needs 60 min, including the first energy minimization of the structure.

The calculation were carried out on the Univac 1106/II of the Rechenzentrum der Universität Freiburg, and on the IBM 370/168 of the Hochschulrechenzentrum der TH Darmstadt. Parts of this work were supported by the Deutsche Forschungsgemeinschaft. The author thanks Professor J. Felsche for valuable discussions, H. Tigges for assistance in programming, and Mrs U. Gebhard for typing the script.

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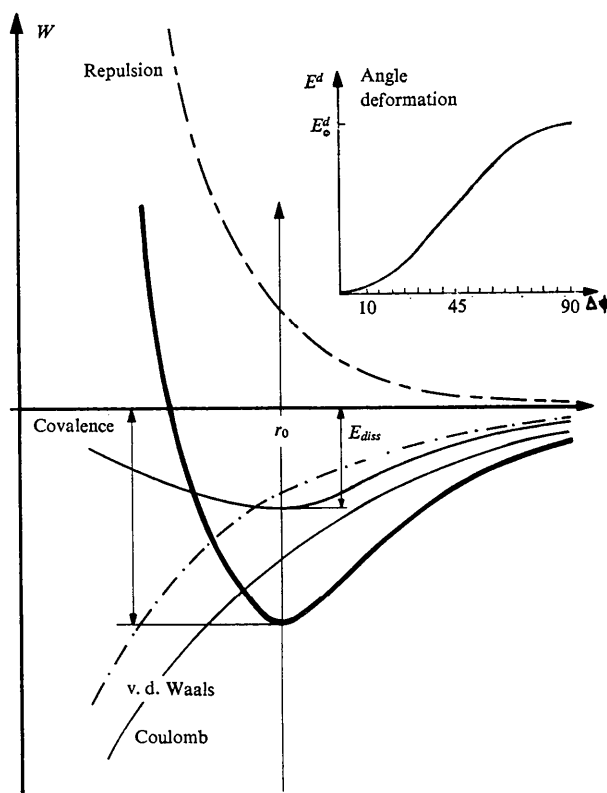


Fig. 1. Graphical representation of all partial energies contributing to the crystal energy.

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