Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: Jacek Rulewski , Piotr Skurski , Paweł Dokurno & Jerzy Błażejowski (1996): Crystal Lattice Energy of Aminoacid Hydrohalides, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 279:1, 219-231

To link to this article: http://dx.doi.org/10.1080/10587259608042192

Mol. Cryst. Liq. Cryst., 1996, Vol. 279, pp. 219–231
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CRYSTAL LATTICE ENERGY OF AMINOACID HYDROHALIDES

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Abstract - Basic relationships concerning thermodynamics of crystalline phases and the process of their formation, as well as energetics of intermolecular interactions in these, were invoked and discussed from the point of view of their application in studies of stability, features and behaviour of solid systems. Further, electrostatic, dispersive and repulsive contributions to the crystal lattice energy of 25 hydrohalides of aminoacids were calculated assuming that each atom of the basic stoichiometric unit interacts with all atoms from surroundings. Energy of electrostatic interactions was obtained assuming 1+ and 1− charges on cation and anion, respectively, and using atomic partial charges resulting from Mulliken population analysis or fitted so as to reproduce molecular electrostatic potential (MEP) around molecules, determined on ab initio Hartree-Fock (HF) or density functional theory (DFT) levels. Dispersive and repulsive contributions were evaluated by either Lennard-Jones or Buckingham equations using atomic (ionic) parameters for dispersive interactions originating from the London or Slater-Kirkwood theory and those for repulsive interactions resulting from the criterion of minimization of energy on separation of atoms (ions) equal to the sum of their van der Waals radii. Coulombic energies arising from charges fitted to MEP seem to be the most reliable. These values show a decreasing tendency with an increase of dimensions of ions (volume of basic stoichiometric units).

INTRODUCTION

Formation of a crystalline phase can be considered as a transfer of entities from a completely disordered gaseous phases (g) to perfectly ordered solid (s) phase which reflect the process,

$$\text{Gaseous entities } (y\ Y_{(g)}) \rightarrow \text{Crystalline phase } (Y_{(s)}) \qquad (1)$$

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where y represents a number of gaseous entities ($Y_{(g)}$) which constitute the simplest stoichiometric unit of a crystalline substance ($Y_{(s)}$). Energy (E) change for the process (1) at 0K ($\Delta_0 E$),

$$\Delta_0 E = E_{(s)} - yE_{(g)} = E_c \tag{2}$$

represents the crystal lattice energy (E_c).[1] When temperature (T) rises above 0 K the energy change can be expressed as $\Delta_T E$ or in terms of the enthalpy change ($\Delta_T H$). Both the above-mentioned quantities are affected by heat capacity (C_v, C_p changes, namely

$$\Delta_T E = E_c + \int_0^T \Delta_T C_v \, dT \tag{3}$$

and

$$\Delta_T H = E_c + \int_0^T \Delta_T C_p \, dT \tag{4}$$

where

$$\Delta_T C_v (\text{or } C_p) = C_{v(s)} (\text{or } C_{p(s)}) - y\, C_{v(g)} (\text{or } C_{p(g)}) \tag{5}$$

Complete thermodynamic description of the process (1) requires consideration of free energy ($\Delta_T F$) or free enthalpy ($\Delta_T G$) changes which combine energy and entropy ($\Delta_T S$) changes, namely

$$\Delta_T F = \Delta_T E - T\, \Delta_T S \tag{6}$$

$$\Delta_T G = \Delta_T H - T\, \Delta_T S \tag{7}$$

At 0K $\Delta_0 S$ and $\Delta_0 C_v$ admit zero values and thus crystal lattice energy remains the only quantity describing the thermodynamics of such phases. As this latter quantity reflects a natural tendency to interaction of entities (the magnitude of cohesive forces) and thus formation of ordered solid phases, its values always becomes negative. If the temperature rises the entropy factor, which reflects a natural tendency to dissipation (decomposition of smaller fragments) and thus formation of disordered systems, becomes more and more pronounced. The entropy change corresponding to the process (1) is always negative and the entropy term ($-T\Delta_T S$) in Equations (6) and (7) is thus positive. As entropy and heat capacity are related through the relationship $(\partial S/\partial T)_v = C_v/T$, the heat capacity terms in Equations (3) and (4) are also always negative, although their values change more slowly than those of the entropy term. At a certain temperature (e.g. sublimation temperature at atmospheric pressure), characteristic for a given substance, the energy terms in Equations (6) and (7) become

equal to the entropy term. Below this temperature the solid phase is more stable, above - the gaseous phase.

Values of the entropy and heat capacity for gaseous and crystalline systems can be predicted, at any temperature, on the basis of statistical thermodynamics - if frequencies of molecular and lattice vibrations are known.[2,3] This issue will not be touched on in this work. Instead, we will focus our attention on the crystal lattice energy problems. Values of this quantity can sometimes be obtained directly from experiment, for example by determining the energy of sublimation of molecular crystals, or through the thermochemical cycle, as in the case of ionic crystals.[1,4,5] Values of lattice energy originating from experiments are available rather for a limited number of compounds[6] and this constitutes a challenge for undertaking efforts directed towards the development of theoretical methods enabling prediction of these characteristics. Considerations concerning the crystal lattice energy must, in fact, touch on the problem of intermolecular interactions, which are nowadays intensively examined.[4] We thus believe that development of a theory describing energetics of crystalline phases will help to understand the nature not only of solids but also intermolecular interactions, being the attribute of the world surrounding us.

This paper is a contribution to this field. In particular, we will show how electrostatic, dispersive and repulsive contributions to the lattice energy of hydrohalides of aminoacids can be evaluated treating all interactions as atom (ion) - atom (ion) interactions. Further, we will discuss how methods of evaluation of partial atomic charges or atomic parameters influence the magnitude of individual contributions. Lastly, we will examine the influence of dimensions of interacting entities on the crystal lattice energy of the compounds studied.

Hydrohalides of aminoacids were selected for examination owing to their simplicity, availability of structural data and also crucial meaning for living matter.

PRINCIPLES OF CRYSTAL LATTICE ENERGY CALCULATIONS

Four contributions are usually considered in the theoretical description of the lattice energy (E_c) of molecular crystals, namely, electrostatic (E_{el}), dispersive (E_d) and repulsive (E_r), as well as the term of zero point energy (E_0),[5,7,8] which gives

$$E_c = E_{el} + E_d + E_r + E_0 . \quad (8)$$

E_{el} in Equation (8) represents Coulombic interactions,[1,4,5]

$$E_{el} = \frac{1}{2} \sum_{i} \sum_{j \neq i} \frac{Ne^2}{4\pi\varepsilon_0} \frac{Q_i Q_j}{R_{ij}} \tag{9}$$

E_0 can be estimated following the relationship,[8]

$$E_0 = \frac{1}{2Z} \sum_{k=1}^{6Z-3} Nhc(\bar{\nu}_L)_k \tag{10}$$

while the sum of E_d and E_r is expressed by various empirical formulae (potentials),[4] those of Lennard-Jones,[9]

$$E_d + E_r = \frac{1}{2} \sum_{i} \sum_{j \neq i} \left[-\frac{D_i D_j}{R_{ij}^6} + \frac{A_i A_j}{R_{ij}^{12}} \right] \tag{11}$$

and Buckingham,[10]

$$E_d + E_r = \frac{1}{2} \sum_{i} \sum_{j \neq i} \left[-\frac{D_i D_j}{R_{ij}^6} + B_i B_j \exp(-C_i C_j R_{ij}) \right] \tag{12}$$

being invoked in this work. In Equations (9)-(12) N is the Avogadro number, h the Planck constant, c the velocity of light, e the elementary charge, ϵ_0 the permittivity of free space, Z the number of molecules per unit cell, $\bar{\nu}_L$ the wavenumber of the lattice vibrations, while Q_i (Q_j) denote relative partial charges at atoms, D_i (D_j), B_i (B_j) and C_i (C_j) atomic parameters, and R_{ij} the distance between interacting centers (summation in Equations (9), (11) and (12) extends over all pairwise interactions between each atom of the basic stoichiometric unit (denoted as i) and all atoms from its surroundings (denoted as j)).

As lattice vibrations fall in the low energy region, their contribution through the E_0 (Equation (10)) term is usually negligible - particularly in the case of ionic crystals whose lattice energies of which attain relatively high values.[5,7]

Crystal lattice energy calculations require knowledge of the solid phase structures. In this work, these structures were extracted from the *Cambridge Structural Database System*.[11] Information concerning the compounds studied is given in Table I, while Figure 1 shows two selected cations in the crystalline phase.

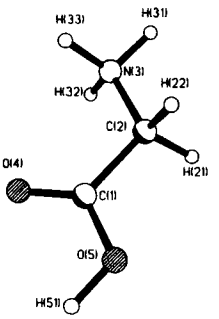
The energy of electrostatic interactions (Equation (9)) was calculated assuming that halide anions and organic cations gain 1− and 1+ charges, respectively, and that the charge in a complex cation is distributed over all the atoms. The corresponding atomic partial charges were derived on the ab initio Hartree-Fock (HF)[45] or density functional theory (DFT)[46] level, as Mulliken charges,[47] or those fitted so as to reproduce the molecular electrostatic potential (MEP fit).[48] These charges were derived

TABLE I Structural data for aminoacid hydrohalides.

No.	Substance	Space group	Z^a	$V/Z(Å^3)^b$	Ref.
1	Glycine.HCl	$P2_1/c$	4	127	12,13
2	Sarcosine.HCl	$P2_1$	2	144	14
3	N,N-DiMeGlycine.HCl	$P2_1/c$	4	175	15
4	Betaine.HCl	$P2_1/c$	4	196	16-18
5	L-Alanine.HCl	$P2_12_12_1$	4	164	13
6	L-Valine.HCl	$P2_1$	2	200	19,20
7	L-Valine.HCl.H_2O	$P2_12_12_1$	4	224	21
8	L-Isoleucine.HCl.H_2O	$P2_12_12_1$	4	249	22
9	L-Phenylalanine.HCl	$P2_12_12_1$	4	261	23,24
10	L-Glutamic acid.HCl	$P2_12_12_1$	4	203	25
11	L-Glutamine.HCl	$P2_12_12_1$	4	202	26
12	L-Tyrosine.HCl	$P2_1$	2	255	27
13	L-Cysteine.HCl.H_2O	$P2_12_12_1$	4	191	28
14	L-Methionine.HCl	$P2_12_12_1$	4	231	29
15	L-Ornithine.HCl	$P2_1$	2	255	30,31
16	L-Lysine.HCl.$2H_2O$	$P2_1$	2	291	32-34
17	1-Methyl-L-prolinium chloride	$P2_12_12_1$	4	212	35
18	cis-3,4-Methylene-L-proline.HCl.H_2O	$P2_12_12_1$	4	224	36
19	N-Methyl-4-hydroxy-L-proline.HCl	$P2_12_12_1$	4	222	37
20	L-Histidine.HCl.H_2O	$P2_12_12_1$	4	235	38-40
21	L-Tryptophan.HCl	$P2_1$	2	286	41
22	Betaine.HBr	$P2_1/c$	4	209	16
23	L-Leucine.HBr	$P2_12_12_1$	4	265	42
24	L-Tryptophan.HBr	$P2_1$	2	296	41,43
25	L-Leucine.HI	$P2_12_12_1$	4	248	44

[a] Number of stoichiometric units in the unit cell.
[b] Ratio of volume of the unit cell to the number of stoichiometric units in the cell.

using the 6-31G** basis sets[49] included in the GAUSSIAN 94 program package.[50] Table II gives such charges in the glycinium and N-methyl-4-hydroxy-L-prolinium cation.



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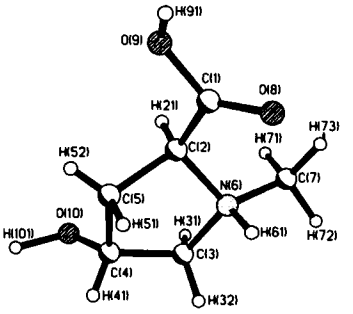

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FIGURE 1 Solid phase structures of glycinaminium (**1**) and N-methyl-4-hydroxy-L-prolinium (**19**) cations.

Parameters occurring in dispersive and repulsive terms (Equations (11) and (12)) were obtained boiling the problem down to the interactions between atoms of complex cations (neglecting their charge) and/or halide anions. At such an assumption, parameters of dispersive interactions between the same entities (atoms or monoatomic ions) were evaluated from either the London,[51]

$$D = \frac{1}{2} P (3I)^{1/2} \tag{13}$$

or the Slater-Kirkwood[52]

$$D = \left[\frac{3}{4} \frac{Neh}{2\pi m_e^{1/2}} \frac{P^2}{(P/n)^{1/2}} \right]^{1/2} \tag{14}$$

equations. The meaning of N, e and h in Equations (13) and (14) is given above, m_e represents the mass of the electron, while P, I and n denote polarizability, ionization potential and number of electrons in the valence shell of a given entity, respectively. Parameters of repulsive interactions can be gauged from relationships (15) and (16) taking into account that relationships (11) and (12) written for pairs of the same interacting entities attain minimum if they are separated at a distance being the sum of their van der Waals radii (R_{VDW}),[53,54] namely

TABLE II Atomic partial charges in glycinaminium (**1**) and N-Methyl-4-hydroxy-L-prolinium (**19**) cations.

Atom(s) (Figure 1)	Method			
	HF		DFT	
	Mulliken	MEP fit	Mulliken	MEP fit
		1		
C(1)	0.782	0.744	0.600	0.617
C(2)	-0.206	0.113	-0.204	0.049
N(3)	-0.619	-0.525	-0.515	-0.501
O(4)	-0.537	-0.560	-0.426	-0.473
O(5)	-0.584	-0.646	-0.447	-0.552
H(21)	0.253	0.108	0.235	0.125
H(22)	0.255	0.112	0.233	0.121
H(31)	0.408	0.385	0.379	0.378
H(32)	0.416	0.381	0.386	0.378
H(33)	0.409	0.375	0.380	0.374
H(51)	0.422	0.513	0.379	0.484
		19		
C(1)	0.799	0.705	0.602	0.589
C(2)	-0.072	0.184	-0.053	0.067
C(3)	-0.176	-0.317	-0.101	-0.443
C(4)	0.199	0.680	0.152	0.587
C(5)	-0.037	-0.142	-0.049	-0.351
N(6)	-0.646	-0.016	-0.459	0.042
C(7)	-0.202	-0.376	-0.228	-0.445
O(8)	-0.543	-0.548	-0.436	-0.462
O(9)	-0.515	-0.683	-0.394	-0.591
O(10)	-0.683	-0.739	-0.557	-0.621
H(21)	0.236	0.101	0.195	0.146
H(31)	0.172	0.124	0.128	0.185
H(32)	0.177	0.067	0.140	0.134
H(41)	0.151	-0.068	0.118	-0.031
H(51)	0.227	0.149	0.200	0.209
H(52)	0.196	0.088	0.172	0.168
H(61)	0.384	0.292	0.341	0.307
H(71)	0.222	0.179	0.187	0.197
H(72)	0.199	0.188	0.187	0.203
H(73)	0.192	0.172	0.204	0.200
H(91)	0.331	0.533	0.305	0.512
H(101)	0.387	0.429	0.344	0.394

$$A = 8DR_{VDW}^{3}/\sqrt{2} \tag{15}$$

$$B = D/(2R_{VDW})^{3}\{3/[CR_{VDW}\exp(-2CR_{VDW})]\}^{1/2} \tag{16}$$

Equation (15) originates from the Lennard-Jones relationship (11), while (16) from the Buckingham dependence (12). To obtain values of B from Equation (16) we took values of C available in the literature. Table III presents dispersive and repulsive parameters derived in the above described manner together with ancillary data used in the evaluation of these.

LATTICE ENERGY OF AMINOACID HYDROHALIDES

Using atomic partial charges derived in the manner described above and parameters given in Table III we evaluated electrostatic, dispersive and repulsive contributions to the lattice energy using two independent programs, PCK 83[62] and WMIN 91.[63,64] The PCK 83 program requires parameters for pairs of atoms. These were easily found by multiplying relevant atomic parameters given in Table III. On the other hand, values of the Coulombic term could not be obtained by WMIN 91 since it does not accept different charges at the same type of atom. Calculations were simplified in the case of hydrates by omitting water molecules.

The results obtained are shown in Table IV. For all the compounds studied the electrostatic contributions dominate and have values comparable to those determined in the case of halide salts of nitrogen organic bases.[65] Dispersive and repulsive contributions differ markedly depending on the method adopted. It is difficult to evaluate which set of atomic parameters (Table III) or models (in the sense of relationships (11) or (12)) used, reflect reliably the above-mentioned contribution to cohesive forces. Values of dispersive and repulsive terms are generally, much higher than those typical for ionic substances (E_d and E_r do not usually exceed 1/10 of E_{el} [5,7,66]). It may thus be that E_d and E_r contributions derived in this work are overestimated. In this situation it seems sufficient to assume that the Coulombic term constitutes a sound reflection of the crystal lattice energy. Such a conclusion is fully supported by the results of our calculations for halide salts of nitrogen organic bases.[65] We found that the electrostatic contribution calculated for charges fitted to the molecular electrostatic potential, compare with experimental values of the crystal lattice energy very well. We thus think that E_{el} values relevant to MEP fit (Table IV),

LE III Dispersive and repulsive parameters together with ancillary data for evaluation of these.

$P^{a,b,c}$ x 10^{24}	$I^{a,b,c}$	n	$R_{VDW}{}^{a,b}$	Parameter[a]						$C^{a,b}$
				Originating from the London equation[51]			Originating from the Slater-Kirkwood equation[52]			
				D	A	B	D	A	B	
0.667 (6,55)	1312.2 (6,57)	1	1.20 (58)	20.9	204.3	37.1	20.3	198.4	36.1	1.64 (61)
1.76 (6,55)	1086.8 (6,57)	2	1.70 (58)	50.2	1395.2	522.4	50.0	1389.6	520.3	1.94 (61)
1.11 (6,55)	1402.2 (6,57)	3	1.55 (58)	35.7	752.0	193.9	39.2	825.8	213.0	1.86 (61)
0.786 (6,55)	1313.5 (6,57)	4	1.52 (58)	25.2	500.6	91.3	32.5	645.6	117.7	1.79 (61)
2.90 (6,55)	999.7 (6,57)	4	1.80 (58)	79.4	2619.5	389.8	86.5	2853.7	424.6	1.79 (61)
3.28 (55,56)	355.8 (6,57)	6	1.61 (59,60)	53.6	1265.4	185.7	105.0	2478.8	363.9	1.76 (60)
4.54 (55,56)	333.3 (6,57)	6	1.74 (59,60)	71.8	2139.7	307.4	134.0	3993.3	573.8	1.78 (60)
6.87 (55,56)	306.1 (6,57)	6	1.92 (59,60)	104.1	4168.0	665.4	182.9	7323.1	1169.1	1.81 (60)

cm^3; I in kJ/mol; R_{VDW} in Å; D in $(kJ/mol)^{1/2}$ $Å^3$; A in $(kJ/mol)^{1/2}$ $Å^6$; B in $(kJ/mol)^{1/2}$; and C in $(Å)^{-1/2}$.
rences are given in parentheses.
n of values taken from references.

LE IV Electrostatic, dispersive and repulsive contributions to the crystal lattice energy of aminoacid hydrohalides (in k

E_{el}				E_d		E_r			
HF[a]		DFT[a]		London[b]	Slater-Kirkwood[b]	London[b]		Slater-Kirkwood	
Mulliken	MEP	Mulliken	MEP			Eqn(11)	Eqn(12)	Eqn(11)	Eqn(12)
-747.6	-757.3	-725.3	-742.7	-136.1	-226.7	144.0	87.9	265.2	155.0
-651.8	-685.3	-640.9	-675.9	-160.1	-241.2	79.1	82.2	124.8	119.5
-616.4	-643.2	-606.8	-636.7	-125.6	-197.8	25.7	36.8	48.9	62.5
-581.4	-602.0	-571.6	-592.6	-131.9	-184.4	18.2	36.2	29.4	51.7
-701.0	-732.4	-684.6	-711.3	-173.3	-316.0	261.6	118.3	536.5	233.5
-656.8	-682.6	-669.5	-696.0	-137.0	-194.8	23.8	48.8	36.0	69.7
-577.3	-603.1	-565.5	-590.8	-107.9	-150.0	16.4	32.9	23.9	44.8
-583.6	-611.0	-568.9	-594.9	-166.0	-250.8	144.5	82.6	265.7	134.5
-677.8	-692.7	-660.5	-680.0	-212.7	-330.5	140.2	105.4	256.4	183.1
-768.8	-791.5	-726.7	-756.3	-231.7	-351.0	467.7	141.2	663.0	222.6
-671.9	-683.1	-648.1	-663.8	-243.4	-385.5	154.3	142.4	265.2	246.5
-720.3	-732.8	-678.9	-706.2	-274.3	-406.5	445.3	145.3	609.6	230.4
-593.8	-593.2	-580.1	-581.5	-126.6	-203.0	54.8	55.1	108.8	97.4
-638.8	-682.9	-627.7	-668.7	-194.2	-324.0	119.4	95.2	238.8	178.5
-843.2	-864.6	-789.1	-820.1	-208.0	-284.0	187.3	98.8	243.0	135.4
-779.3	-844.6	-730.1	-792.6	-181.5	-264.3	189.7	98.3	265.7	150.0
-574.7	-605.2	-555.0	-569.7	-145.2	-214.8	33.7	44.8	63.0	72.1
-564.8	-579.3	-569.3	-597.5	-111.8	-157.9	26.4	35.5	46.0	54.2
-641.3	-667.7	-622.9	-653.6	-183.3	-314.0	78.4	73.5	162.2	141.0
-577.5	-611.9	-561.8	-570.2	-172.9	-255.8	64.1	75.7	101.5	119.1
-688.7	-696.4	-666.0	-686.8	-233.8	-331.0	51.5	85.7	81.3	133.7
-580.2	-591.8	-558.3	-571.0	-190.3	-250.9	64.9	89.7	95.1	123.2
-596.3	-618.7	-592.1	-606.4	-160.5	-237.3	50.6	70.7	83.0	112.3
-529.2	-526.3	-528.9	-522.7	-267.3	-386.7	87.0	117.7	137.3	187.7
-585.2	-608.1	-573.8	-595.5	-171.6	-246.3	56.2	43.0	87.6	58.0

od of atomic charges evaluation in the cation.
origin of dispersive and repulsive parameters (Table III).

best represent the crystal lattice energy of hydrohalides of aminoacids at the present stage of our knowledge of this problem.

It is interesting how electrostatic contributions to the lattice energy change with dimensions of ions. To reveal this, in Figure 2 we plotted Coulombic energies originating from charges fitted to MEP on the DFT level against *V/Z* ratio. Despite the fact that the points are scattered, the general tendency is clearly seen, namely $-E_{el}$ values show a decreasing tendency with an increase in volume of the basic stoichiometric unit and thus dimensions of ions. This remains in accordance with well-known empirical rules.[67]

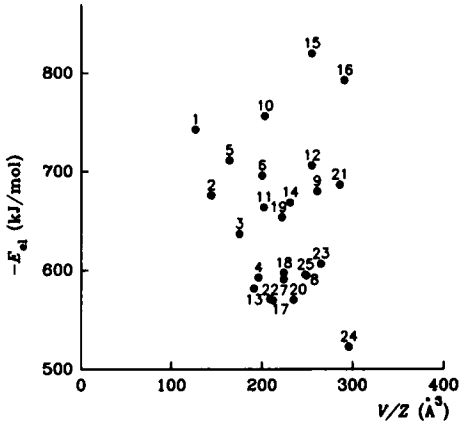

FIGURE 2 Coulombic energy (values relevant to DFT/MEP fit, Table IV; compounds numbers are given at points) versus volume of a basic stoichiometric unit (Table II).

CONCLUDING REMARKS

Basic relations concerning energy and entropy changes upon crystal formation are invoked and discussed in brief, to show how the thermodynamics of ordered solid phases can be considered.

Theoretical calculations performed by us provided important characteristics concerning energetics of aminoacid hydrohalides - substances of basic importance in nature, biology and chemistry. We also believe that the results obtained will help us understand the origin of intermolecular interactions and contribute to the development of methods enabling prediction of structure, properties and reactivity of solids.

Acknowledgements We are greatly indebted to Dr. W. Busing (Oak Ridge National Laboratory, TN, USA) for supplying the FORTRAN version of WMIN 91. We would like also to thank A. Konitz for his valuable comments and the Polish State Committee for Scientific Research (KBN) for financial support of this work (under grants BW/8000-5-0200-5 and DS/8000-4-0026-5).

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