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Ab initio study of the structural properties of LiF, NaF, KF, LiCl, NaCl, and KCl

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The lattice energy (LE), equilibrium lattice parameter (a_0), elastic constants (C_{ij}), and central-zone phonon frequencies (ν) of LiF, LiCl, NaF, NaCl, KF, and KCl have been evaluated with CRYSTAL, a periodic *ab initio* Hartree-Fock linear combination of atomic orbitals program. The mean error with respect to experiment is 5.7%, 3.4%, 14.6%, and 8.8% for LE, a_0, B [bulk modulus; $B = \frac{1}{3}(C_{11} + 2C_{12})$], and ν, respectively. The errors increase systematically with increasing size of the cation or anion. Correlation effects (both intraionic and interionic) are the main reason for the discrepancies with respect to experiment.

I. INTRODUCTION

Since the early works of Madelung,[1] Ewald,[2] and Born and Huang,[3] alkali halides have been the subject of a large number of theoretical investigations, concerning energy-related properties such as the elastic tensor and the phonon dispersion curves. The simple Born-type semiempirical formula for the interatomic potential energy (a Coulomb or "Madelung" long-range term and a short-range repulsive term) used in the early studies was supplemented in the 1960's by dipole,[4] quadrupole,[5] and/or breathing[6] shell terms. In the 1970s a more fundamental approach, still partially empirical and based on the electron-gas theory,[7,8] was applied systematically to alkali halides and other ionic compounds. The earliest quantum mechanical work due to Löwdin[9] involved numerous approximations in the theory, but in the past decade the implementation of reasonably reliable fully *ab initio* computational schemes allowed the nonempirical evaluation of the structural properties of ionic systems with reference both to density functional[10] and to Hartree-Fock[11,12] Hamiltonians. Many of these pioneering *ab initio* calculations were still biased by problems related to numerical accuracy, basis set limitations, or simply reliability of the computer programs. In the past few years, however, considerable progress has been made in the direction of the standardization, generalization, and improvement of the numerical accuracy of the algorithms of many computational schemes. Time is ripe for systematic applications that should show the limits and merits of the adopted Hamiltonians, schemes of solution of the Schrödinger equation, and basis sets. In the present paper we report results obtained with CRYSTAL, the *ab initio* Hartree-Fock (HF) linear combination of atomic orbital (LCAO) self-consistent-field (SCF) computer program implemented by the authors and collaborators.[13] General information on the method can be found elsewhere.[12] As regards ionics, recent applications concern Li_2O, Na_2O, K_2O,[14] CaF_2,[15] and MgF_2.[16] In the present study, no use has been made of pseudopotentials. The results are shown and discussed in the next section. In the Appendix the basis sets adopted are reported, and related problems are discussed.

II. RESULTS AND DISCUSSION

For each system, the following quantities have been calculated: the lattice energy (LE), the equilibrium lattice parameter (a_0), the bulk modulus (B), the three non-null components of the elastic tensor (C_{11}, C_{12}, C_{44}), and the central zone phonon frequency (ν). In all cases the required quantity has been obtained from a point-by-point calculation referring to different geometries; from a polynomial fit of the curve $E(a)$, LE, a_0, and B have been obtained. With reference to the calculated geometry minimum (a_0), a tetragonal distortion allows the evaluation of $C_{11}-C_{12}$; from $B = (C_{11} + 2C_{12})/3$, C_{11} and C_{12} have been obtained. In a similar way, C_{44} is evaluated from a rhombohedral distortion. Finally a central zone phonon frequency ν is obtained by displacing one sublattice with respect to the other in the direction [100]. Again, the numerical data are obtained from polynomial fits of the curve $C_{ij}(\delta)$ and $\nu(\delta)$, where δ is the distortion from the

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equilibrium position. The estimated error due to the fitting procedure is 0.001 Å, 10^{-6} hartree, 0.1 GPa, and 0.1 THz for the equilibrium lattice parameter a_0, total energy E, elastic constants C_{ij}, and central zone phonon frequency ν, respectively. The results are summarized in Tables I, II, and III.

The experimental values are all extrapolated from room temperature data to the static limit, i.e., to 0 K temperature without zero point motion. The difference between the room temperature and the static limit data is relatively small for the equilibrium lattice constants (maximum difference 1.3% for KCl), but very significant for the elastic constants, the biggest difference being 25% for the C_{11} constant of LiF.

A. Lattice parameter, lattice energy

Let us consider first the results for the equilibrium lattice parameter a_0. The calculated data are always larger than the experimental, as expected; typically the HF error for the bond lengths of the III-V semiconductors obtained with the same method ranges from 0.0 to +2.3% with an average of +1.2%.[17] In the present case the error increases along the series Li-Na-K, but even more when passing from the F to Cl series. The error is the superposition of two effects, both linked to the fact that the HF approach disregards the interelectronic correlation motion. First, concerning the intraionic correlation, the F^- and Cl^- ions from the HF calculation are too large; electronic correlation effects would serve to reduce the size of the anions. The error is larger in Cl^- than in F^- because (a) the electrostatic field created by the lattice, which tends to contract the anion, is smaller for the chlorides, which have a larger lattice parameter; (b) the valence shell in Cl is more diffuse than in F; as a consequence, the electrostatic effects due to nuclear attraction are less effective than in F. Second, concerning the interionic correlation, dispersion forces are approximately proportional to the polarizability of the ions, which is much larger in Cl^- than in F^-; similar considerations apply to the cations, but on a reduced scale. The previous discussion justifies the (regular) trend of the Δ% column for a_0.

As regards the LE, which is the difference of the energies of the bulk and isolated ions, the error ranges from −2.6% to −9.0 %. As the LE is evaluated with reference to the ions, the error cannot be attributed to the formation (or breaking) of electron pairs. It is to be attributed to (a) dispersion forces; (b) changes in intra-ionic correlation energy, particularly associated with the contraction of the anion upon crystallization, due both to the short-range repulsive effects and the effects of the Madelung potential. We will return later to the dispersion effects. The experimental lattice energy is evaluated by a Born-Haber thermochemical cycle (see, for example, Ref. 18, Sec. 4.2, p. 91), using the data from Ref. 19 (Sec. 4, p. 51).

B. Bulk modulus, elastic constants, and central zone phonon frequency

The bulk modulus (B) is always underestimated as a consequence of the overestimation of the lattice parameter (B is evaluated at the calculated a_0). Figure 1 shows that the error in the bulk modulus (ΔB) and in the lattice energy [Δ(LE)] is to a good approximation linearly correlated to the error in the lattice parameter (Δa_0).

As regards C_{11} and C_{12} the behavior is again similar to that of B [to which they are directly related through the relation $B = 1/3(C_{11} + 2C_{12})$]. A large dispersion

TABLE I. Calculated and experimental lattice energy (LE), lattice constant (a_0), and bulk modulus (B). Δ% is the percentage difference between calculated and experimental data. The calculated data shown in parentheses refer to the HF data plus dispersion effects evaluated from Sangster and Atwood's parameters (Ref. 21). LE, a_0, and B are in kcal/mol, Å, and GPa, respectively.

	LE			a_0			B		
Syst.	Calc.	Expt.[a]	Δ%	Calc.	Expt.[b]	Δ%	Calc.	Expt.[c]	Δ%
LiF	245.3	251.9	−2.6	4.02	3.99	+0.8	75.9	76.9	−1.3
	(247.0)		(−1.9)	(3.99)		(0.0)	(77.5)		(+0.8)
NaF	217.0	222.9	−2.6	4.63	4.57	+1.3	51.1	53.8	−5.0
	(219.6)		(−1.5)	(4.59)		(+0.4)	(53.2)		(−1.1)
KF	187.2	198.3	−5.6	5.49	5.29	+3.8	29.7	35.5	−16.3
	(190.3)		(−4.0)	(5.42)		(+2.5)	(31.4)		(−11.5)
LiCl	191.5	207.0	−7.5	5.28	5.07	+4.1	30.0	36.9	−18.7
	(196.2)		(−5.2)	(5.24)		(+3.4)	(30.0)		(−18.7)
NaCl	176.1	189.2	−6.9	5.80	5.57[d]	+4.1	22.3	28.6	−22.0
	(178.6)		(−5.6)	(5.74)		(+3.1)	(23.5)		(−17.8)
KCl	156.9	172.4	−9.0	6.57	6.20	+6.0	15.7	20.8	−24.5
	(162.7)		(−5.6)	(6.51)		(+5.0)	(16.0)		(−23.1)

[a] From Ref. 19 [Sec. 4, pp. 51].
[b] From Ref. 30.
[c] From Ref. 31.
[d] From Ref. 32.

TABLE II. Calculated and experimental elastic constants C_{11}, C_{12}, C_{44} in GPa. Experimental data are from Ref. 31.

	C_{11}			C_{12}			C_{44}		
Syst.	Calc.	Expt.	Δ%	Calc.	Expt.	Δ%	Calc.	Expt.	Δ%
LiF	125.8	135.8	−7.4	50.9	47.4	+7.4	76.1	68.7	+10.8
NaF	107.8	115.4	−6.6	22.8	23.0	−0.9	33.6	29.8	+12.8
KF	66.1	79.7	−17.1	11.9	13.4	−11.2	15.6	13.3	+17.3
LiCl	60.9	63.2	−3.6	14.6	23.8	−38.7	33.5	27.6	+21.4
NaCl	47.4	61.1	−22.4	9.8	12.3	−20.3	15.3	13.6	+12.5
KCl	36.3	50.9	−28.7	5.4	5.8	−6.9	7.6	6.7	+13.4

with respect to experiment (maximum error for $C_{11} = -28.7\%$, for $C_{12} = -38.7\%$) is mainly related to the correlation between the two quantities, both experimentally and computationally. Note, for example, that the maximum error for C_{12} (LiCl) is associated with the minimum error for C_{11} and vice versa (KCl, −28.7% for C_{11} and −6.9% for C_{12}). The situation is different for C_{44}. It is well known that the dependence of C_{44} on the pressure (and therefore on the lattice parameter) is quite small, much smaller than for C_{11} and C_{12} (see, for example, Ref. 20). This means that the calculated C_{44} of Table II are not heavily biased by the HF error in a_0, and show the "usual" HF overestimation of force constants (from +10% to +20% to be compared with a mean error of +6.5% for the III-V semiconductors[17]).

The error for ν, the central zone phonon frequencies (max −22.7%; min −1.3%, mean −8.8%), follows the pattern of B, although the trend is less regular along the series; the mean error is smaller than for B, probably because short-range repulsive forces play a more important role in this case than for B.

C. Correction for dispersion forces

We tried to estimate the importance of the interionic correlation by using dispersion coefficients due to Sangster and Atwood.[21] The dispersion energy, evaluated through r^{-6} and r^{-8} terms summed over the infinite crystal, is attractive, and tends to reduce the HF error. The results for LE, a_0, and B, obtained by adding to the HF energy at each energy point the dispersion contribution, are shown in Table I (in parentheses). By comparison with the HF data it turns out that the dispersion energy, at least when evaluated with Sangster and Atwood's parameters, corrects a large fraction of the HF error in the case of the fluorites (the mean correction is 32.6%, 70.2%, and 55.7% for LE, a_0, and B, respectively) whereas it is much less effective for the chlorides (only 36.5%, 20.9%, and 8.3% of the HF error for LE, a_0, and B, respectively) where the HF error is much larger. This relatively rough estimate seems to indicate that intraionic correlation effects are at least as important as (probably more important) the interionic contributions.

TABLE III. Calculated and experimental central zone phonon frequencies ν in THz. Experimental data are from Ref. 33.

	ν		
Syst.	Calc.	Expt.	Δ%
LiF	9.0	9.5	−5.3
NaF	7.7	7.8	−1.3
KF	5.8	6.0	−3.3
LiCl	5.1	6.6	−22.7
NaCl	4.7	5.3	−11.3
KCl	4.1	4.5	−8.9

D. Comparison with previous *ab initio* calculations

A certain number of *ab initio* calculations of the structural properties of NaCl have been performed with density functional (DF) Hamiltonians,[22,23] in conjunction with pseudopotential plane waves or linearized augmented plane waves (LAPW) schemes; the results for a_0 vary from 5.28 Å to 5.64 Å, where the discrepancy seems to be due to both incompleteness in the PW expansion,[23] use of different local exchange-correlation functions, and/or numerical inaccuracies in the methods;

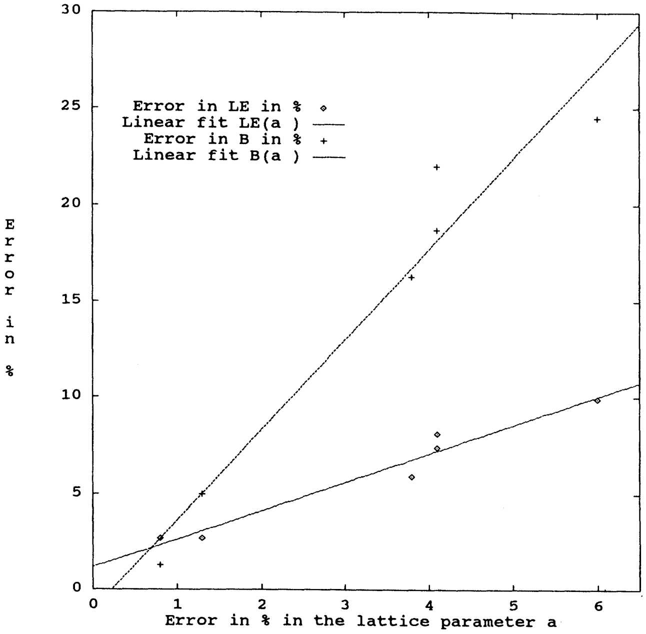

FIG. 1. The error in lattice energy (LE) and bulk modulus (B) depends almost linearly on the error in the equilibrium lattice parameter (a_0). On the ordinate axis the absolute values of the relative errors are depicted. The straight lines are obtained by fitting.

on the whole, the DF Hamiltonian tends to underestimate a_0 by some 1–2% and overestimate B by about 8%. The figures for the most recent (and very accurate) calculations are -1.6% (a_0) and $+10.1\%$ (B).[24] A more complete comparison of the different results for NaCl has been made elsewhere,[25] with reference in particular to the $B1$-$B2$ phase transition.

As far as we know, there is only one previous systematic study of the structural properties of alkali halides with an *ab initio* scheme, due to Pueyo *et al.*[26] who employed the Hartree-Fock perturbed ion (PI) method. The PI method is based on the theory of electronic separability (TES) of Huzinaga *et al.*[27] It assumes that the crystal electronic density is the sum of the densities of the individual ions. The wave function is obtained by minimizing the effective energy of each ion in the field of the crystal lattice. A projection operator enforces the cluster-lattice orthogonality. A HF Hamiltonian and local (Slater) functions are used, so that, in principle, if the hypotheses of the method are justified, one should find quite good agreement with the present results. However, the PI a_0 data are systematically larger than the present ones: $+0.03$, $+0.11$, $+0.11$, $+0.32$, $+0.31$, and $+0.65$ (in Å) from LiF to KCl, respectively. The corresponding LE differences are -3.2, -1.9, -4.12, -1.5, -8.1, and -8.9 (in kcal/mol). As regards B, the differences are even larger (12 GPa for KCl, to be compared with 15.7 GPa from Table I).

The large difference between the present periodic HF and the PI-HF results can scarcely be attributed to basis set differences. The discrepancies must probably be attributed to some inaccuracy in the implementation of the PI scheme, or to some weakness in the formal scheme itself.

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APPENDIX: BASIS SET INFORMATION

Tables IV, V, and VI give the basis set for the anions and the cations adopted in the present study. The contraction scheme is as follows: F, 7-311G; Cl, 8-6-311G; Li, 6-1G; Na, 8-5-11G; K, 8-6-5-11G, where the usual notation[28] is adopted. Each coefficient multiplies individually normalized Gaussian functions. For reasons of computational efficiency s and p orbitals share the same exponent. The exponents and the coefficients have been optimized in the isolated ions (charge ± 1). The isolated ion total energies which correspond to the basis sets of Tables IV, V, and VI and are used for the evaluation of the lattice energy of the six compounds are reported in Table VII with the kinetic energy.

In the bulk calculation the exponents of the two most diffuse shells of the two ions have been reoptimized; the

TABLE IV. Exponents (α in bohr^{-2}) and coefficients (c_s, c_p) of the Gaussian-type functions (GTO's) of the isolated F$^-$ and Cl$^-$ anions.

	Fluorine			Chlorine		
Shell	Exponents	Coefficients		Exponents	Coefficients	
type	α	c_s	c_p	α	c_s	c_p
1*s*	13770.000	0.000877		135320.000	0.000225	
	1589.000	0.009150		19440.000	0.001910	
	327.600	0.048600		4130.000	0.011100	
	91.460	0.169100		1074.000	0.049890	
	30.500	0.370700		323.400	0.170300	
	11.460	0.416500		111.100	0.368300	
	4.660	0.131600		43.400	0.403600	
				18.180	0.145900	
2*sp*	19.290	−0.118300	−0.122200	324.800	−0.007630	−0.082000
	4.586	−0.127700	0.532000	73.000	−0.082900	0.060500
	1.387	1.000000	1.000000	23.710	−0.104600	0.211500
				9.138	0.254000	0.376500
				3.930	0.695000	0.396700
				1.329	0.399000	0.186000
3*sp*	0.431	1.000000	1.000000	4.755	−0.374000	−0.034000
				1.756	−0.475400	0.161700
				0.785	1.340000	0.925000
4*sp*	0.121	1.000000	1.000000	0.294	1.000000	1.000000
5*sp*				0.090	1.000000	1.000000

TABLE V. Exponents and coefficients of the GTO's of the two isolated cations Li^+, Na^+.

Shell	Lithium			Sodium		
	Exponents	Coefficients		Exponents	Coefficients	
type	α	c_s	c_p	α	c_s	c_p
$1s$	840.000	0.002640		56700.000	0.000225	
	217.500	0.008500		8060.000	0.001910	
	72.300	0.033500		1704.000	0.010500	
	19.660	0.182400		443.600	0.050060	
	5.044	0.637900		133.100	0.169100	
	1.500	1.000000		45.800	0.365800	
				17.750	0.399800	
				7.380	0.149400	
$2sp$	0.514	1.000000	1.000000	119.000	−0.006730	0.008030
				25.330	−0.079800	0.063900
				7.800	−0.079300	0.207400
				3.000	0.305600	0.339800
				1.289	0.563900	0.372600
$3sp$				0.542	1.000000	1.000000
$4sp$				0.229	1.000000	1.000000

results are shown in Table VIII. On the basis of the exponents of the most diffuse shell, it results that in the crystalline environment the anion is always more contracted than when isolated. For the cation apparently something similar is true for Li and Na, but not for K; however, for the cations the energy versus exponent curves are so flat that interpretation of numerical minima may be misleading.

The bulk and the isolated ion calculations have been performed with basis sets containing the same number of functions, the only difference being that the exponent of the most diffuse shell has been reoptimized separately for each system. One can wonder if the two basis are of the same variational quality, the description of the tails of the wave function in the isolated system being more critical than in the bulk. Moreover, in the crystal each atom can exploit the functions of the neighboring atoms. These effects can lead to an overestimation of the lattice energy [basis set superposition error (BSSE) (Ref. 29)]. Taking into account that in the present study high quality core functions have been used, the BSSE effect, if any, must involve mainly the valence electrons. In order to estimate how incomplete the basis sets for the isolated atoms are, we repeated the isolated ion calculations adding one extra diffuse *sp* shell to the basis sets of Tables IV, V, and VI, and reoptimizing the exponents of the two most diffuse *sp* shells. The energy lowering due to those extra functions is shown in Table VII, last column; the sum of the Δ values for the cation and the anion can be assumed as the upper limit of the uncertainty on the LE due to basis set effects.

The other point to be shortly discussed is the im-

TABLE VI. Exponents and coefficients of the GTO's of the isolated cation K^+.

Shell	Potassium		
	Exponents	Coefficients	
type	α	c_s	c_p
$1s$	172500.000	0.000220	
	24320.000	0.001920	
	5140.000	0.011090	
	1343.900	0.049920	
	404.500	0.170200	
	139.400	0.367900	
	54.390	0.403600	
	22.710	0.145900	
$2sp$	402.000	−0.006030	0.008410
	93.500	−0.080500	0.060200
	30.750	−0.109400	0.211700
	11.920	0.258000	0.372600
	5.167	0.684000	0.402200
	1.582	0.399000	0.186000
$3sp$	17.350	−0.007400	−0.032100
	7.550	−0.129000	−0.062000
	2.939	−0.683400	0.169100
	1.190	1.080000	1.500000
	0.674	1.030000	1.060000
$4sp$	0.404	1.000000	1.000000
$5sp$	0.221	1.000000	1.000000

TABLE VII. Total (TE) and kinetic (KE) energy in Hartrees of the isolated ions with the basis sets reported in Tables IV, V, and VI. Δ is the lowering of TE in mhartrees when an extra diffuse *sp* shell is added to the basis sets of Tables IV, V, and VI (see text).

Ion	TE	KE	Δ
F^-	−99.42473	99.26578	0.52
Cl^-	−459.54320	459.47021	2.26
Li^+	−7.23526	7.23098	0.03
Na^+	−161.67001	161.65951	0.01
K^+	−598.98038	598.70491	0.79

TABLE VIII. Exponents of the two most diffuse shells (one in the lithium case), in cations and anions, optimized for each system.

	Cation		Anion	
System	α_a	α_b	α_a	α_b
LiF	0.525		0.437	0.147
NaF	0.568	0.313	0.437	0.157
KF	0.378	0.200	0.437	0.137
LiCl	0.510		0.322	0.116
NaCl	0.578	0.323	0.320	0.125
KCl	0.389	0.216	0.333	0.117

portance of polarization functions; *d* orbitals have been added to the basis sets of Tables IV, V, and VI, and the energy in the calculated minima has been computed; the energy lowering is quite small (1.2 mH for KCl). The reason for the negligible importance of *d* orbitals is due both to the complete shell structure of the cations and anions, and to the high symmetry of the systems. In a previous study devoted to alkali oxides,[14] it has been found that *d* orbitals on potassium have a negligible importance for all properties except C_{44} which reduces by as much as 40%. The reason is the following: In the C_{44} deformation, the atomic site symmetry dramatically reduces; in particular the K site symmetry is no longer centrosymmetric. The lowest order polarization of the cation, namely, the dipolar *p*-*d* effect, may occur. Such effect is very important in K_2O, due to the relatively small energy difference between 3*p* and 3*d* orbitals, whereas it is much smaller in Li_2O and Na_2O, due to the larger energy differences. The situation for alkali halides is different, because such a polarization mechanism is not possible for symmetry reasons. A complete set of calculations has been repeated for KCl with *d* orbitals on K, the percentage variation being −0.5%, 0.0%, and +1.0% for a_0, B, and C_{44}, respectively. The effect of *d* orbitals on Cl is even smaller.

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