Structural properties and electron density of NaCl

H. J. F. Jansen* and A. J. Freeman

Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60201

(Received 15 October 1985)

The validity of all-electron total-energy local-density calculations for ionic insulators is investigated for NaCl using our full-potential linearized augmented-plane-wave method. We find that the experimental zero-temperature structural parameters are accurately described within the local-density approximation. Comparison of theoretical and experimental form factors shows large discrepancies for odd high-indexed reflections which is attributed to the procedure used to extract $T=0$ results from the room-temperature measurements. We conclude that a more stringent test of the charge density awaits the availability of more precise experimental form factors measured at low temperatures.

It has often been debated whether the electronic structure of NaCl could be determined accurately from total-energy calculations within the local-density approximation. Since NaCl is an ionic insulator, the electrons are localized on a very long time scale. Density-functional theory pertains to the ground state and in principal considers an average over all times to obtain the minimal ground-state energy. In the local-density approximation one performs this average in an approximate way, which works very well for metals, but there is no clear theoretical a priori justification why it should yield accurate results for insulators where the electrons are highly localized. There exist, however, a posteriori proofs because actual calculations for atoms and molecules give results in agreement with experiment. For NaCl, the work of Williams et al.,[1] based on the augmented spherical wave method, indicated that good agreement could be obtained for the structural properties (lattice constant, heat of formation, bulk modulus).

Subsequent pseudopotential calculations, however, produced inconsistent results: Froyen and Cohen[2] have published results which were in good agreement with experiment, whereas previously Andreoni et al.[3] obtained relatively large differences with experiment.

We have investigated the electronic structure of NaCl with our precise all-electron full-potential linearized augmented-plane-wave (FLAPW) method[4] in which all numerical approximations are controlled and as a result all numerical errors can be made as small as is desired. We have used the Hedin-Lundqvist form of the exchange and correlation potential.[5] In our final iterations we use more than 200 basis functions, and we obtained the energy eigenvalues at 50 points in the irreducible wedge of the Brillouin zone. This yielded a sufficient precision for our total-energy values. In this paper we present our results for the structural properties and the charge density of NaCl and we find good agreement with experiment for the structural properties. The charge density is compared with its semiexperimental counterpart which is derived from the room-temperature experimental form factors. Here we find good global agreement, but large differences for some reflections with high, odd indices.

Table I summarizes theoretical and experimental results for the lattice constant, the cohesive energy, and the bulk modulus. Our numerical error is 1% in the lattice constant and 10% in the bulk modulus.[4] Table I shows that within these errors the local-density approximation yields an accurate description of the structural properties of NaCl. The theoretical value of the cohesive energy is too low by 0.2 eV. This discrepancy is mainly due to the description of the atom, where we make small errors in the low-density outer regions, which affects the valence electrons. We did not try alternative forms of the exchange and correlation potential, but one expects the cohesive energy to change most by using approximations which have a different low-density behavior, like the Wigner interpolation formula. Because of the simple structure of the atoms (only one electron in the open valence shell) there are no multiplet effects on the total energy of the atom. (When more valence electrons are present, the local-density approximation introduces much larger errors up to 1 eV in the atomic total energy[6] and hence in the cohesive energy.)

The electronic charge density is the fundamental quantity in density functional theory. It is therefore of great importance to compare the theoretical density with its experimental counterpart as derived from x-ray diffraction[7-10] measurements. Unfortunately, the only experimental data we have been able to find are x-ray atomic form factors measured at room temperature. These form

TABLE I. Structural parameters of NaCl: lattice constant a, cohesive energy E_c (with respect to neutral atoms), and bulk modulus B. The values within parenthesis are corrected for zero-point motion.

	a (Å)	E_c (eV)	B (GPa)
This work	5.64	6.61	30.4
Expt.	5.60	6.39	26.6
Ref. 1	5.40	6.57	32.0
Ref. 2	5.52 (5.56)		31.2 (28.4)
Ref. 3	5.28		24.0

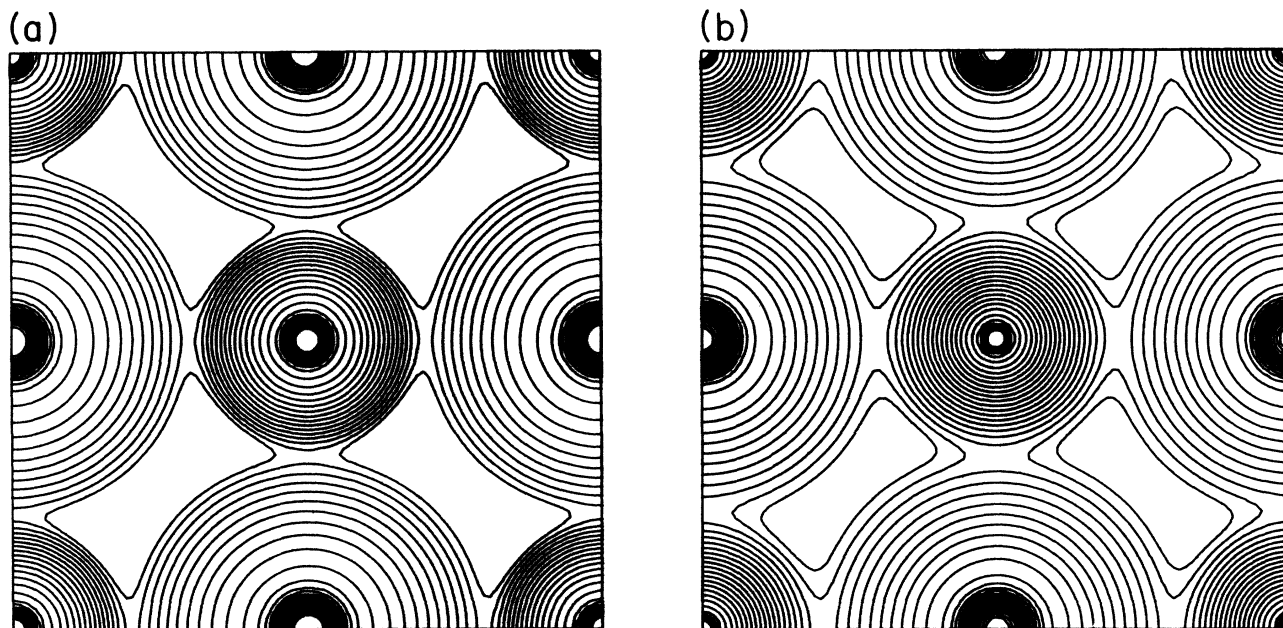**(a)**   **(b)**

FIG. 1. (a) Experimental and (b) theoretical charge density contours in a (100) plane. The same set of contour levels is used in both cases.

factors are analyzed in terms of several parametrized atomiclike form factors[7] which allow extrapolation to large scattering angles so that a Fourier transform procedure can be used to obtain the charge density. In order to obtain $T = 0$ values of the form factors from the room-temperature values, which include the effects of lattice vibrations, one can take out these effects in an approximate way using for each atom its appropriate Debye-Waller factor.[7] In this way one obtains semiempirical form factors at $T = 0$ for all reciprocal-lattice vectors.

Figure 1 compares the experimentally derived and theoretical contour plots of the densities in a (100) plane. The qualitative agreement of the two pictures in quite good. The ions are spherical to a high degree and the interstitial density is low. The contour levels in both figures have the same values and are on a logarithmic scale. The

TABLE II. Form factors of NaCl. The experimental data at each reflection ($hlkl$) are from (a) Ref. 10, (b) Ref. 9, (c) Ref. 8, and (d) Ref. 7. Column (e) gives the standard deviation (in %) of the four measurements, while column (f) displays the experimental error (in %) as given in Ref. 7. The form factors of Ref. 7 are then fitted to a sum of parametrized form factors (see text) and given in column (g). The values extrapolated to $T = 0$ are given in column (h). Our theoretical results are displayed in column (i), and column (j) shows the error (in %) between "experiment" [column (h)] and theory [column (i)].

| ($hlkl$) | Experiment at room temperature | | | | | | Analysis | | | |
	a	b	c	d	e	f	g	h	i	j
111	4.36	4.81	4.71	5.05	6	2	4.80	4.80	4.65	−3
200	19.65	20.55	20.19	20.50	2	4	20.74	21.51	21.19	−1
222	14.01	14.35	14.42	13.80	2	4	14.48	16.15	15.86	−2
400	12.24	12.52	12.45	12.46	1	2	12.84	14.84	14.59	−2
331	2.28	2.52	2.49	2.58	5	1	2.73	2.73	2.65	−3
333	2.27	2.55	2.64	2.85	9	2	2.83	2.95	2.92	−1
600	7.18	7.85	8.00	8.37	6	1	8.36	11.50	10.91	−5
442	7.10		8.00	8.27	8	1	8.36	11.50	10.74	7
533	2.04		2.30	2.48	10	2	2.61	2.98	3.12	+5
444	5.72	6.17	6.20	6.72	7	2	6.78	10.35	9.47	+9
551	2.08		2.19	2.35	6	3	2.41	2.85	3.11	+9
800	4.03	4.74	4.68	4.97	9	2	5.10	9.20	8.39	−9
555	1.87	1.71	1.77	1.65	5	6	1.79	2.31	2.95	+28
771	1.01		1.34	1.24	14	10	1.28	1.76	2.55	+45
1000	2.30	2.58	2.73	2.88	9	2	3.03	7.31	6.56	−10
666	2.01	2.40	2.58	2.89	15	4	2.70	6.98	6.16	−12
1200	1.13		1.50	1.56	17	6	1.58	5.64	5.20	−8
777	0.83		0.74	0.62	14	10	0.66	0.94	1.89	+101
1400	0.65		0.73	0.69	6	6	0.73	4.20	4.23	+1

lowest contour in the interstitial region corresponds to a density of 0.007 electrons per $\mathring{A}^3$ and adjacent contours differ by a factor of $\sqrt{2}$. On the average, the experimental density in the interstitial is lower by about 30%. The origin of this discrepancy may be found in the extrapolation to zero temperature, as we discuss next.

In Table II we make a quantitative comparison of the form factors themselves. We are not aware of more recent experimental data, and therefore we only show this older work,[7-10] which was performed at room temperature. In general, the theoretical and experimental data (see last three columns in Table II) agree within the errors of the measurements, although these error bars are too large to consider very fine details. One large discrepancy, however, is very striking: the form factors corresponding to directions with odd integers are completely different for higher q values. This indicates that there is a problem in extracting from the experimental data the $T=0$ values, i.e., to properly account for the effect of the optical phonons. In such an extraction, the use of atomic Debye-Waller factors is essential. One assumes that the charge density at finite temperature can be obtained by broadening the $T=0$ atomic charge densities independently.

In the NaCl structure the Fourier components of the charge density with even integers correspond to plane waves which have a value $+1$ on all atomic nuclei and -1 in the center of the interstitial. The all-odd components belong to plane waves which are $+1$ on the Na atoms, -1 on the Cl atoms, and zero in the interstitial. Hence the (111) component of the charge density gives the overall charge transfer from Na to Cl, while the higher-order all-odd components give the redistribution of charge on one atom due to the presence of the other. Furthermore, the high-order all-odd components are modified in the presence of optical phonons, where the different ions move in opposite directions and where each atom induces changes in the charge distribution on the other atom. As a result, these terms cannot be extracted accurately from finite-temperature measurements analyzed in terms of rigidly moving ions. In our opinion this is the main cause of the differences in Table II, and in order to make a direct comparison one needs experimental data obtained at low temperatures; otherwise, meaningful quantitative conclusions cannot be drawn.

To summarize, we have performed precise numerical all-electron total-energy calculations of the electronic structure of NaCl. By comparing with experimental data we find that the local-density approximation yields an accurate description of the ground-state structural properties of this ionic crystal. A more stringent test of the charge density, however, awaits experimental form factors measured at low temperature.

*Present address: Physics Department, Oregon State University, Corvallis, OR 97331-6507.

[1] A. R. Williams, J. Kübler, and C. D. Gelatt, Jr., Phys. Rev. B 19, 6094 (1979).

[2] S. Froyen and M. L. Cohen, Phys. Rev. B 29, 3770 (1984).

[3] W. Andreoni, K. Maschke, and M. Schlüter, Phys. Rev. B 26, 2314 (1982).

[4] H. J. F. Jansen and A. J. Freeman, Phys. Rev. B 30, 561 (1984).

[5] L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971).

[6] J. W. Davenport, R. E. Watson, and M. Weinert, Phys. Rev. B 32, 4883 (1985).

[7] Von G. Schoknecht, Z. Naturforsch. 12, 983 (1957).

[8] H. Witte and E. Wölfel, Z. Phys. Chem. 3, 296 (1955).

[9] M. Renninger, Acta Crystallogr. 5, 711 (1952).

[10] R. Brill, H. C. Grimm, C. Hermann, and Cl. Peters, Ann. Phys. (Leipzig) 34, 393 (1939).