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Hartree-Fock study of crystalline lithium nitride

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The electronic structure of crystalline lithium nitride has been theoretically investigated within the Hartree-Fock approximation. The basis set comprises 28 atomic orbitals per unit cell and has been defined following strictly variational criteria. Energy data, band structure, and Mulliken populations are provided and discussed; the calculated x-ray structure factors and Compton profiles are compared with the experimental ones. All these data confirm in an unbiased way the hypothesis that nitrogen is present in Li_3N as the N^{3-} ion, which does not exist as a free species, but is stabilized in the crystal by the surrounding Li^+ ions.

I. INTRODUCTION

Lithium nitride is an unusual ionic conductor whose structural and electronic properties are now relatively well known, especially due to intense investigations performed at, or in collaboration with, the Max-Planck-Institut für Festkörperforschung in Stuttgart. A comprehensive discussion of work performed up to 1978 has been provided by Rabenau.[1] Subsequent relevant contributions include, in particular, the study of the electron momentum distribution[2,3] (EMD), new x-ray structure-factor data, and the associated study of the defect structure,[4] the measurement of the quadrupole constants,[5] the calculation of electric field gradients at all atomic positions,[6] and the analysis of anharmonic vibrations.[7] Lithium nitride is a good candidate for accurate theoretical investigations. Its unit cell contains only four lightweight atoms and its crystal structure, though rather uncommon, is highly symmetric. The space group is $p6/mmm$ with $a=3.655$ Å and $c=3.874$ Å; Li_2N layers alternate with pure lithium layers along the c direction; in the Li_2N layers, the lithium atoms, labeled Li(2), are arranged in a graphitelike structure with the nitrogen atoms at the center of the hexagons; in the pure-lithium layers, the Li(1) atoms are atop the nitrogen atoms. A detailed analysis of x-ray diffraction data[8] has shown that lithium nitride is not too far away from the ideal ionic structure, $(Li_3^+)N^{3-}$, although in the past there have been suggestions of a partially covalent character of N—Li bonds.[9,10] To our knowledge, only one *ab initio* theoretical treatment exists, that is, one recently performed by Kerker.[11] He used a pseudopotential Hamiltonian containing a local exchange and correlation term[12] for describing valence electrons; the basis set (BS) included over 200 plane waves, supplemented by one s- and three p-Gaussian-type orbitals (GTO's) centered on nitrogen atoms, in order to improve the description of the electronic structure in the neighborhood of the nitrogen cores. The results are in generally good agreement with experiment. The calculated charge-density maps exhibit small, although not entirely negligible, departures from the ideal ionic structure, in qualitative agreement with diffraction data; however, no direct comparison is provided with experimental structure factors. The calculated Fourier transform of the EMD, the so-called autocorrelation function $B(\vec{r})$, reproduces the experimental data with surprising accuracy; residual discrepancies are tentatively attributed to an improper accounting of core-valence orthogonalization effects, which is an intrinsic defect of all frozen-core pseudopotential calculations.

This represents an additional, and, in a sense, complementary, contribution to the theoretical description of lithium nitride. We report the results of Hartree-Fock (HF), exact-exchange, all-electron calculations, which were performed by means of a previously described[13] computer program (CRYSTAL). The basis functions employed are atomic orbitals (AO's) obtained as a linear combination of s-, p-, and d GTO's, with suitable contraction coefficients. The extended basis set used here was chosen within a rich functional space following a variational criterion. This procedure reduces the risks of predetermining the character of the solution, as can happen, for instance, when minimal BS's are adopted for the calculation of ionic systems:[14] in those cases, the pure ionic character of the wave function is a mere consequence of the level of its description. Kerker's solution is not exempt from similar risks as recognized by the author himself, especially due to the rather poor description of the neighborhood of the nitrogen cores. The use of extended and highly polarizable basis sets for the description of ionic systems requires, however, that far-reaching Coulomb effects are very accurately taken into account both in the calculation of the Fock matrix and in the evaluation of total energy. These kind of problems have been discussed in detail in a previous study concerning lithium hydride,[15] where a minimal and an extended BS solution were critically compared. A similar investigation had been performed some years ago by Hayns and Dissado[16] in conjunction with a semiempirical Hamiltonian. Here, we have used the procedure described in our previous paper for taking into account the "Madelung potential" due to all the charge distributions external to the sphere where the one- and two-electron integrals are exactly or approximately evaluated.

After commenting about the basis set and the computational conditions (Sec. II), the results are presented in Sec. III in a rather detailed way. Particular attention is devoted to a comparison between calculated and experimental data concerning charge and momentum densities. All results appear to confirm, in an unbiased way, the essentially ionic nature of lithium nitride.

II. CHOICE OF BASIS SET AND OTHER COMPUTATIONAL ASPECTS

Scores of computations were performed in order to define the BS reported in Table I, which was finally used for calculating the crystal properties. The essential guideline in the choice of the BS parameters was the variational criterion of minimizing the total energy. As usual, the optimization was performed by steps, by exploring in turn the usefulness of additional GTO's of different types on lithium and nitrogen, and by trying different contraction schemes. The exploration of the parameter space occurred, however, under two constraints: The total number of AO's, which directly determines the computational cost, had to be kept within reasonable limits, and their spatial extent could not exceed certain bounds in order to avoid linear-dependence catastrophes. The main indications resulting from our investigation can be summarized as follows.

The optimization process resulted on the whole in a considerable energy gain, of the order of several electron volts, starting from an atomiclike BS; on the other hand, the energy changes associated with individual tests were often as small as 0.1 eV, which shows the importance of very accurate numerical methods for this kind of investigation. As was to be expected, the choice of the nitrogen AO's was the most critical problem. In fact, in agreement with previous findings,[8,11] we found the crystal to be markedly ionic, and a satisfactory description of the unusual N^{3-} ion required much attention. In order to insure ample variational freedom, three *sp* shells were assigned to nitrogen for describing its valence electrons. When trying to optimize the exponent of the outermost shell we met with a linear-dependence catastrophe at $\alpha=0.10$ a.u. We therefore adopted the safety value $\alpha=0.13$ a.u.; by extrapolating available data we estimated the optimum exponent to be located around 0.08 a.u., with a further energy gain of about 0.4 eV. The usefulness of *d* functions of different sizes was also explored; practically no gains in crystal energy were observed (less than 0.001 a.u.). The contraction scheme of the core orbital was finally optimized, which resulted in a slight expansion with respect to the core of the isolated atom and in an energy gain of about 0.3 eV. For lithium, both atomiclike and ioniclike BS's were tried; it was finally found that the set previously employed for lithium hydride[15] performed quite satisfactorily. It supplements a corelike AO with an outer *sp* shell apt to increasing the variational freedom in the immediate vicinity of the lithium core. The value of the optimum exponent for the outer shell ($\alpha=0.5$ a.u.) corresponds, in fact, to a much more localized function than is needed for valence electrons of lithium. The contribution to energy of the *p* functions on lithium is small but not negligible since it amounts to 0.01 a.u. The

TABLE I. Exponents (in a.u.) and coefficients of the Gaussian functions used in the present calculation. The contraction coefficients multiply normalized individual Gaussians.

Atom	Shell	Type	Exponent	Coefficient *s*	*p*
Nitrogen	1	*s*	8100.	0.000 823	
			1027.83	0.008 872	
			188.45	0.053 12	
			52.722	0.170 3	
			18.111	0.360 2	
			7.0332	0.402 3	
			2.8967	0.155 1	
	2	*sp*	19.15	−0.027 58	0.01755
			3.920	−0.109 0	0.09620
			1.250	0.195 7	0.2312
	3	*sp*	0.48	1.0	1.0
	4	*sp*	0.13	1.0	1.0
Lithium	1	*s*	700.0	0.001 421	
			220.0	0.003 973	
			70.0	0.016 390	
			20.0	0.089 954	
			5.0	0.315 65	
			1.5	0.494 59	
	2	*sp*	0.5	1.0	1.0

present BS can describe the effects of the anisotropic coordination of lithium atoms in the crystal and account for the different electronic structure around the cores of Li(1) and Li(2). The transferability of the lithium BS from one to another kind of ionic crystal is gratifying: BS studies such as those reported here are difficult and extremely ponderous, and apparently of little reward. However, it is hoped that they will provide valuable indications when similar subsystems are considered in different crystalline environments, analogous to what happens in molecular quantum chemistry.

Once the BS was fixed, the other computational parameters were chosen so as to ensure a numerical precision of the order of 0.1 eV/cell in total energy. With respect to previous calculations,[13] a relatively large "quantum zone" was needed for an accurate evaluation of the Coulomb terms, probably due to the large size of the nitrogen ion. Under those conditions, the most important multipole correction from the surrounding "one-electron" zone was associated with the high hexadecapole moment of the nitrogen ion and amounted to about 0.02 eV/cell.

The problem of $\vec{k}$-space integrations is, of course, far from critical with insulating systems; only six $\vec{k}$ points in the irreducible part of the Brillouin zone were sufficient for reconstructing, with sufficient precision, the Fock matrix during the self-consistent iterative procedure.

III. RESULTS AND DISCUSSION

A. Energy data

The relevant energy data corresponding to the experimental equilibrium structure are reported in Table II. The HF cohesive energy has been calculated by subtracting the HF energy of the four constituent atoms from the total crystal energy per cell.[17] The experimental cohesive energy has been obtained starting from the thermodynamic data for lithium nitride reported by Rabenau:[1] $\Delta G^0_{f,298\,\mathrm{K}} = -129$ kJ mol^{-1}, $H^0_{298\,\mathrm{K}} - H^0_0 = 11.6$ kJ mol^{-1}, and $S^0_{298\,\mathrm{K}} = 65.7$ J mol^{-1} K^{-1}. We see that the present calculation accounts for less than half of the cohesive energy. This is slightly surprising at first, since for lithium hydride the HF cohesive energy practically coincided with the experimental one.[15] It was already pointed out that the present BS for nitrogen is not fully optimized; however, the main reason for the observed discrepancy is certainly to be attributed to correlation effects, which are much less important in lithium hydride; the difference in the correlation energy of the N^{3-} ion with respect to the atom can, in fact, be estimated to be around 0.22 a.u. by extrapolating to $Z = 7$ the series of the differences in correlation energy between the atomic systems with ten and seven electrons which have been calculated[18] down to $Z = 8$.

In Table II we also report results of an energy-minimization study with respect to the lattice parameter. When performing such a study, care must be taken that the level of description is about the same for all of the geometrical configurations considered; the problem is more serious when the basis set is not fully optimized with respect to all the variational parameters, as is the case here for the exponent α_0 of the outermost AO's on nitrogen. We have proceeded in two steps. First, we have changed all of the crystal parameters by a factor q and correspondingly altered α_0 so that $\alpha_0 q^2 = \mathrm{const}$; the minimum corresponded to a slight contraction of the crystal, namely by less than 1%. We then let the c parameter vary independently with constant α_0; practically no change was observed here. This kind of calculations is too questionable for reliable elastic constants to be obtained; however, we can mention that from an analysis of second derivatives the compressibility in a direction parallel to the c axis could be estimated to be nearly twice as large as in a perpendicular direction.

TABLE II. Energy data and equilibrium parameters.

Total energy (a.u.)	−76.8945
Kinetic energy (a.u.)	76.8970
Virial coefficient	1.000 02
HF cohesive energy (a.u.)	0.196
Experimental cohesive energy (a.u.)	0.42
Calculated crystal parameter (Å)	a; 3.61
	c; 3.84

B. Band structure

Figure 1 shows the portion of the band structure of lithium nitride which includes the lowest conduction bands and the uppermost valence bands, the latter essentially associated with p electrons of nitrogen. The other occupied bands are located between −24.19 and −23.96 eV (N $2s$ band), between −64.69 and 64.04 eV (lithium-core bands) and at −420.08 eV (nitrogen-core band). The separation between the $2s$ and the $2p$ bands of nitrogen is similar to that reported by Kerker;[11] for the rest, the two calculated band structures are very different from each other. In particular, the lowest p band exhibits a maximum at A in our calculation, presenting there, according to Kerker the absolute minimum. Since the qualitative description of valence bands is usually correct at a HF level, there might be some numerical inconsistencies in the pseudopotential calculation. The variational basis set used

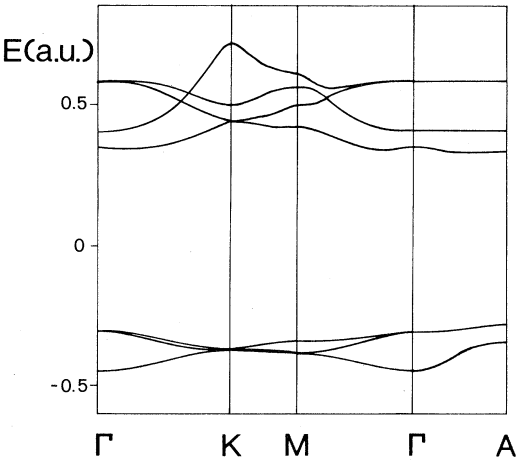

FIG. 1. Portion of the band structure of lithium nitride.

TABLE III. Contributions to the Mulliken populations of the different species of AO's, corresponding to the different bands and shells. Shells are numbered as in Table I.

			Nitrogen			Li(1)			Li(2)	
		s	p_x+p_y	p_z	s	p_x+p_y	p_z	s	p_x+p_y	p_z
Band	1	2.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2	0.004	0.000	0.006	1.990	0.000	0.000	0.000	0.000	0.000
	3	0.004	0.002	0.000	0.004	0.000	0.000	1.990	0.000	0.000
	4	0.000	0.002	0.000	0.000	0.000	0.000	1.998	0.000	0.000
	5	1.992	0.000	−0.002	0.000	0.000	0.004	−0.004	0.010	0.000
	6	0.000	1.184	0.838	−0.008	0.006	−0.006	−0.034	0.016	0.006
	7	−0.002	1.572	0.404	−0.004	0.006	0.002	−0.020	0.040	0.002
	8	0.000	1.196	0.772	−0.012	0.006	0.004	−0.002	0.034	0.006
Shell	1	2.001			1.629			1.626		
	2	0.204	0.848	0.427	0.337	0.017	0.004	0.340	0.049	0.007
	3	0.888	1.048	0.468						
	4	0.905	2.058	1.123						
Total		3.998	3.954	2.018	1.966	0.017	0.004	1.966	0.049	0.007

in the present calculation is obviously not designed to properly describe virtual states. In fact, the gap obtained here is far too large; the experimental gap is about 2.2 eV (Ref. 19) and Kerker obtains 1 eV. Increasing the size of the outermost s-type Gaussian orbitals on lithium atoms causes a dramatic reduction of the gap, but impairs the ground-state solution. In addition, the HF calculations exaggerate, as a rule, the separation between levels in the proximity of the Fermi energy. The latter effect could partly explain the larger width of the nitrogen p bands with respect to Kerker's local-exchange results: 4.6 eV versus 3 eV.

C. Population data

The population data to be presented in the following have been obtained according to a Mulliken population analysis, that is, by attributing half of the overlap populations $P_{\mu\nu}S_{\mu\nu}$ to each of the involved orbitals χ_μ and χ_ν, independently of their size. It is known that such an analysis of the charge density is not free from ambiguities; in the present case, however, the smallness of the overlap populations makes this problem less serious. In fact, we have also tried an alternative "weighted" partition,[13] but the results were practically the same. Table III shows the Mulliken populations subdivided per band and per atomic shell, in units of the electron charge. When the band populations are considered, it is seen that the assignment of the different bands to the different AO's is quite unambiguous. Note that band 2, the lowest core band of lithium, is almost entirely associated with Li(1). Analogously, the nitrogen p_z AO has the highest weight in band 6, the most stable among the p bands of nitrogen. The analysis of the populations in the different AO's can help us to ascertain the relative importance of the different functions in the BS; except for the p AO's on the lithium atoms, the participation of the other orbitals is relatively well balanced. All of the overlap populations between nitrogen and its neighboring atoms are negative [N-Li(1): −0.054; N-Li(2): −0.026; N-N interlayer: −0.027; N-N interlayer: −0.069]. Lithium-lithium—overlap populations are obviously negligible. On the whole, the description of lithium nitride as an ionic compound $(\mathrm{Li}^+)_3\mathrm{N}^{3-}$, is strongly confirmed *a posteriori* by the present results; the covalent character of the crystal, if any, is very slight. Finally, it is interesting to comment on the lowest nonzero multipole moments of the charge distribution attributed to the different atoms (see Table IV). According to the sign of the quadrupole moment ($L=2, m=0$), the Li(1) distribution is slightly flattened in the c-axis direction due to the antibonding interaction with the two nitrogen atoms above and below the Li(1); for the same reason, namely, antibonding interaction with neighboring nitrogen atoms, the Li(2) distribution is slightly oblong in the c-axis direction. The hexadecapole ($L=4$) moments are very low for both lithium atoms. On the contrary, nitrogen has very small quadrupole moments and a large hexadecapole one. The latter is probably an artifact of the Mulliken partition of charge; owing to the large size of the nitrogen ion, its Mulliken distribution contains pointlike charges in correspondence with the surrounding lithium atoms, which give relatively important contributions to high moments. This is probably the main reason why we had to choose a relatively large radius of the quantum zone for a precise evaluation of the total energy (see Sec. II): The contributions to energy by high-order multipoles are in fact, critically dependent from that radius, and rapidly become negligible with its increase.

D. Structure factors

Schulz and co-workers[4,6] have produced a very rich set of experimental structure factors, including 125

TABLE IV. Lowest nonzero multipole moments, expressed in a.u., of the electron charge distributions attributed to the atoms according to the Mulliken partition of charge.

	N	Li(1)	Li(2)
$L=0$	9.970	1.987	2.022
$L=2$, $m=0$	−0.007	−0.057	0.039
$L=4$, $m=0$	−32.66	−0.02	−0.08

symmetry-independent reflections at 153, 233, and 293 K and about 80 at 393, 488, 588, and 678 K. They have analyzed their data following a theoretical model that used standard scattering curves for the Li^+ ions, and calculated scattering data for an N^{3-} ion immersed in a stabilizing Watson-sphere potential.[20,21] In order to account for thermal motion, they used ten parameters for each temperature: six anisotropic temperature factors (two per atomic species), the isotropic extinction factor,[22] the scaling factor, and the occupation probability of the two lithium positions, or, as otherwise stated, the density of vacancies of Li(1) and Li(2). The radius of the Watson sphere was also optimized for best agreement with experimental data. Here, we have followed a similar procedure for the thermal corrections, but we first had to subdivide the electronic charge density into ionic contributions, which was accomplished according to a Mulliken analysis (see preceding subsection). It is rather questionable to assume (especially at high temperatures) that such ionic charge distributions rigidly follow the thermal motion of the corresponding nuclei. We have therefore confined the present analysis to the three lower temperatures, where thermal corrections are less important and a simple harmonic model of vibration appears to be adequate.[7] The thermal parameters were refined, as usual, by minimizing the agreement factor R; since the weighting factors derived from counting statistics were not available to us, the unweighted expression was used,

$$R=\sum |F^{\text{obs}}-F^{\text{cal}}| \Big/ \sum F^{\text{obs}} .$$

The results are reported in Table V. In the same table the best agreement factors, $R^{<}$ and $R^{>}$, are shown, obtained by considering reflections only at low and high angles, respectively; following Schulz and Schwarz,[8] we fixed the limit between the two sets at $\sin\theta/\lambda=0.65$ Å^{-1}.

In all cases the agreement is noticeably much better for the low-angle reflections; this result can partly be ascribed to the poorer quality of the experimental data at the highest angles, where the present results are much nearer to the calculated than to the observed intensities of Ref. 8. On the whole, both the theoretical model used by Schulz and co-workers and ours provide a very good description of the charge density of lithium nitride, although the former seems to be slightly better in this respect. The present calculation can, in principle, very accurately account for anisotropies of the electron density due to crystal-field effects, but the description of the tail of the nitrogen-ion distribution is rather unsatisfactory (see subsection A); furthermore, the partition into ionic contributions suffers from some arbitrariness. Schulz's model is certainly rougher that ours, since it ignores ionic-charge anisotropies and neglects orthogonality effects. On the other hand, it can apparently describe correctly the essential features of the charge distribution of a nearly ideal ionic compound such as lithium nitride; the use of the Watson-sphere radius as an adjustable parameter makes an important contribution to the correctness of the calculated results. Schulz's simple model also permits an interesting analysis to be performed, via a difference synthesis, on the deviations from an ideal ionic-bonded crystal.[8] Such deviations appear to be markedly dependent on temperature, and at 233 K there seems to be a nearly perfect compensation of thermal and electronic anisotropies, corresponding to the best agreement of Schulz's model with experiment. The fact that our data give the best agreement at the higher temperatures could be interpreted as an implication that the present calculation overestimates the anisotropies of the electron distribution in the field of the static nuclei. However, to make more definite statements about this point, structure-factor data collected at much lower temperatures would be valuable, since thermal corrections and related problems would be much less important.

We can now take a closer look at the refined thermal parameters as reported in Table V. The mean-square dis-

TABLE V. Refined thermal parameters. $U^{\perp}$ and $U^{\parallel}$ are the thermal mean-square displacements, perpendicular and parallel to the c direction, in units of 10^{-4} Å^2. K is the absolute scale factor, g is the extinction coefficient, oc1 and oc2 are the occupation probabilities of the two lithium sites, and R, $R^{<}$, and $R^{>}$ are the agreement factors referring to all reflections and to those with $\sin\theta/\lambda$ less than or greater than 0.65 Å^{-1}, respectively. The numbers in parentheses are the corresponding results from Ref. 8; the authors did not provide the unweighted agreement factors in 153 and 293 K, so their corresponding weighted R's are reported, marked with an asterisk.

Temperature (K)	153	233	293
$U^{\perp}_{\text{N}}$	85.7(62.2)	105.4(77.5)	125.9(92.9)
$U^{\parallel}_{\text{N}}$	61.2(58.5)	75.0(77.5)	97.1(95.0)
$U^{\perp}_{\text{Li(1)}}$	176.1(125)	219.1(160)	259.8(189)
$U^{\parallel}_{\text{Li(1)}}$	73.0(71)	94.0(86)	109.0(107)
$U^{\perp}_{\text{Li(2)}}$	131.9(88)	154.0(108)	181.6(126)
$U^{\parallel}_{\text{Li(2)}}$	189.9(181)	253.5(248)	308.7(307)
oc1	0.996(0.997)	1.002(0.998)	0.996(1.003)
oc2	0.994(0.990)	0.994(0.989)	0.992(0.982)
K	1.021	1.015	1.023
g (10^{-6})	175	180(480)	627
R	0.0167(0.0095*)	0.0121(0.0080)	0.0125(0.0130*)
$R^{<}$	0.0102	0.0093(0.0050)	0.0077
$R^{>}$	0.0199	0.0125(0.0140)	0.0168

TABLE VI. Directional Compton profiles. The core and valence contributions to the CP's (labeled as c and v) correspond to the four lowest bands and to the subsequent four ones, respectively. In the column labeled t^*_{calc}, the total calculated CP is reported, after convolution with the experimental resolution function (full width at half maximum equal to 0.41 a.u.), for direct comparison with the observed CP's (Ref. 2), the latter is being reported in the column headed t_{obs}. All data are in a.u.

	(001)				(110)				(100)			
p_z	v	c	t^*_{calc}	t_{obs}	v	c	t^*_{calc}	t_{obs}	v	c	t^*_{calc}	t_{obs}
0.0	4.640	2.261	6.679	6.731	4.417	2.262	6.539	6.571	4.557	2.258	6.622	6.613
0.1	4.564	2.246	6.615	6.678	4.381	2.245	6.493	6.509	4.499	2.246	6.565	6.561
0.2	4.386	2.217	6.426	6.506	4.285	2.213	6.357	6.335	4.336	2.214	6.396	6.401
0.3	4.112	2.171	6.127	6.191	4.125	2.166	6.131	6.096	4.084	2.165	6.129	6.139
0.4	3.714	2.105	5.743	5.788	3.828	2.097	5.820	5.782	3.766	2.102	5.783	5.770
0.5	3.296	2.024	5.303	5.318	3.495	2.018	5.437	5.377	3.408	2.024	5.378	5.338
0.6	2.887	1.933	4.838	4.808	3.123	1.930	5.000	4.926	3.028	1.934	4.935	4.878
0.7	2.521	1.831	4.372	4.322	2.729	1.830	4.524	4.454	2.639	1.834	4.470	4.404
0.8	2.164	1.724	3.918	3.854	2.316	1.726	4.027	3.974	2.262	1.728	4.000	3.948
0.9	1.824	1.615	3.486	3.411	1.878	1.619	3.529	3.493	1.892	1.619	3.534	3.513
1.0	1.504	1.507	3.084	3.014	1.463	1.512	3.052	3.039	1.532	1.511	3.089	3.077
1.2	1.039	1.300	2.376	2.299	0.824	1.305	2.244	2.257	0.915	1.302	2.303	2.323
1.4	0.623	1.110	1.792	1.756	0.506	1.115	1.684	1.710	0.531	1.111	1.712	1.727
1.6	0.342	0.942	1.343	1.351	0.340	0.945	1.316	1.332	0.316	0.943	1.302	1.333
1.8	0.201	0.798	1.035	1.054	0.238	0.797	1.056	1.072	0.195	0.798	1.024	1.053
2.0	0.136	0.675	0.831	0.837	0.169	0.673	0.862	0.871	0.137	0.674	0.835	0.845
2.5	0.071	0.447	0.526	0.540	0.086	0.446	0.540	0.555	0.096	0.446	0.547	0.555
3.0	0.060	0.303	0.361	0.364	0.047	0.304	0.353	0.363	0.054	0.303	0.360	0.359
3.5	0.029	0.214	0.246	0.249	0.026	0.214	0.241	0.255	0.022	0.214	0.239	0.241
4.0	0.012	0.156	0.170	0.180	0.016	0.155	0.172	0.181	0.015	0.155	0.170	0.172
4.5	0.011	0.115	0.126	0.138	0.010	0.115	0.125	0.131	0.012	0.115	0.127	0.125
5.0	0.008	0.087	0.095	0.102	0.006	0.087	0.094	0.097	0.006	0.087	0.094	0.092
6.0	0.002	0.051	0.053	0.057	0.002	0.051	0.053	0.057	0.003	0.051	0.054	0.057
7.0	0.001	0.031	0.033	0.034	0.000	0.031	0.032	0.034	0.000	0.031	0.032	0.034

placements are somewhat larger with respect to those of Ref. 8; the anisotropy of the vibrational ellipsoid of Li(1), and especially of N, is larger, while the reverse is true for Li(2); on the whole, however, the main results of Schulz are confirmed. One of the important conclusions of Schulz's work[4,7,8] was that the lithium content of their crystals was slightly below stoichiometry, corresponding to a percentage of vacancies at the Li(2) positions between 1% and 2%, while no vacancies were found at the Li(1) sites, within experimental error. This result is relevant to explaining the mechanism of ionic conductivity, and the high concentration of the defects might also justify the red color of the crystals. The present study leads to similar conclusions, although the distinction between the two occupancies is less clear cut (the uncertainty in the estimated occupancies is about 0.4%).

E. Compton profiles

We defer to a subsequent paper a thorough discussion of the EMD of lithium nitride, essentially based on the autocorrelation function $B(r)$, for which abundant experimental information is available.[2,3] In this section we simply present the Compton profiles along the main three crystallographic directions and compare them with the experimental ones of Ref. 2. Table VI reports the valence and core contributions to the three profiles, and the total CP's convoluted with the experimental resolution function for comparison with the observed data. The agreement is quite reasonable; the observed anisotropy is also satisfactorily reproduced as documented in Fig. 2.

Pattison and Schneider[2] have compared their experimental profiles with the theoretical isotropic ones obtained using the same model as employed by Schulz (see preceding section). The Watson-sphere radius $r_W = 1.38$ Å, resulting from x-ray-diffraction—data analysis, gave poor agreement with the experimental CP's, the peak height being in error by as much as 5%, vice versa, $r_W = 1.20$ Å, which gives the best agreement for CP's performs badly for x-ray structure factors [see Fig. 4(a) in Ref. 20].

According to Pattison, the main reason of the relative failure of the Schulz model lies in its neglect of overlap effects, which are much more important in the description of the EMD than of charge densities. The fact that the present results are so far better than those obtainable with that model, even with the optimum r_W, could have essentially the same explanation. Since the anisotropy of the EMD is also correctly described, we could infer that the partially unsatisfactory results described in the preceding subsection are mainly ascribable to the arbitrary partition of the charge density into independently vibrating ionic contributions, and to neglect of electron correlation in the N^{3-} ions.

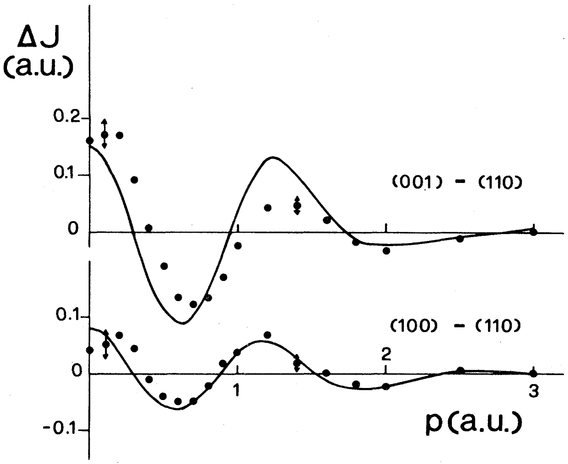

FIG. 2. Different Compton profiles. The dots represent the experimental data and the double arrows indicate the estimated errors. The calculated data (solid curve) have been convoluted for limited experimental resolution.

F. Concluding remarks

This work strongly supports the hypothesis that nitrogen is present in Li_3N as the N^{3-} ion, which does not exist as a free species, but is stabilized in the crystal by the surrounding Li^+ ions. Such ionic character resulted automatically following a pure variational criterion of total-energy minimization within the HF approximation; the addition of correlation terms would further favor a purely ionic, with respect to a partially covalent, structure. The use of the variationally optimized basis set has provided a ground-state wave function which accurately reproduces the experimental cohesion energy (after inclusion of correlation energy according to a reasonable estimate), structure factors, and Compton profiles. We can thus confirm what we already stated with reference to the lithium hydride calculation,[15] namely that an accurate HF calculation performed with an extended basis set selected according to variational criteria can satisfactorily describe the most important ground-state properties of ionic crystals. Within the present computational scheme, the main residual problem concerns a more adequate description of the tail of the distribution of the large negative ions.

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