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Electric Field Gradients and Charge Density in Lithium Nitride

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Abstract

The magnitudes of the electric field gradients at all atomic positions in Li_3N are known from NQR experiments. High-temperature NQR data indicate the gradients at Li(1) and Li(2) to be of opposite sign. In this paper, we calculate the field gradients from X-ray data and refine the parameters of the multipole deformation functions together with scale, extinction and temperature factors against X-ray and NQR data simultaneously, assuming various sign combinations for the gradients at Li(1), Li(2) and N. Despite an ill-defined scale factor of the X-ray intensities, negative signs at both Li(2) and N are obtained, and the sign at Li(1) is thus positive. The same signs are obtained from an ionic point-charge model. The extinction correction is important and dependent on the assumed signs. The model deformation map for the signs +, −, − at Li(1), Li(2) and N shows nearly spherical Li ions, whereas N appears to be strongly polarized perpendicular to **c**. With the assumption of the incorrect negative sign at Li(1), a strongly polarized Li(1) ion but approximately the same reliability indices for the X-ray data are obtained. Inclusion of NQR data in the charge-density refinement results in a better definition of the quadrupolar components of the deformation density close to the atomic centres.

Introduction

Schwarzenbach & Ngo Thong (1979) suggested that structure factors inferred from X-ray diffraction be combined with electric field gradient tensors at the sites of the nuclei measured with nuclear quadrupole resonance spectroscopy (NQR) to obtain an electron distribution satisfying both types of data. The field gradient $\nabla\mathbf{E}$ at any site can, in principle, be computed from the electron-density distribution in the crystal and thus from structure factors. It is evaluated as the sum of two terms, $\nabla\mathbf{E} = \nabla\mathbf{E}(\text{overlap}) + \nabla\mathbf{E}(\text{deformation})$. The first term is the gradient in the structure composed of neutral spherical atoms whose electron densities overlap at the nuclear site. The second term arises from the static deformation density which, in our model, is represented by deformation functions (Hirshfeld, 1977). The computed field gradient may be compared with the observed quantity $\nabla\mathbf{E}(\text{obs})$, or $\nabla\mathbf{E}(\text{obs}) - \nabla\mathbf{E}(\text{overlap})$ may be introduced as an observation in the least-squares determination of the deformation parameters.

The structure of the ionic conductor lithium nitride, Li_3N, appears to be well suited for an application of this procedure. It is hexagonal, space group $P6/mmm$, $a = 3{\cdot}646\ (1)$, $c = 3{\cdot}874\ (1)$ Å at 233 K. The unit cell contains one formula unit. The N atom occupies the Wyckoff position 1(*a*) (000), Li(1) occupies 1(*b*) $(00\frac{1}{2})$ and Li(2) 2(*c*) $(\frac{1}{3}\frac{2}{3}0, \frac{2}{3}\frac{1}{3}0)$. The point symmetries are respectively $6/mmm$, $6/mmm$ and $\bar{6}m2$. N is coordinated by six Li(2) at 2·105 Å and two Li(1) at 1·937 Å. Accurate X-ray diffraction data at 153, 233 and 293 K have been reported by Schulz & Schwarz (1978). They compared structure refinements assuming neutral atoms $Li_3^0N^0$ and assuming an ionic structure $Li_3^+N^{3-}$. The scattering factor curve for N^{3-} was derived from a Watson sphere model (Schwarz & Schulz, 1978). Excellent agreement between observed and calculated structure factors was obtained for the ionic structure with a Watson radius of 1·39 Å. The high ionicity of the compound is also suggested by polarized infrared and Raman spectra (Chandrasekhar, Bhattacharya, Migoni & Bilz, 1978), by Compton scattering (Pattison & Schneider, 1980) and by a theoretical calculation of the electronic structure (Kerker, 1980).

The quadrupole coupling constants $|eQ\,\nabla E_{33}/h|$ of all atomic sites in Li_3N have been measured by ^{7}Li, ^{6}Li and ^{14}N NQR by Brinkmann, Freudenreich & Roos (1978), Brinkmann, Mali & Roos (1979) and Differt & Messer (1980); eQ is the nuclear quadrupole moment, h is Planck's constant and ∇E_{33} is the field gradient along **c**. Owing to the hexagonal site symmetries, the gradient tensors are axially symmetric, $\nabla E_{11} = \nabla E_{22} = -\frac{1}{2}\nabla E_{33}$, $\nabla E_{12} = \nabla E_{13} = \nabla E_{23} = 0$. Taking $Q = -0{\cdot}041b$ for ^{7}Li (Orth, Ackermann & Otten, 1975) and $0{\cdot}016b$ for ^{14}N (*Handbook of Chemistry and Physics*, 1978), the errors of which may be as large as 15%, the magnitudes of $|\nabla E_{33}|$ are 5·87, 2·88 and 13·04 × 10^{20} V m^{-2} at Li(1), Li(2) and N, respectively. These values are nearly constant between 220 and 350 K. The signs of the quadrupole coupling constants are not determined

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experimentally. However, high-temperature NQR experiments indicate *opposite signs* for the field gradients at Li(1) and Li(2) (Messer, Birli & Differt, 1980; Brinkmann, Mali & Roos, 1980). This is in agreement with the ionic point-charge model which predicts the signs +, −, − at Li(1), Li(2) and N respectively, and a ratio ∇E_{33}(Li1)/∇E_{33}(Li2) of −2·36. The Sternheimer quadrupole antishielding factor of N^{3-} is estimated as 20 which implies a highly polarizable ion (Differt & Messer, 1980).

Charge density refinements

The 125 X-ray intensities and their e.s.d.'s, measured at 233 K with graphite-monochromated Mo $K\alpha$ radiation to a maximum $\sin\theta/\lambda$ of 1·07 Å^{-1}, were obtained from Professor Heinz Schulz (Schulz & Schwarz, 1978). Only three intensities were $<3\sigma$. Charge-density refinements were carried out with *LSEXP* (Hirshfeld, 1977), modified according to Schwarzenbach & Ngo Thong (1979).* The latest amendments to the program allow calculation of e.s.d.'s of field gradients from the inverse least-squares matrix, and refinement of secondary extinction according to Becker & Coppens (1975). The neutral-atom structure was chosen as the starting point. The free-atom scattering factors in analytical form were taken from *International Tables for X-ray Crystallography* (1974). All independent parameters of the deformation functions from $n = 0$ to $n = 4$ were refined. In terms of orthogonalized spherical harmonics, there are three monopolar, two quadrupolar and one hexadecapolar functions per atom; Li(2) has also an octopolar term. There are thus 19 independent population parameters and three exponents α of the radial functions $r^n \exp(-\alpha r)$. Eight standard parameters were refined, *viz* two temperature coefficients per atom, one scale factor and one extinction parameter (type I crystal, Lorentzian mosaic distribution). The extinction correction is important for the reflection 001 (Table 1), and has a minor effect on 002, 100 and 110. The population parameters of the Li atoms were not varied. Any underoccupancy of these sites as described by Schulz & Schwarz (1978) is accounted for by monopolar terms which are themselves dependent on the scale factor (see below). All refinements were carried out with respect to $|F|^2$, with weights $\sigma^{-2}(|F|^2)$. Field gradients introduced as observations were given a weight of 1100 and the differences $|\nabla E_o - \nabla E_c|$ were smaller than 3×10^{18} V m^{-2} at convergence. The field gradients ∇E_{33}(overlap) are −1·972, 3·270 and 0·366 × 10^{20} V m^{-2} for Li(1), Li(2) and N respectively. They were evaluated by summing the contributions of neighbouring atoms to a maximum distance of 10 Å. The following difficulties were encountered during refinement:

(i) The scale factor, defined by $F_0 \simeq$ scale × F_c, is 28·56 for the ionic structure $Li_3^+N^{3-}$ and 29·46 assuming neutral atoms. In the charge-density refinements, it increased to 31·5 (4). The correlation coefficients with the $n = 0$ functions of Li(1), Li(2) and N, and the temperature parameters of N are, respectively, −0·73, −0·87, −0·97, 0·94 and 0·87. The correlation with the extinction parameter is small. Corresponding deformation maps (not reproduced here) show deep holes at *all* atomic positions. The X-ray data are thus insufficient to obtain reliable estimates of the scale factor together with the populations of the monopolar functions. The monopolar functions are able to simulate the scattering of the core electrons at high angles and the deformation model has enough parameters to describe the intensities of the few low-order reflections. The scale factor indicated by the lowest reliability indices is certainly wrong. All refinements with variable scale were therefore repeated with a scale fixed at the free-atom value of 29·456, in order to judge the effect on the calculated field gradients. The true value of the scale factor is probably within a few percent of 29·0.

Table 1. *Reliability factors obtained from 16 refinements*

Definitions: GOF($|F|^2$) = $\{\sum \text{weight} \times (|F_o|^2 - |F_c|^2)^2/(n-m)\}^{1/2}$, n = number of observations, m = number of variable parameters; $R(|F|) = \sum |F_o - F_c| / \sum |F_o|$;
$R_w(|F|^2) = \{\sum \text{weight} \times (|F_o|^2 - |F_c|^2)^2 / \sum \text{weight} \times |F_o|^4\}^{1/2} \simeq 2R_w(|F|)$;
y_{min} = smallest extinction factor, $F_0 \simeq yF_{corr}$. The sums include all structure factors.
Radial exponents α were varied in refinements *c*2–*h*2, and kept at 5·0 Å^{-1} in all other refinements.

	Sign of ∇E_{33} at Li(1), Li(2), N			GOF-($|F|^2$)	$R(|F|)$	$R_w(|F|^2)$	$n-m$	y_{min}
Variable scale								
*a*1				1·199	0·00680	0·0119	99	1·000
*b*1				1·129	0·00619	0·0111	98	0·9037
*c*1	+	−		1·134	0·00643	0·0113	100	0·9120
*d*1	−	−		1·160	0·00659	0·0115	100	0·9442
*e*1	+	+		1·188	0·00699	0·0118	100	0·9357
*f*1	−	+		1·235	0·00720	0·0123	100	0·9634
*g*1	+	−	−	1·204	0·00686	0·0120	101	0·9027
*h*1	+	−	+	1·589	0·00866	0·0159	101	0·9311
Fixed scale								
*a*2				1·373	0·00783	0·0137	100	1·000
*b*2				1·361	0·00767	0·0135	99	0·9479
*c*2	+	−		1·247	0·00722	0·0123	98	0·9553
*d*2	−	−		1·233	0·00732	0·0122	98	0·9514
*e*2	+	+		1·309	0·00759	0·0129	98	1·000
*f*2	−	+		1·302	0·00793	0·0128	98	0·9947
*g*2	+	−	−	1·251	0·00747	0·0124	99	0·9453
*h*2	+	−	+	1·346	0·00769	0·0133	99	0·9774

* This paper is in error on p. 654, 2nd column, line 12. The constraint for spherical symmetry and $n = 4$ should read $(100) = 8/(2 + A^2)^2\{(A11)\}$, *i.e.* the constant is the same as for cylindrical symmetry.

(ii) Some refinements, in particular those with variable scale factor and those against structure factors only, diverged if the radial exponents α were varied. Several correlation coefficients of α(N) with population parameters were >0·99. As remarked by Schulz & Schwarz (1978), there are only a few reflections with $\sin\theta/\lambda < 0{\cdot}4$ Å^{-1} where the scattering factor curves for N^0 and N^{3-} differ appreciably, *i.e.* the deformation density is expected to be quite flat. The high correlations indicate that we use too many parameters for its description. Whenever the α's could not be refined, they were therefore fixed at 5·0 Å^{-1}.

Eight refinements with a variable scale factor (*a*1 to *h*1) and eight with a fixed scale factor (*a*2 to *h*2) were carried out. The reliability indices are shown in Table 1. Firstly, the charge density was refined against structure factors only (refinements *a*1, *b*1, *a*2, *b*2). The field gradients and their e.s.d.'s were computed at convergence and are shown in Table 2. The signs of ∇E_{33} at Li(2) and N are shown to be probably *negative*, independent of the scale factor. The sign at Li(1) is not indicated by the structure factors, except if extinction is neglected and the scale factor is too large (refinement *a*1).

The extinction parameters obtained are 0·20 (7) × 10^4 for *b*1 and 0·09 (7) × 10^4 for *b*2; the corresponding mosaic spreads are 17″ and 35″ (crystal diameter 0·3 mm).

Next, the field gradients at Li(1) and Li(2) were introduced as observations, assuming the sign combinations +−, −−, ++ and −+ (refinements *c*1–*f*1 and *c*2–*f*2). This considerably improved the convergence to the least-squares minimum. The correlations of the exponents α with population parameters generally decreased; the α's could be varied in *c*2–*f*2. The temperature factors for the four sign combinations agree within 2σ. The computed values for the field gradient at N are −5·7, −0·9, −5·4, −0·9 × 10^{20} V m^{-2} for *c*1–*f*1 (e.s.d. 1·8 × 10^{20}) and −7·5, −7·2, −5·4, −6·0 × 10^{20} V m^{-2} for *c*2–*f*2 (e.s.d. 4·2 × 10^{20}). The sign at N is thus again determined to be *negative*, except in *d*1 and *f*1 where it is indeterminate. The reliability indices show the sign at Li(2) to be probably *negative*, but they are not able to indicate the sign at Li(1). However, since these signs are *different* according to NQR, the sign combination +− is to be preferred.

Finally, in refinements *g*1, *h*1, *g*2 and *h*2, all field gradients were introduced as observations, starting from refinements *c*1 and *c*2. They again show the sign at N to be clearly *negative*.

Static model maps resulting from refinements *g*2 (+−−) and *d*2 (−−?), fixed scale, were obtained with Fourier summations of the structure factors calculated with the deformation functions only. The plane $(\bar{1}2\bar{1}0)$ is shown in Figs. 1 and 2. The e.s.d. of the deformation density was estimated with *DEFSYN* (Hirshfeld, 1977)

Table 2. *Calculated field gradients* ∇E_{33} *from refinements a*1, *b*1 (*variable scale*) *and a*2, *b*2 (*fixed scale*)

In *a*1 and *a*2, secondary extinction is neglected; in *b*1 and *b*2, it is included. Units are 10^{20} Vm^{-2}, e.s.d.'s are given in parentheses.

	Li(1)	Li(2)	N	Probable signs
*a*1	−3·9 (3·3)	−5·1 (2·4)	−1·8 (2·1)	− − ?
*b*1	−0·3 (3·6)	−8·7 (2·4)	−3·6 (2·1)	? − −
*a*2	−1·2 (3·9)	−8·4 (2·7)	−4·5 (2·7)	? − −
*b*2	+1·2 (4·8)	−10·5 (3·3)	−4·5 (3·0)	? − −
$\lvert\nabla E_{33}(\text{obs})\rvert$	5·87	2·88	13·04	

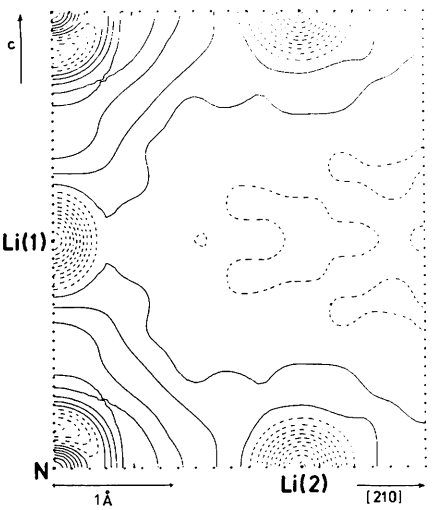

Fig. 1. Static model deformation map in the plane $(\bar{1}2\bar{1}0)$ containing Li(1), Li(2) and N, obtained from refinement *g*2, gradient signs +, −, −. Negative contours broken, contour interval 0·05 e Å^{-3}.

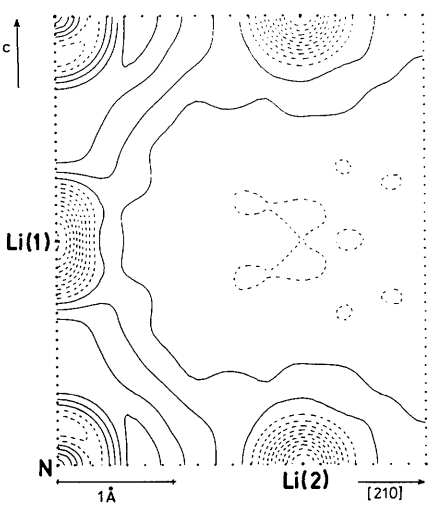

Fig. 2. Model deformation map as in Fig. 1, obtained from refinement *d*2, with negative signs at Li(1) and Li(2), *i.e.* in contradiction with the NQR data.

by summing the variances and covariances of the deformation parameters for each grid point. It is approximately 0·01 e Å^{-3} between the atoms, and increases to 0·1 e Å^{-3} at the atomic sites.

Discussion

The calculations show that only some of the signs, and not the absolute values of the field gradients may be inferred with sufficient precision from structure factors. Since the signs at Li(1) and Li(2) are opposite, +, −, − is predicted respectively at Li(1), Li(2) and N, independently of the scale factor and in agreement with the ionic model. A change of the scale factor affects mainly the monopolar deformation terms, *i.e.* the heights of the peaks and holes at the atomic positions of the deformation map.

The model map of Fig. 1, computed with the most probable signs +, −, − of the gradients shows nearly spherical Li ions. Both density minima are slightly ellipsoidal with an axial ratio of 1·1 and elongated towards N, *i.e.* the electron distributions of both Li are contracted along the Li—N bonds. The diameter of the hole is 10% smaller at Li(1) than at Li(2). The N atom, on the other hand, is strongly polarized and contracted along **c**. Near its centre, the peak is an oblate ellipsoid with an axial ratio of about 1·4, followed by a trough on **c**. Similar polarizations of the atoms have been obtained by Kerker (1980). In terms of orthogonalized spherical harmonics, the main contributors to the deformation density are the monopolar functions of all atoms and the quadrupolar function of N, followed by the quadrupolar functions of both Li. The contributions of octopolar and hexadecapolar terms are insignificant. The model map of Fig. 2 was obtained with negative gradients at both Li positions and is thus in disagreement with the NQR data. The reliability indices with respect to the X-ray data are, however, about the same as for Fig. 1. The observed gradient of $-13{\cdot}04 \times 10^{20}$ V m^{-2} at N was not used as an observation; its value computed from refinement $d2$ is $-7{\cdot}2 \times 10^{20}$ V m^{-2}. The map is very similar to Fig. 1 everywhere except at Li(1) where the density minimum is now strongly polarized along **c**. This shows clearly that the field gradient information modifies the deformation map considerably in the vicinity of the atoms. It is thus complementary to the information contained in the structure factors. The weaker field gradient at N does not change the form of this ion; it results only in a lower peak and a shallower trough than in Fig. 1.

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