PHYSICAL REVIEW B VOLUME 9, NUMBER 4 15 FEBRUARY 1974

# Calculated properties of the $N_2^-$ defect in sodium azide*†

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(Received 27 July 1973)

A self-consistent-field molecular-orbital calculation was performed for the $^2\Pi_g$ ground state of an $N_2^-$ molecule ion embedded in an array of point ions simulating the sodium azide lattice. The equilibrium internuclear separation for $N_2^-$ was determined to be 2.17 a.u. The crystal-field splitting of the ground state and the equilibrium orientation of $N_2^-$ in the monoclinic phase ($\alpha$-$NaN_3$) were calculated using an expansion of the crystal potential of $\alpha$-$NaN_3$ together with wave functions calculated for the rhombohedral phase ($\beta$-$NaN_3$). Results of the calculation are compared with properties of $N_2^-$ inferred from ESR spectra by Gelerinter and Silsbee (GS). The orientational energy of the $N_2^-$ quadrupole moment in the crystal field is minimum for a tilt angle of 4.67°, in excellent agreement with experiment, but the sense of rotation is reversed. The splitting of the partially occupied $1\pi_g$ level, which GS attribute to Jahn-Teller distortion, is explained here instead by the monoclinic structure of $\alpha$-$NaN_3$, and has the value $\Delta = 366\ \text{cm}^{-1}$. The predicted $3\sigma_g - 1\pi_g$ energy separation is $\Delta' = 68\,800\ \text{cm}^{-1}$. These values are in reasonable agreement with the measurements of GS, as are calculated values of the dipole-dipole contribution to the hyperfine tensor: $A_{xx} = -8.19$ G, $A_{yy} = +15.71$ G, and $A_{zz} = -7.56$ G.

## I. INTRODUCTION

Color centers in the alkali azides and alkaline-earth azides have been of interest for some time, since the corresponding defects are thought to be involved in photolysis and thermal decomposition.[1-7] Among the defects produced by ionizing radiation which have been identified by electron-spin resonance is an $N_2^-$ molecular ion trapped at an anion site in potassium azide ($KN_3$),[8,9] sodium azide ($NaN_3$),[10,11] and barium azide ($BaN_6$).[12] In $KN_3$, this $N_2^-$ defect has been tentatively correlated with a prominent optical absorption band at 565 nm.[13]

Gelerinter and Silsbee (GS)[10] found it necessary to measure the ESR spectrum of $N_2^-$ in $NaN_3$ at liquid-helium temperature, because of very short spin-lattice relaxation time. They interpreted their results in terms of the rhombohedral $NaN_3$ crystal structure established by Hendricks and Pauling[14] in 1925. The space group is $D_{3d}^5$, with the rhombohedral unit cell shown in Fig. 1. The point symmetry at the anion site, $D_{3d}$, is high enough to preserve the degeneracy of the $^2\Pi_g$ ground state of $N_2^-$. Nevertheless, GS infer from the ESR spectrum that the orbital degeneracy is split by 500 $\text{cm}^{-1}$, and that the $N_2^-$ ion is tilted 4.6° with respect to the crystal *c* axis. These effects they attribute to Jahn-Teller distortion.

In 1963, it was discovered by Miller and King,[15] and independently by Pringle and Noakes,[16] that $NaN_3$ undergoes a second-order phase transition at room temperature (~ 19 °C) and that the structure is monoclinic at lower temperatures. The nature of the distortion of the pseudorhombohedral unit cell is shown in Fig. 2. The monoclinic phase has been investigated in detail by Parsons and Yoffe,[17] and by Pringle and Noakes[18] who designate it $\alpha$-$NaN_3$ to distinguish it from the rhombohedral

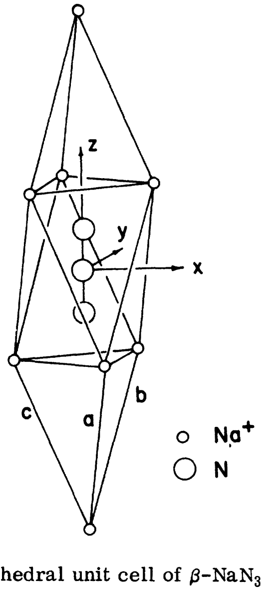

FIG. 1. Rhombohedral unit cell of $\beta$-$NaN_3$ (high-temperature phase).

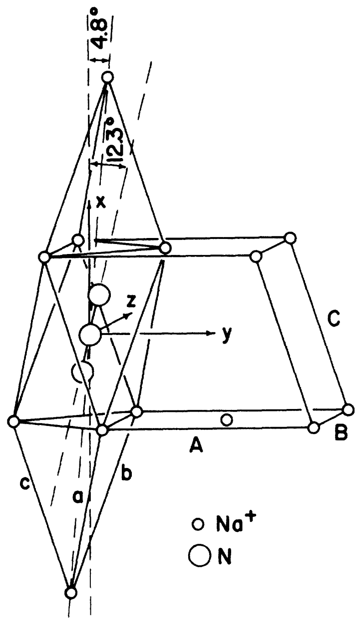

FIG. 2. Pseudorhombohedral unit cell of $\alpha$-$NaN_3$ (low-temperature phase). Also shown are the cations associated with a conventional, base-centered-monoclinic unit cell.

phase $\beta$-$NaN_3$. The space group of $\alpha$-$NaN_3$ is $C_{2h}^3$, and the point symmetry at the azide site is $C_{2h}$. Evidently the observations of GS need to be reinterpreted in terms of the monoclinic structure of $\alpha$-$NaN_3$. The crystals grow as thin platelets with the $c$ axis perpendicular to the large face. This large face remains perpendicular to the $x$ axis in Fig. 2 after cooling through the phase transition; thus the 4.6° tilt of the $N_2^-$ ion observed by GS is presumably with respect to the $x$ axis. Both the tilt and the splitting of orbital degeneracy may well be explained by the phase transition, rather than by Jahn-Teller distortion, as Gelerinter[19] has subsequently suggested.

The object of the present investigation is to verify the model of an $N_2^-$ ion in an anion site by accounting quantitatively for some of its observed properties, and, in particular, to test the foregoing conjecture. This object is accomplished by combining an *ab initio* molecular orbital calculation in a simulated crystalline environment, presented in Sec. II, with crystal-field calculations, Sec. III. Spin-Hamiltonian parameters are derived in Sec. IV, and compared with experiment in Sec. V. The results and conclusions are summarized in Sec. VI.

## II. MOLECULAR ORBITAL CALCULATIONS

Self-consistent-field molecular-orbital calculations were performed for the $^2\Pi_g$ ground state of $N_2^-$ by the Hartree-Fock-Roothaan open-shell procedure.[20] The CDC 6600 version of the POLYATOM system of computer programs was employed for these calculations. A general description of this system of programs, which utilizes a Gaussian basis, may be found in the paper by Csizmadia *et al.*,[21] and in the documentation of the POLYATOM system available through the Quantum Chemistry Program Exchange.

The basis set for the present calculation was chosen as follows: Huzinaga's[22] ($9s$, $5p$) basis for the nitrogen atom was supplemented by a $d$-type Gaussian function, whose orbital exponent $\xi$ was varied to minimize the energy of $N_2$ at the experimental internuclear separation, $R = 2.068$ a.u. The total energy obtained with the optimum value, $\xi = 1$, was $-108.969$ hartree, which compares very favorably with the value $-108.970$ hartree obtained by Nesbet,[23] thus establishing confidence in the basis set. This ($9s$, $5p$, $1d$) basis was subsequently employed in the $N_2^-$ calculation.

In order to ensure a reasonable equilibrium internuclear separation, it was considered essential to simulate the crystalline environment of the molecule ion. This was accomplished by constructing an array of point ions representing the $\beta$-$NaN_3$ crystal structure. Only integral charges were employed; i.e., the azide ion was represented by a single point ion, with charge $-e$, at the central N position. The lattice contained 238 ions. The $N_2^-$ ion was placed at the central azide-ion site, symmetrically disposed with respect to the central N position, and with the same orientation as the missing azide ion. This representation of the crystalline environment was thought to be adequate for the purposes of stabilizing the molecule ion and computing molecular orbitals; a more realistic model is presented in Sec. III in connection with crystal-field calculations.

The ground configuration of $N_2^-$ is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 1\pi_g$. In $\beta$-$NaN_3$, with the $N_2^-$ ion oriented parallel to the $c$ axis, the two $1\pi_g$ orbitals are degenerate, so the ambiguity was resolved by assigning a fractional occupancy of 0.5 to each orbital, in accordance with the open-shell procedure.[19] The internuclear separation $R$ was varied to minimize the total energy, which is plotted as a function of $R$ in Fig. 3. It can be seen from this curve that the equilibrium internuclear separation is $R = 2.17$ a.u.

The one-electron energies corresponding to the equilibrium internuclear separation are shown schematically in Fig. 4, and are listed in Table I, together with the total electronic energy. (It should be noted that the energies shown in Fig. 3 and Table I incorporate an additive constant determined by the arbitrary specification of the size of the point-ion lattice used in these calculations.

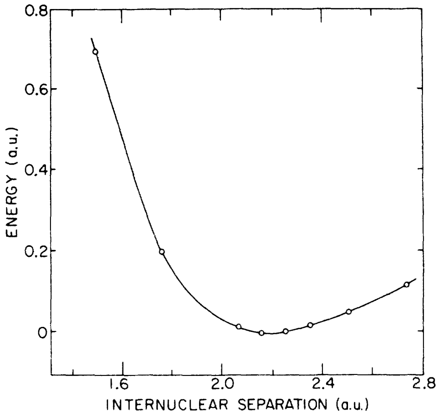

FIG. 3. Potential curve for $N_2^-$ in $\beta$-$NaN_3$.

TABLE I. One-electron and total energies for $N_2^-$ in $\beta$-$NaN_3$, calculated for the equilibrium internuclear separation, 2.17 a.u.

| Orbital | Energy (hartree) |
|---|---|
| $1\pi_g$ | $-0.1145$ |
| $1\pi_u$ | $-0.3908$ |
| $3\sigma_g$ | $-0.4338$ |
| $2\sigma_u$ | $-0.6071$ |
| $2\sigma_g$ | $-1.2001$ |
| $1\sigma_u$ | $-15.4354$ |
| $1\sigma_g$ | $-15.4377$ |
| Total | $-133.9527$ |

However, relative energies are significant for a given lattice.) The corresponding wave functions were used to calculate molecular properties, which are presented in Table II. Quadrupole moments $Q_{ii}$ are given both for the entire molecule ion, including nuclei, and for the $1\pi_g$ orbitals alone. The corresponding electronic operators are permutations of $-\frac{1}{2}(3x^2 - r^2)$. The coordinate system is chosen such that the $z$ axis coincides with the molecular axis, and the origin is at the center of the molecule. In addition, the $y$ axis has been chosen to coincide with the twofold symmetry axis of the crystal field. Also shown are electric field gradients $F_{ii}$, which are expectation values of permutations of $(3x^2 - r^2)/r^5$, for the $1\pi_g$ orbitals only; here, the origin is at one nucleus. These molecular properties are used in the calculation of spin-Hamiltonian parameters.

## III. CRYSTAL-FIELD CALCULATIONS

The crystal-field splitting of the degeneracy of the $1\pi_g$ orbitals requires a more precise determination of the crystal potential than is needed for wave functions and equilibrium internuclear separation. For this purpose, the point-ion potential was refined to incorporate the substantial quadrupole moment of the azide ion. We chose to represent the azide ion by a linear array of three point ions, separated by 1.17 Å, with charges of $0.714e$ assigned to the central ion and $-0.857e$ assigned to each end ion.[24] The resulting potential was expanded about the center of the anion vacancy in the form (in hartree)

$$V(r) = -\sum_{L=0}^{\infty} \sum_{M=-L}^{L} e_{LM} r^L Y_L^M(\theta, \phi), \tag{3.1}$$

where

$$e_{LM} = \sum_{\alpha=0}^{\infty} \frac{4\pi Q_\alpha}{(2L+1) r_\alpha^{L+1}} Y_L^{M*}(\theta_\alpha, \phi_\alpha). \tag{3.2}$$

Here $Q_\alpha$ is the charge on ion $\alpha$ whose polar coordinates with respect to the vacancy center are $r_\alpha$, $\theta_\alpha$ and $\phi_\alpha$, and $Y_L^M(\theta, \phi)$ is a spherical harmonic. Each term in Eq. (3.1), which is valid within the first spherical shell of ions, is a solution of the Laplace equation. The coefficients $e_{LM}$ are constrained by symmetry; only combinations of spherical harmonics which transform as bases for the identity representation of the crystallographic

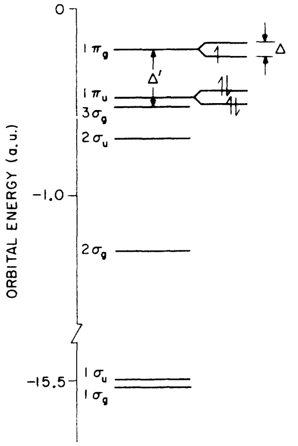

FIG. 4. Orbital-energy-level diagram for $N_2^-$ in $\alpha$-$NaN_3$.

TABLE II. Calculated properties of $N_2^-$ in $\beta$-$NaN_3$. Quadrupole moments $Q$ and electric-field gradients $F$ are in atomic units, and are referred to the coordinate axes shown in Fig. 5.

| | $Q_{xx}$ | $Q_{yy}$ | $Q_{zz}$ |
|---|---|---|---|
| $1\pi_{gx}$ | 1.7375 | $-0.2373$ | $-1.5002$ |
| $1\pi_{gy}$ | $-0.2373$ | 1.7375 | $-1.5002$ |
| Total (including nuclei) | 2.0057 | 2.0057 | $-4.0013$ |
| | $F_{xx}$ | $F_{yy}$ | $F_{zz}$ |
| | $-0.5715$ | $+1.0914$ | $-0.5199$ |

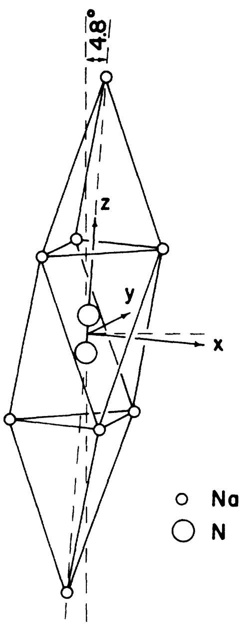

FIG. 5. Orientation of the $N_2^-$ ion in an azide-ion vacancy in $\alpha$-$NaN_3$.

point group at the anion site can contribute. The infinite lattice sums in Eq. (3.2) were evaluated by the method of Nijboer and DeWette.[25,26]

The crystal potential was treated by first-order perturbation theory, using the wave functions calculated for $\beta$-$NaN_3$ as unperturbed functions. Of course, the total energy already contains a contribution of the simulated $\beta$-$NaN_3$ lattice; it is not necessary to subtract this off, however, since we are interested only in changes in energy with electronic state and orientation. The energy of the molecule ion in the crystal potential is given by

$$E=\sum_{L=0}^{\infty}\sum_{M=-L}^{L}(-1)^M e_{LM}q_{L,-M}e^{iM\phi}, \tag{3.3}$$

where $\phi$ is the angle through which the molecule ion is tilted from the $x$ axis toward the $y$ axis (see Fig. 2), and $q_{LM}$ is a multipole moment of the molecular charge distribution defined by

$$q_{LM}\equiv-\sum_i(\psi_i,\ r^L Y_L^{M*}(\theta,\phi)\psi_i). \tag{3.4}$$

The sum in Eq. (3.4) is over all occupied molecular spin orbitals $\psi_i$. Only multipole moments with even $L$ are nonvanishing. Because of the compactness of the molecular wave functions, it is an adequate approximation to retain only the quadrupole terms in Eq. (3.3). (The $L=0$ term is just an additive constant which may be disregarded.)

It was assumed in Eq. (3.3) that the multipole moments of Eq. (3.4) are defined with respect to a set of axes chosen such that the $x$ axis coincides with the molecular axis, and the $z$ axis with that of Fig. 2 (i.e., the twofold symmetry axis of the crystal field). In calculating molecular wave functions and properties, however, the $z$ axis was chosen to coincide with the molecular axis in order to conform to prior usage; this has been done in Table II. In addition, the $y$ axis has been chosen to coincide with the twofold symmetry axis of the crystal field, as shown in Fig. 5.

The quadrupole moments $q_{2M}$ defined by Eq. (3.4) are then related to the quadrupole moments $Q_{ii}$ of Table II by

$$q_{20}=(5/4\pi)^{1/2}Q_{yy}, \tag{3.5a}$$

$$q_{2,\pm1}=0, \tag{3.5b}$$

and

$$q_{2,\pm2}=(5/24\pi)^{1/2}(Q_{zz}-Q_{xx}). \tag{3.5c}$$

The potential expansion coefficients $e_{2M}$, calculated with reference to the coordinate axes shown in Fig. 2, are listed in Table III. Note that, by symmetry, $e_{2,\pm1}=0$ and $e_{2,-2}=e_{2,2}^*$. It then follows from Eqs. (3.3) and (3.5) that the energy of orientation is given by

$$E=(5/4\pi)^{1/2}e_{20}Q_{yy}+(5/6\pi)^{1/2}(Q_{zz}-Q_{xx})\times[\mathrm{Re}(e_{22})\cos2\phi-\mathrm{Im}(e_{22})\sin2\phi]. \tag{3.6}$$

Since $Q_{zz}-Q_{xx}$ is negative for both components of the degenerate ground state, the equilibrium orientation $\phi_0$ is given by

$$\tan2\phi_0=-\mathrm{Im}(e_{22})/\mathrm{Re}(e_{22}). \tag{3.7}$$

It follows from Eqs. (3.6) and (3.7) that the difference in energy between the two $1\pi_g$ orbitals, $\Delta[\equiv E(1\pi_{gy})-E(1\pi_{gx})]$, is given in terms of the difference in quadrupole moments $\delta Q$ by

$$\Delta=(5/4\pi)^{1/2}\delta Q[e_{20}+\tfrac{2}{3}{}^{1/2}\mathrm{Re}(e_{22})/\cos2\phi_0], \tag{3.8}$$

where

$$\delta Q\equiv Q_{yy}(1\pi_{gy})-Q_{yy}(1\pi_{gx})=Q_{xx}(1\pi_{gx})-Q_{xx}(1\pi_{gy}). \tag{3.9}$$

The quantitative results of these crystal-field calculations are presented in Sec. V.

## IV. HYPERFINE INTERACTIONS

The Hamiltonian for the magnetic hyperfine interaction of an electron with one of the nuclei is[27]

TABLE III. Expansion coefficients of the crystal potential in atomic units, defined by Eq. (3.2).

| $M$ | $e_{2M}$ |
|---|---|
| 0 | $-0.010460$ |
| $\pm1$ | 0 |
| $\pm2$ | $0.015876\pm i0.0026057$ |

$$H_1 = 2g_n\mu_B\mu_N\left(\frac{\vec{I}\cdot(\vec{l}-\vec{s})}{r^3}+\frac{3(\vec{I}\cdot\vec{r})(\vec{r}\cdot\vec{s})}{r^5}+\frac{8\pi}{3}\vec{I}\cdot\vec{s}\,\delta(\vec{r})\right), \tag{4.1}$$

where $\mu_B$ is the Bohr magneton; $g_n I$ is the nuclear magnetic moment in nuclear magnetons $\mu_N$; $\vec{l}$ and $\vec{s}$ are the electron orbital and spin angular momenta, respectively; $\vec{I}$ is the nuclear spin; and $\vec{r}$ is measured from the nucleus. The corresponding term in the spin Hamiltonian has the form

$$H_I = \vec{I}\cdot\overleftrightarrow{A}\cdot\vec{s}, \tag{4.2}$$

where, by symmetry, the hyperfine tensor $\overleftrightarrow{A}$ is diagonal in the chosen coordinate system.

The Fermi contact term [the last term on the right-hand side in Eq. (4.1)] contributes an isotropic hyperfine interaction given by

$$\overleftrightarrow{A}_c = \overleftrightarrow{I} g_n \mu_B \mu_N (\tfrac{16}{3}\pi)\,|\psi(0)|^2; \tag{4.3}$$

this contribution appears to vanish because the unpaired spin is assigned to a $1\pi_g$ orbital, which has a node at the internuclear line. In reality, the contact term makes a significant contribution via core polarization, but the present treatment is inadequate to deal with it; one requires either configuration mixing or unrestricted Hartree-Fock (different orbitals for different spins).[28]

The contribution of the dipole-dipole interaction to the anisotropic hyperfine interaction is

$$\overleftrightarrow{A}_s = 2g_n \mu_B \mu_N \langle\psi\,|(3\vec{r}\cdot\vec{r}-r^2\overleftrightarrow{I})/r^5|\,\psi\rangle, \tag{4.4}$$

whose components are simply proportional to the electric-field gradients listed in Table II.

Finally, the term in Eq. (4.1) involving $\vec{l}$ contributes to the hyperfine tensor in second-order perturbation theory, in combination with the spin-orbit interaction $\lambda l_z s_z$, giving

$$A_{Lzz} = -4g_n \mu_B \mu_N (\lambda/\Delta)\langle\psi\,|r^{-3}|\,\psi\rangle, \tag{4.5}$$

where $\Delta$ is the splitting between the $1\pi_g$ levels.

## V. RESULTS

Gelerinter and Silsbee (GS)[10] were able to infer a number of properties of the $N_2^-$ defect in $NaN_3$ from its ESR spectrum. They established the angle through which the $N_2^-$ ion is tilted with respect to the $x$ axis in Fig. 2 (i.e., with respect to the direction perpendicular to the crystal face). The departures of the $g$ values from the free-electron value were interpreted in terms of the splitting $\Delta$ of the $1\pi_g$ levels and the separation $\Delta'$ of the $3\sigma_g$ and $1\pi_g$ levels, using a value for the spin-orbit coupling constant derived by extrapolation from an isoelectronic sequence. Finally, they measured the principal values of the hyperfine tensor $\overleftrightarrow{A}$. All of these data are summarized in Table IV.

The theoretical equilibrium orientation was determined from Eq. (3.7) and Table III. The calculated tilt angle, $\phi_0 = 4.67°$, is in almost exact agreement with the measured value. Theoretically, the $N_2^-$ ion is tilted as shown in Fig. 5, in the same sense and by nearly the same amount as the long axis of the pseudorhombohedral unit cell. Note that Eq. (3.7) involves only the crystal field and not the quadrupole moments; accordingly, any prolate spheroid would be tilted through the same angle, including the azide ion. Actually, the azide ion is tilted much more than the $N_2^-$ ion, presumably because of steric constraints.

TABLE IV. Comparison of calculated properties of $N_2^-$ in $NaN_3$ with those inferred from ESR spectra.

| Property | Theory | Experiment[a] |
|---|---|---|
| $\phi_0$ | 4.67° | 4.6° |
| $\Delta$ | 366 $cm^{-1}$ | 500 $cm^{-1}$ |
| $\Delta'$ | 68 800 $cm^{-1}$ | 45 000 $cm^{-1}$ |
| $A_{sxx}$ | −8.19 G | |
| $A_{syy}$ | 15.71 G | |
| $A_{szz}$ | −7.56 G | |
| $A_{xx}$ | −3.19 G | −3.9 ± 0.5 G |
| $A_{yy}$ | 20.71 G | 23.5 ± 0.5 G |
| $A_{zz}$ | −9.56 G | −11 ± 2 G |

[a] E. Gelerinter and R. H. Silsbee, J. Chem. Phys. 45, 1703 (1966).

The crystal-field splitting $\Delta$ was determined from Eq. (3.8), and the $3\sigma_g - 1\pi_g$ energy difference $\Delta'$ from the one-electron energies in Table I. These quantities are compared with experiment in Table IV.[29] The crystal-field calculation also confirms that the $1\pi_{gy}$ orbital lies lower in energy than the $1\pi_{gx}$, in agreement with GS.

The dipole-dipole contribution to the anisotropic hyperfine interaction was calculated from Eq. (4.4) and the electric-field gradients of Table II for the $1\pi_{gy}$ orbital. The corresponding hyperfine constants are listed in Table IV. These values cannot be compared directly with experiment, however, because the measured values contain both isotropic and orbital contributions. The orbital contribution, Eq. (4.5), was not calculated. However, one can infer an approximate value from experiment. It is evident from the form of the wave function that the dipole-dipole interaction is dominated by the $p_y$ atomic orbital centered on the nucleus in question, and accordingly, its contributions to $A_{xx}$ and $A_{zz}$ should be nearly equal; this surmise is supported by the calculation. Accordingly, the orbital contribution to $A_{zz}$ must be about − 7 G; this estimate agrees well with the value calculated by GS from a simple approximate wave function, − 5 G. The same assumption allows one to infer an isotropic contribution of + 5 G, since the dipole-dipole part is traceless. These inferred contributions have been included in the theoretical values in Table IV, to permit direct comparison with experiment.

## VI. DISCUSSION

The calculated ground-state properties of $N_2^-$ in $NaN_3$ are generally in good agreement with measured properties, as can be seen from Table IV.

The agreement of calculated and measured angles through which the $N_2^-$ ion is tilted is impressive. However, there is some ambiguity about the experimentally determined direction in which the $N_2^-$ ion is tilted, and we are uncertain as to whether there is a discrepancy between theory and experiment. Gelerinter[19] appears to agree with our conclusion that the ion is tilted in the same sense in which the planes are sheared, as shown in Fig. 5. On the other hand, the description of GS[10] suggests that the tilt is in the opposite sense. Experimentally, the sense of rotation was established indirectly from a comparison of the intensities of both ESR spectra and x-ray reflections of a twinned crystal. We are unable to assess the reliability of such a determination, but would like to suggest that it is at least subject to misinterpretation.

The energy intervals $\Delta$ and $\Delta'$ appear to be in satisfactory agreement with values inferred from ESR spectra. Note that GS allow a 50% error in the determination of $\Delta'$. The discrepancy in $\Delta$ could be related to the fact that the lattice parameters for $\alpha$-$NaN_3$ which were used here were established at a temperature between − 90 and − 100 °C,[18] whereas the ESR measurements were made at liquid He temperature. A significant increase in monoclinic distortion is expected as the temperature is reduced below − 100 °C,[18] and consequently the crystal-field splitting $\Delta$ should be larger than calculated.

The calculated dipole-dipole contribution to the hyperfine tensor is consistent with measured values. It remains to calculate orbital and isotropic contributions.

The results of the present calculation support the model of an $N_2^-$ molecular ion in an anion vacancy, but the observed crystal-field splitting is explained in terms of a low-temperature phase transition, as suggested by Gelerinter,[19] rather than the Jahn-Teller distortion proposed by GS.

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[*] Supported in part by the U. S. Army Research Office-Durham under Grant No. DA-ARO-D-31-124-71-G35, and in part by the U. S. Army, Picatinny Arsenal, Dover, New Jersey.

[†] Computations performed at Brookhaven National Laboratory and at the Computer Center of the University of Connecticut, which is supported in part by the National Science Foundation Grant. No. GJ-9.

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[28] Reference 27, pp. 695–706.

[29] A preliminary account of this work is given in Bull. Am. Phys. Soc. 18, 349 (1973). The value $\Delta = 974$ cm$^{-1}$ quoted there was based on a less adequate model of the $\alpha - NaN_3$ lattice in which azide ions were represented by single point charges, $-e$.