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Commentationes

Stability and Crystal Field Splitting of N_2^- in Barium Azide

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The crystal field splitting of the ground $^2\pi_g$ state and the equilibrium orientation of the N_2^- radical in the monoclinic barium azide are calculated employing a point ion representation of the lattice potential and assuming three different plausible trapping sites for the radical. When the N_2^- is assumed to replace an azide ion which is parallel to the *c* axis of the unit cell, the previously suggested trapping site, the calculated crystal field splitting is in order of magnitude agreement with the value deduced from the *g* shift in the ESR spectrum. The calculated orientational angle of the molecular axis with the *c* axis of the unit cell is 9.0 degrees which compares favorably with the experimentally determined angle of 5.0 ± 1.5 degrees. Possible reasons why the N_2^- can not be trapped at the site of an azide ion which is perpendicular to the *c* axis are suggested from the calculation.

Key words: Barium azide – Crystal field splitting

1. Introduction

Studies of irradiated azides indicate that many defects arise from dissociation of the azide ion, N_3^- [1–3]. When barium azide is subjected to UV irradiation, ESR spectra attributable to N_2^- and N_3^{2-} are observed [1–3]. Irradiation with X-rays at 77 k produces trapped nitrogen atoms [4]. The trapping sites of these species in the unit cell are not unambiguously determined from the ESR experiment. In the case of barium azide the question of the trapping site of the N_2^- radical has some puzzling features. Barium azide has a monoclinic unit cell with $a = 9.6$ Å, $b = 4.4$ Å, and $c = 5.42$ Å [5]. The angle between *a* and *c* is 99.75 degrees. A projection of the unit cell is shown in Fig. 1. The linear azide ions lie parallel to the

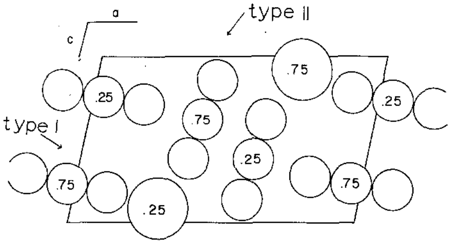

Fig. 1. Projection of the unit cell of barium azide on the *ac* plane is shown indicating the two different kinds of azide sites

ac plane and have two orientations roughly parallel and perpendicular to the *c* axis which have previously been labelled type II and type I azides respectively [5]. From the ESR experiment the axis of the N_2^- is deduced to be parallel to a type II azide which prompted the suggestion that the radical was trapped at a type II site [3]. Why the radical can be trapped at one azide site (type II) and not at the other azide site (type I) is not understood. An alternate possibility is that the radical is trapped at another site in the lattice but that the orientational energy at this other site is such that the axis of the radical is parallel to a type II azide ion. In order to shed some light on this question of the trapping site of the N_2^- in barium azide, an *a priori* calculation of the orientational energy, the angle of orientation and the crystal field splitting of the orbital of the unpaired electron was undertaken assuming three different plausible trapping sites for the radical. The formalism developed by Bartram *et al.* [6] to treat the N_2^- in sodium azide was employed.

2. Determination of Crystal Field Splitting from g and A Tensors

Molecular orbital calculations of the N_2^- indicate that the ground configuration of the radical is $1\sigma_g^2$, $1\sigma_u^2$, $2\sigma_g^2$, $2\sigma_u^2$, $1\pi_u^4$, $3\sigma_g^2$, $1\pi_g$ [6]. For the free N_2^- the π orbitals are degenerate but in the lattice the lower symmetry of the crystal field removes this degeneracy. A schematic of the energy levels of the N_2^- in a crystal lattice is shown in Fig. 2. The largest hyperfine tensor component is measured when the dc magnetic field is perpendicular to the axis of the radical which is consistent with the fact that the unpaired electron is in a π_{gy} orbital [1, 6]. The g shifts in a paramagnetic radical are well known to be a result of the perturbation due to the combined effect of the spin orbit interaction and the applied dc magnetic field. Using the formalism of Stone [7] the parallel g shift, δg_z can be shown to be,

$$\delta g_z = \frac{2\lambda}{\Delta} \langle \pi_{gy} | L_z | \pi_{gyx} \rangle \langle \pi_{gx} | L_z | \pi_{gy} \rangle \tag{1}$$

where λ is the spin orbit coupling constant of nitrogen and Δ is the crystal field splitting shown in Fig. 2. The L_z is the sum of the z component of the angular

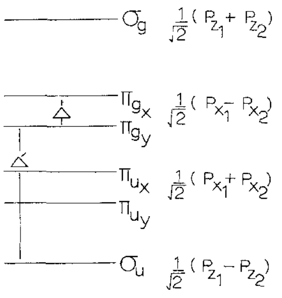

Fig. 2. A schematic of the energy levels of the N_2^- showing the crystal field splitting, Δ, of the π_g orbital

momentum centered about each of the nuclei. A somewhat over simplified form of the orbitals is assumed in order to calculate the g shift in Eq. (1).

$$\pi_{gy}=as(1)+cP_y(1)-cP_y(2)+as(2) \tag{2}$$
$$\pi_{gx}=as(1)+cP_x(1)-cP_x(2)+as(2) \tag{3}$$

Using these orbitals in Eq. (1), δg_z is obtained to be

$$\delta g_{zz}=\frac{-2|\lambda|}{\Delta}(2c^2)^2 \tag{4}$$

The amount of p unpaired spin density in the molecular orbital of the unpaired electron can be estimated in the usual way from the hyperfine tensor components which are, $A_y=20.0$ G., $A_x=-3.6$ G. and $A_z=-4.1$ G. The signs of the tensor components are chosen based on predictions from molecular orbital calculations of hyperfine splittings in N_2^- [6, 8]. From these components, the anisotropic part of the hyperfine interaction is estimated to be 16.0 G. leading to a value of 0.471 for C^2. Taking λ as $-60\ \text{cm}^{-1}$ and using the above value of c^2, Δ is estimated to be 4570 cm^{-1} from the measured g_z shift of -0.0233.

3. *A priori* Calculation of Crystal Field Splitting

The point ion approximation is used to calculate the crystal potential at type I, type II and the interstitial site. The interstitial site lies equidistant from two barium ions on a line joining the ions and parallel to the b crystal axis. In the point ion approximation the barium ions are taken to have a charge of $+2$ and the linear triatomic azide ion is represented by a linear array of three point charges separated by a distance of 1.17 Å. The charge on the center of the ion is -0.857e and on the ends of the ion is 0.714e [9]. The potential is expanded in spherical harmonics about the center of the trapping sites and has the form,

$$V(r)=-\sum_{L=0}\ \sum_{M=-L} e_{LM}r^L Y_L^M(\theta,\phi) \tag{5}$$

where,

$$e_{LM}=\sum\frac{4q_\alpha}{(2L+1)r}{}^{L+1}\ Y_L^M(\theta_\alpha,\phi_\alpha) \tag{6}$$

the charge on the αth ion is q_α and r_α, θ_α and ϕ_α are the polar co-ordinates of the ion. The z axis for the calculation was chosen parallel to the crystalographic b axis and the x axis was parallel to the a axis of the unit cell. It should be pointed out that this co-ordinate system is different from the co-ordinate system of the g and A tensor of the N_2^- in which the z principal axis is parallel to the N_2^- axis and thus a type two azide ion. The only non vanishing spherical harmonics in Eq. (6) are those which transform as a basis for the identity representation of the point group which describes the symmetry at the various sites. The infinite lattice sums in the potential expansion were evaluated by the method of Nijboer and

De Wette [10, 11]. The orientational energy of the N_2^- in the crystal field potential is [6]

$$E=(5/4\pi)^{\frac{1}{2}}\, e_{20}\, Q_{yy}+(5/6\pi)^{\frac{1}{2}}\, (Q_{zz}-Q_{xx})\, (\mathrm{Re}(e_{22}) \cos 2\phi-\mathrm{Im}(e_{22}) \sin 2\phi) \quad (7)$$

where ϕ is the angle through which the molecular ion is tilted from the x axis toward the y axis of the co-ordinate system in which the crystal field is calculated. The Q_{xx} and the Q_{yy} are the quadrupole moments of the radical. The equilibrium orientational angle, ϕ_0, is obtained by minimizing the total energy E with respect to ϕ and is given by

$$\tan 2\phi_0=-\mathrm{Im}(e_{22})/\mathrm{Re}(e_{22}) \quad (8)$$

The crystal field splitting, Δ, of the π_{gy} from the π_{gx} is given in terms of the difference of the quadrupole moments of the π_{gx} and the π_{gy} orbitals [6],

$$(5/4\pi)^{\frac{1}{2}}\, \delta Q(e_{20}+0.81649\ \mathrm{Re}(e_{22}))/\cos 2\phi_0 \quad (9)$$

4. Results

The calculated non-vanishing expansion coefficients of the point ion potential at the three sites considered are given in Table 1. The crystal field splitting, Δ, and the equilibrium orientational angle of the axis of the diatomic radical measured in the *ca* plane with respect to the *c* axis calculated for the three assumed trapping sites are given in Table 2. The δQ in the calculation was taken as 1.98748 a.u. which is the value calculated for the N_2^- in NaN_3 [6]. The use of the δQ value appropriate to the NaN_3 lattice is not an unreasonable approximation because the molecular orbital wavefunctions of the N_2^- were found to be relatively in-

Table 1. Expansion coefficients, e_{LM}, of point ion potential in atomic units at three sites in the unit cell of barium azide

site	e_{20}	e_{22}
interstit	0.120568	$-0.003252-0.001200\,i$
azide I	-0.007819	$0.004495-0.001301\,i$
azide II	-0.006662	$-0.007287-0.005617\,i$

Table 2. The calculated crystal field splitting of the $^2\pi_g$ ground state and the orientational angle of the N_2^- for the three assumed trapping sites of the radical in barium azide

	θ[a] (degrees)	Δ (cm^{-1})
interstit.	0.37	16858.5
azide I	-1.68	546.4
azide II	9.06	1936.4

[a] θ is the angle between the axis of the N_2^- and *c* axis of the unit cell in the *ca* plane of the lattice.

sensitive to lattice environment [6, 12]. This is supported by the similarity in the magnitudes of the principal components of the hyperfine tensors of the N_2^- in $Ba(N_3)_2$ and NaN_3.

5. Discussion

The calculated crystal field splitting of the π_g level of the N_2^- agrees best with the value estimated from the experimental data when the N_2^- is assumed to be located at a type II azide site. The calculated results for the other sites are in substantial disagreement with the experimental estimate. The calculated equilibrium angle, ϕ_0, of 9.0 degrees is in reasonable agreement with the value of 5.0 ± 1.5 degrees determined from the experimental data. The calculations support the conclusion that the N_2^- is trapped at a type II azide site as has been previously suggested. It should be pointed out that the calculation has not taken into account overlap between the N_2^- molecular orbitals and the orbitals of the nearest neighbor ions. The negative shift of g_y has been suggested to arise from a slight covalent bonding between the N_2^- and the barium ions [1].

A possible reason why the type II site is more favorable to trapping the N_2^- than the type I site is suggested in a comparison of the e_{00} terms in the potential expansion at both sites. The e_{00} represents the electrostatic Madelung contribution to the potential and it has a larger value at a type II site than at a type I site indicating that a negatively charged species would be more tightly bound to a type II site.

Although the complete details of the mechanism of formation of the N_2^- by UV light in $Ba(N_3)_2$ are not known, some plausible speculation is possible. It has been established that the N_2 is produced by 230 nm light which is believed to correspond to an internal transition of the azide ion [1]. Investigations of $Ba(N_3)_2$ in which the end nitrogen of the linear azide ion is an N^{15} isotope indicate that the defect is produced by the removal of an end nitrogen [2]. Perhaps what occurs is that both type I and II azides are excited and subsequently dissociate into N_2^- and N^0. In the case of the type II site, the neutral nitrogen atom diffuses away from the site leaving the N_2^- trapped. For the type I site both the N_2^- and the N^0 diffuse from the site because the site can not trap the radical.

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