

be defined as

$$\frac{1}{L_{\text{eff}}} \equiv -\frac{1}{\mathcal{R}} \frac{d\mathcal{R}}{dt} = \frac{\alpha}{e^{\alpha t} - 1} - \frac{\int_0^{h(\nu-\nu_0)} \frac{\Delta E [-\alpha e^{-\alpha t} + (1/L) e^{-t/L}]}{-\alpha + 1/L} d\Delta E}{\int_0^{h(\nu-\nu_0)} \frac{\Delta E (e^{-\alpha t} - e^{-t/L})}{-\alpha + 1/L} d\Delta E}$$

When $\alpha L \gg 1$ and $\alpha t > 1$,

$$\frac{1}{L_{\text{eff}}} \approx \int_0^{h(\nu-\nu_0)} \frac{\Delta E}{L} e^{-t/L} d\Delta E \bigg/ \int_0^{h(\nu-\nu_0)} \Delta E e^{-t/L} d\Delta E.$$

If $1/L$ is expanded in a Taylor series in ΔE and if quadratic and higher order terms in ΔE can be neglected, then L_{eff} is the electron attenuation length of an electron with an energy $h\nu_0 + \frac{2}{3}h(\nu-\nu_0)$ above the Fermi energy.

Irradiation-Produced Paramagnetic Oxides of Nitrogen in Single-Crystal Potassium Azide

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A magnetic resonance absorption centered about $g=2$ and showing no evidence of fine structure is reported in x-irradiated single crystals of potassium azide. Six absorption lines are detected which appear to exhibit axial symmetry about the crystal C direction. These lines are shown to be a composition of two distinct spectra each consisting of three nuclear hyperfine components. For one set of lines, an anisotropic hyperfine splitting varying from 38 to 3 Oe is observed as the magnetic field is rotated from the crystal C axis to a direction perpendicular to this axis. The other set similarly exhibits splittings between 62 and 31 Oe. The inner and outer sets of lines are believed to be due to NO and NO₂ molecules, respectively, with both molecules located at crystal sites having axial symmetry. These molecular species are formed during the irradiation process, perhaps from nitrate and/or nitrite impurities known to be contained in the lattice. Each of the three components of the outer set of lines exhibits a partially resolved seven-line multiplet structure which is interpreted to be the result of an interaction between the paramagnetic electron and the nuclei of two crystallographically equivalent nearest-neighbor potassium ions.

I. INTRODUCTION

IN the past several years, the effects of radiation on single crystals of potassium azide (KN₃) have become the source of some considerable interest.¹⁻⁴ From the optical work reported by Tompkins and Young² and Cunningham and Tompkins,³ it is clear that the irradiation of potassium azide presents a manifold of problems related to defects whose properties are to some extent dependent on the radiation energy, on the total irradiation dosage, and on the temperature at which these defects are generated. Since it has been

shown that some of these defects are paramagnetic,⁵⁻⁷ a magnetic resonance absorption study was undertaken in ultraviolet- and x-irradiated potassium azide single crystals containing trace amounts of oxides of nitrogen to determine the nature of these defects. This work as well as that of others has demonstrated the existence of a number of distinct paramagnetic defects, some being stable only at temperatures considerably below 0°C and some produced only after specific irradiation and thermal treatment.

As a consequence of the over-all complexity of the problem, this report concerns itself with only those defects which are responsible for a spectrum consisting of six strong absorption lines observed in crystals which are permitted to thermally bleach at room temperature after irradiation at temperatures below 50°C.

* Part of a dissertation submitted by D. Mergerian in partial fulfillment of the requirement for a Ph.D. at the Illinois Institute of Technology.

¹ P. W. M. Jacobs and F. C. Tompkins, Proc. Roy. Soc. (London) **A215**, 254 (1952).

² F. C. Tompkins and D. A. Young, Proc. Roy. Soc. (London) **A236**, 10 (1956).

³ J. Cunningham and F. C. Tompkins, Proc. Roy. Soc. (London) **A251**, 27 (1959).

⁴ J. E. Mapes, R. W. Dreyfus, and P. W. Levy, "Watertown Arsenal Conference on Radiation Effects in Ordnance Materials," 1957 (unpublished).

⁵ R. Horst, J. H. Anderson, and D. E. Milligan, J. Phys. Chem. Solids (to be published).

⁶ A. J. Shuskus, C. G. Young, O. R. Gilliam, and P. W. Levy, J. Chem. Phys. **33**, 622 (1960).

⁷ D. W. Wylie, A. J. Shuskus, C. G. Young, O. R. Gilliam, and Paul W. Levy, Phys. Rev. **125**, 451 (1962).

II. APPARATUS

The spectrometer used in this investigation is of conventional design utilizing a balanced hybrid tee junction. A klystron oscillator, padded by a ferrite isolator, supplies 3-cm wavelength radiation to the input arm of the tee junction. The klystron frequency is locked to that of the sample cavity by a feedback loop coupled to the klystron repeller voltage supply. Microwave power is detected either directly by a selected crystal diode or by a 30-Mc/sec superheterodyne system. Magnetic field modulation for phase sensitive lock-in detection is provided at either 200 cps by flat coils fastened to the magnet pole faces or at 100 kc/sec by a loop of wire wrapped directly around the specimen. The sample with the wire loop is placed at the center of a cavity operating in the cylindrical TE_{011} mode. With this mode of operation, the wire loop is found to have negligible effect upon the quality factor of the cavity. Spectroscopic splitting factor values are determined from proton resonance measurements which determine Zeeman field strengths, and from microwave frequency measurements utilizing the harmonics of a quartz, crystal-controlled oscillator.

III. EXPERIMENT

Potassium azide has the body-centered tetragonal structure of potassium bifluoride (KHF_2).⁸ When a single crystal of this salt is exposed to ultraviolet light or x irradiation at 77°K, a deep blue coloration is produced which is unstable at or above room temperature. The optical absorption spectrum for a crystal colored

in this manner shows two well defined maxima, one at 570 $m\mu$ and another at 750 $m\mu$. If such a crystal is allowed to stand for several days at approximately 30°C, the blue coloration changes to yellow with an optical density dependent on the total radiation dosage. This optical absorption spectrum shows no clearly resolved maxima, but gradually covers most of the visible region. (For a more detailed description of these optical absorptions, see references 2, 3, and 4.) The yellow coloration is quite stable and is found to persist indefinitely at temperatures below 30°C.

Both blue and yellow colored potassium azide single crystals exhibit magnetic resonance absorption in the region of $g=2$ with spectra which differ markedly in both symmetry and hyperfine characteristics. No paramagnetic resonance absorption is observed in the un-irradiated crystals.

The magnetic resonance absorption spectrum of yellow colored single-crystal potassium azide is observed to consist of 14 partially resolved lines. Of these 14 lines, six seem to exhibit symmetry about the crystal C axis and have intensities which are between five to ten times the intensities of the remaining eight, the ratio being dependent on the irradiation history of the specimen. This report is concerned with a description and tentative interpretation of the more intense six-line spectrum.

Figure 1 is a recorder tracing of the magnetic resonance absorption spectrum in yellow colored potassium azide taken at 77°K with the crystal C axis oriented parallel and perpendicular to the Zeeman field direction.

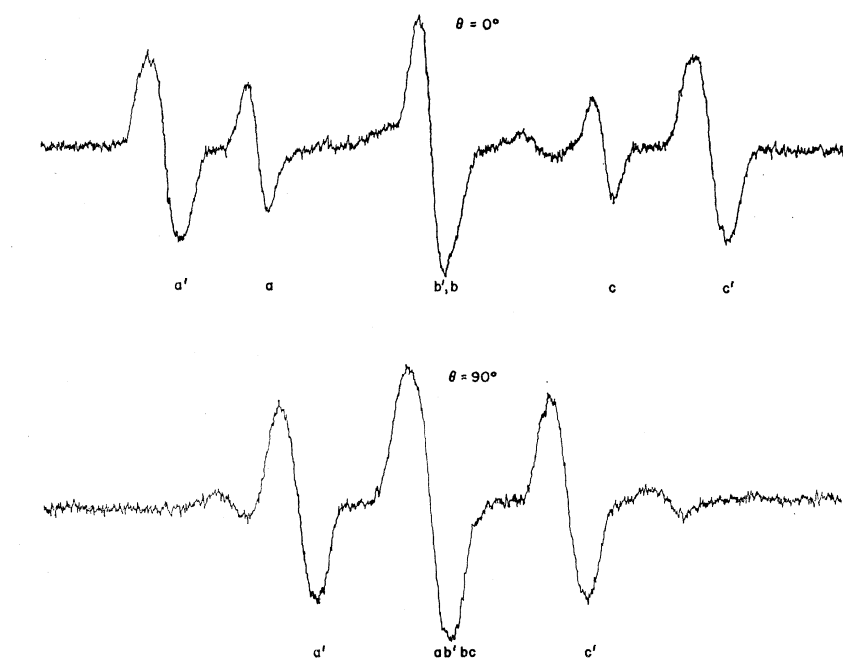


FIG. 1. First derivative recorder tracing of the magnetic resonance absorption in yellow-colored single-crystal potassium azide taken at 77°K with the crystal C axis parallel and perpendicular to the Zeeman field direction.

⁸ R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1953).

For purpose of identification, the six lines are labeled a , b , c and a' , b' , and c' . From the asymmetry of the center line as best seen for H parallel to C , it appears that two resonance absorptions occur at the central field position. Further evidence for the presence of two lines at this position is obtained by examining the saturation behavior of the spectrum. It is possible to trace through the spectrum at microwave power levels sufficient to wipe out, by saturation, lines a' , b' , and c' , while maintaining some strength in the lines a , b and c . Under such conditions, the high-field asymmetry of the central line disappears and it is found that lines a , b , and c are of equal width and strength and are, to within measurement errors, equally spaced. It thus appears that the resonance absorption shown in Fig. 1 is a consequence of the superposition of two distinct spectra, each consisting of three equally spaced hyperfine components, see Fig. 2. The best fit constants to a spin Hamiltonian having the form

$$\mathcal{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} \quad (1)$$

are given in Table I.

The two sets of lines are observed to grow at different rates during the irradiation process. In crystals which are only slightly colored, the primed set of lines is observed to be considerably more intense than the unprimed set. Further irradiation leads to a more rapid growth of the unprimed set of lines as compared to the primed set so that in very densely colored crystals the unprimed set of lines is several times more intense than the primed set. Other characteristics that have been studied for this six-line spectrum are the line shapes and the manner in which the two sets of lines change upon saturation. Under conditions of low microwave power and low amplitude field modulation, conditions necessary to produce undistorted line shapes, and with the sample at 77°K, it is observed that lines a and c exhibit shapes which are strongly Gaussian in character while at all orientations lines a' and c' are neither Gaussian nor Lorentzian. Each of the latter exhibits a structure of seven partially resolved multiplets (Fig. 3), each multiplet having a width at points of inflection of approximately two oersteds. The saturation behavior of these two sets of lines is determined by varying the cavity resonator power and taking recorder tracings of the six-line spectrum. It is found that the unprimed set of lines show saturation effects which are quite distinct from the effects shown by the primed set of lines.

TABLE I. Best-fit constants to the spin Hamiltonian given by Eq. (1) and linewidths.

Set	g_{11}	g_{\perp}	A_{11} (Oe)	A_{\perp} (Oe)	Widths (Oe)
Primed	1.9994	2.0039	62	31	5
Unprimed	2.0001	2.0061	38	3 ^a	3

^a Estimated.

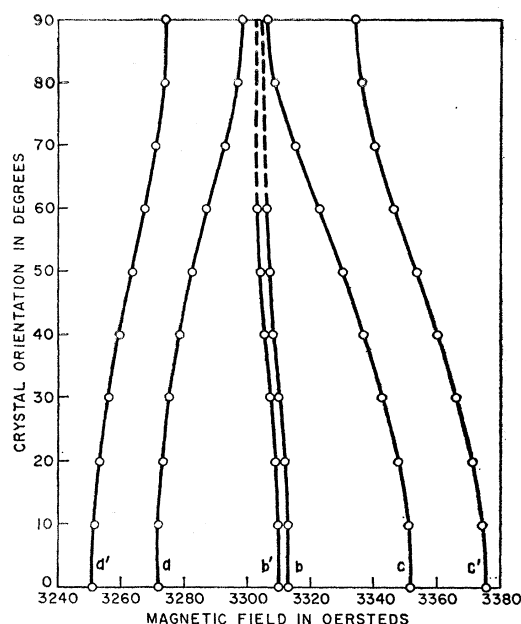


FIG. 2. Zeeman field strength vs crystal orientation for the six lines of the primed and unprimed spectra.

Each of the lines in the unprimed set shows no change in line shape and exhibits a variation in peak absorption, as is characteristic of inhomogeneous broadening, Fig. 4(a). On the other hand, the primed set shows a gradual increase in linewidth and a variation in peak absorption, as is to some extent characteristic of homogeneous broadening,⁹ Fig. 4(b). This difference in saturation behavior in the two spectra is exhibited to within measurement errors at all orientations, except perhaps for the nearly perpendicular orientation where the central region of the spectrum is crowded by the near superposition of four resonance lines, Fig. 2.

IV. DISCUSSION

With evidence obtained from the decomposition of the central field line by saturation effects, differences in linewidths and from the observation of partially re-



FIG. 3. First derivative recorder tracing of the seven partially resolved lines observed in each of the three lines of the primed set of resonance absorption lines.

⁹ A. M. Portis, Phys. Rev. **91**, 1071 (1953).

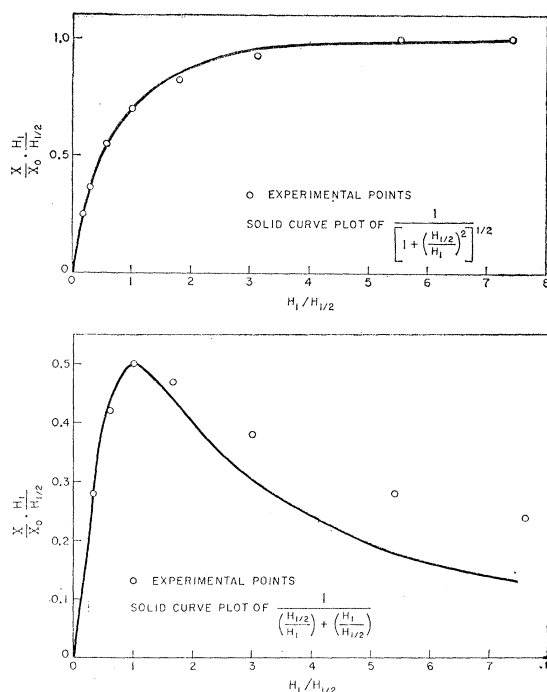


FIG. 4. Effect of saturation on the two sets of resonance lines. The points are experimental while the solid curves correspond to the case of (a) inhomogeneous and (b) homogeneous broadening.

solved multiplet structure in the primed set of lines, it is concluded that this six-line resonance absorption spectrum is a superposition of two sets of three lines, each set being due to a distinct paramagnetic defect. Furthermore, the absence of fine structure established by observing this six-line spectrum at two different frequencies leads to the conclusion that these spectra are due to either doublet electron spin states or to singlet orbital terms or both. In either case, the electron paramagnetism is associated with a triplet nuclear spin state. The observation that both defects are associated with a triplet nuclear spin state suggests that each defect center contains a single nitrogen nucleus. Such a center could then consist of a neutral nitrogen atom with no zero-field splitting, a paramagnetic state of ionic nitrogen, or a molecule or molecule-ion involving one nitrogen nucleus together with constituents of zero-spin nuclei. Furthermore, the fact that the observed six-line spectrum exhibits no measurable asymmetry about the crystal C axis suggests that these defects are located at sites having axial symmetry. In the potassium azide structure, we consider four such sites: the normal azide-ion site which has a slight orthorhombic component, the normal potassium-ion site, and two interstitial sites (the α site, located midway between two adjacent azide ions, and the β site located midway between two adjacent potassium ions, both along the crystal C axis direction, Fig. 5). Before discussing the possible location of all the defects, consideration will be given to those atoms, atomic ions, mole-

cules, and molecular ions which could be responsible for such a magnetic resonance absorption spectrum.

Consider first the six $2p$ states of the various charge states of nitrogen. Of these six states, only three, the $^4S_{3/2}$, $^2P_{1/2}$, and the $^2P_{3/2}$, which correspond, respectively, to the neutral, positive divalent, and negative divalent states of nitrogen, could exhibit a magnetic resonance absorption without fine structure. Of the remaining three states, the 3P_0 and the 3P_2 states would exhibit fine structure in fields of axial symmetry while the 1S_0 state would be nonmagnetic.

The anisotropy of the observed spectra can be used to rule out the possibility of a neutral nitrogen atom, since the anisotropic magnetic dipole and the electric quadrupole interactions vanish for this state so that the only term to contribute to the hyperfine splitting of neutral nitrogen would be the isotropic Fermi contact term. The two remaining ionic states of nitrogen, the $^2P_{1/2}$ and the $^2P_{3/2}$ can also be ruled out on the basis that these two ionic states would most probably be unstable at room temperature, while the defects responsible for these two spectra are found to have long time stability at temperatures up to 100°C . Furthermore, the energy required to produce these doubly ionized states of nitrogen are well beyond the energies available from ultraviolet photons which, as stated previously, can be used to produce these defect centers.

We next consider those molecular species which contain a single nitrogen nucleus in combination with other zero-spin nuclei. A chemical analysis of the KN_3 powder and single crystals shows that NO_2^- and NO_3^- ions are contained in these crystals in amounts of the order of 100 parts per million. We therefore consider NO , NO^- , NO_2 , NO_3 , and NO_3^+ , which constitute the more stable, paramagnetic irradiation products of the NO_3^- and NO_2^- ions. The divalent ions produced by the irradiation are not considered because they would not be expected to be stable at room temperature.

Of these five molecules and molecule ions, NO^- and NO_3^+ can be ruled out due to the lack of fine structure in the observed spectrum. Also, NO_3 can be ruled out since the magnetic center appears to consist of a hole in a non-bonding orbital on an oxygen atom and would consequently yield almost no hyperfine interaction with

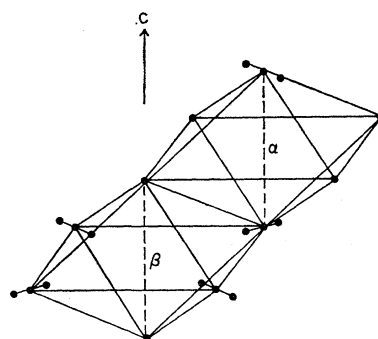


FIG. 5. View of the two fourfold axially symmetric interstitial sites of the potassium azide structure.

the nitrogen nucleus.¹⁰ As a result of this process of elimination, only the NO and NO_2 molecules remain as possible sources of the observed spectrum.

A. Primed Spectrum

Identification of the defect center responsible for this spectrum is based on a comparison of the anisotropic hyperfine splitting and its space average with the hyperfine splittings observed in other systems containing NO_2 molecules and on an acceptance of the arguments which exclude the NO_3 molecule and any divalent molecule-irradiation products of NO_3^- and NO_2^- as possible sources for either of the two observed spectra. Of the numerous reports on paramagnetic resonance absorption spectra attributed to NO_2 ,¹⁰⁻¹⁶ the least ambiguous as far as identification is concerned, appear to be those on gaseous NO_2 reported by Castle and Beringer,¹¹ NO_2 trapped in solid argon reported by Jen *et al.*,¹² and NO_2 trapped in solid carbon bisulfide and carbon tetrachloride reported by Bird *et al.*¹³ The nuclear hyperfine splittings observed in these systems are given in Table II along with the spectroscopic splitting factors. It is to be noted that even in these three systems, where the identity of the paramagnetic center is quite unambiguous, there exists very little in common in the spectral characteristics other than the triplet structure. In the case of the solid solutions of NO_2 , the situation is complicated by the fact that the hyperfine splittings are a consequence of an isotropic Fermi contact interaction potential and a randomized dipole-dipole interaction potential. Since the space average of the latter interaction splitting does not in general vanish, it is generally not possible to separate the individual contributions to the total hyperfine splitting. In a gas or low-viscosity liquid, however, the situation is conveniently simplified by the rapid tumbling motion of the molecules. If the molecular tumbling frequency is large compared to the equivalent frequency of the anisotropic hyperfine splitting, which is surely the case for low moment of inertia gas molecules at 300°K, the only observable splitting of consequence will be that due to the isotropic Fermi contact interaction. It thus seems reasonable to accept the 47.3 Oe splitting in gaseous NO_2 as a signature for this molecule in its ground electronic state.

The eigenvalues to Eq. (1), assuming a condition of axial symmetry, taken to first order in the nuclear spin

TABLE II. Spectral parameters for gaseous NO_2 and NO_2 trapped in noncrystalline matrices.

	g	A (Oe)
NO_2 (gaseous) ^a	1.9951	47.3
NO_2 (in solid argon) ^b	2.0037	57.8
NO_2 (in solid CS_2 and CCl_4) ^c	2.008	107

^a See reference 11.

^b See reference 12.

^c See reference 13.

quantum number M_I , are given by

$$E = \pm g\beta H \pm \frac{1}{2} \times [(A_{11}^2 g_{11}^2 \cos^2 \theta + A_1^2 g_1^2 \sin^2 \theta) / g^2]^{1/2} M_I, \quad (2)$$

where $g^2 = g_{11}^2 \cos^2 \theta + g_1^2 \sin^2 \theta$, A_{11} and A_1 are the components of the \mathbf{A} tensor in Eq. (1), and the tensors \mathbf{g} and \mathbf{A} have the same principal axes. The principal components to \mathbf{A} can be rewritten as

$$A_{ii} = K + T_{ii}, \quad (i = x, y, z) \quad (3)$$

where K is the strength of the Fermi contact interaction and T_{ii} are the principal components to the traceless dipole-dipole interaction.

Since only the magnitudes of A_{ii} are observable, we must consider Eq. (3) and the solution for the Fermi contact term K under eight possible sign combinations.¹⁷ Out of the eight possible sign combinations for the primed spectrum, five yield either negative or vanishing values for K which we consider to be unacceptable. Of the remaining three combinations, the one corresponding to all positive values for the principal values of the \mathbf{A} tensor yields a value of 41.3 Oe for K while the two combinations corresponding to equal and opposite values of A_{xx} and A_{yy} yield a value of 21.3 Oe for K . On the basis that the primed spectrum is due either to NO or NO_2 molecules, the first of these combinations seems to be the best assignment since the 41.3-Oe solution for K is only twelve percent less than the Fermi contact term for gaseous NO_2 . The latter two sign combinations yield a solution for K which is much too far removed from 47.3 Oe for gaseous NO_2 or 14.2 Oe for NO molecules trapped in potassium chloride.¹⁸ Finally, the combination corresponding to all positive values of A_{ii} requires, under conditions of axial symmetry, that $T_{xx} = T_{yy} = -\frac{1}{2}T_{zz}$ which is a result that can be shown for an orbitally quenched paramagnetic electron whose orbital state is a linear combination of s and p functions.

From the fact that the primed spectrum exhibits, to within measurement error, axial symmetry, it is concluded that the NO_2 molecules are located at crystal sites having such symmetry and that these molecules have a configuration similar to the gaseous molecules and that the molecules are oriented in such a manner as to produce no measurable x - y anisotropy in the \mathbf{g}

¹⁰ B. Bleaney, W. Hayes, and P. M. Llewellyn, *Nature* **179**, 140 (1957).

¹¹ J. G. Castle and R. Beringer, *Phys. Rev.* **80**, 114 (1950).

¹² C. K. Jen, S. Foner, E. L. Cochran, and V. A. Bowers, *Phys. Rev.* **112**, 1169 (1958).

¹³ G. R. Bird, J. C. Baird, and R. W. Williams, *J. Chem. Phys.* **28**, 738 (1958).

¹⁴ W. B. Ard, *J. Chem. Phys.* **23**, 1967 (1955).

¹⁵ H. Zeldes and R. Livingston, *J. Chem. Phys.* **35**, 563 (1961).

¹⁶ J. Cunningham (to be published).

¹⁷ M. H. Cohen, W. Känzig, and T. O. Woodruff, *Phys. Rev.* **108**, 1096 (1957).

¹⁸ C. Jaccard, *Phys. Rev.* **124**, 60 (1961).

and **A** tensors. Of the four crystal sites having axial symmetry, the two interstitial positions α and β , Fig. 4, do not have sufficiently large volumes to accommodate an NO₂ molecule. On the other hand, the two remaining axially symmetric sites, the normal azide-ion and normal potassium-ion sites, have volumes sufficient to accommodate an NO₂ molecule. Each potassium-ion site has eight nearest-neighbor azide ions and two next-nearest neighbor potassium ions, the nearest and next-nearest distances being 3.521 and 3.528 Å respectively. On the other hand, each azide-ion site has eight nearest-neighbor potassium ions and two next-nearest-neighbor azide ions, the distance being the same as those for the potassium-ion site. Of these two sites, the seven-line multiplet structure exhibited by each triplet component of the primed spectrum seems best accounted for by locating the NO₂ molecule at a potassium-ion site.

Assume an NO₂ molecule to be located at a potassium-ion site. If there exists some overlap between the NO₂ paramagnetic electron and the neighboring nuclei, a multiplet structure would be expected due to an interaction with the nuclei of the eight nearest-neighbor azide ions and the two next-nearest-neighbor potassium ions. The interaction of the paramagnetic electron with the potassium-ion nuclei would cause a seven-line multiplet structure, while such an interaction with the nuclei of the azide ions, assuming all nitrogen nuclei to be equivalent, would result in a 49-line multiplet structure. Although there exists no available data sufficiently reliable to provide estimates to the strengths of these interactions, it seems reasonable to attribute the partially resolved seven-component multiplet structure observed in each of the three lines of the primed spectrum to an interaction between two equivalent potassium-ion nuclei. The interaction with the eight nearest-neighbor azide-ion nuclei should cause an unresolved multiplet structure which could account for the widths of the seven-component multiplet structure.

B. Unprimed Spectrum

Before presenting arguments for the identification of the defect center responsible for this spectrum, a brief discussion of the paramagnetic nature of NO seems in order. In the gas, NO has a $^2\pi$ ground term which is twofold degenerate in orbital angular momentum. Under spin-orbit interaction, this term is split into a low-lying $^2\pi_{1/2}$ term separated by 121 cm⁻¹ from a $^2\pi_{3/2}$ term.¹⁹ If the spin and orbital angular momenta are antiparallel as is thought to be the case for the NO ground state, then the spin and orbital magnetic moments cancel. The paramagnetic character of this molecule will therefore be a consequence of the degree to which the $^2\pi_{3/2}$ state is populated. For an NO molecule trapped in a solid and unable to rotate, consideration must be given to the possible perturbing effects of

crystalline electric fields or the possibility of the molecule having a $^2\Sigma$ ground term if one is to account for the presence of paramagnetism at thermal energies considerably below 121 cm⁻¹, as in the spectra attributed to molecular NO trapped in single crystals of KNO₃ and KCl.^{16,18}

In considering the effect of a crystalline electric field on the $^2\pi$ state of NO it can be shown that the π_x and π_y degeneracy will be lifted under a perturbing crystalline electric field having orthorhombic or lower symmetry, since these functions transform in the same manner as do p_x and p_y orbitals.²⁰ The magnitude of such a splitting of the $^2\pi$ state of NO will of course depend upon the strength of the orthorhombic component of the crystalline electric field. Such a field would also contribute to the removal of axial symmetry in the hyperfine splitting. We may imagine two extreme cases for NO: one in which there is no crystalline field and the $^2\pi$ state is split into $^2\pi_{1/2}$ and $^2\pi_{3/2}$ states by the action of the spin-orbit potential and the second in which there exists a crystalline electric field whose orthorhombic component is overwhelmingly greater than the 121 cm⁻¹ spin-orbit coupling constant. In the second case, the $^2\pi$ state is split into π_x and π_y states, each being twofold degenerate in spin. Under simultaneous action of both perturbations, the actual splitting of the $^2\pi$ state will be intermediate to these two extremes. Eigenvalues for the intermediate case are given by

$$E = \pm [\Delta^2 + (\lambda/2)^2]^{1/2} \quad (4)$$

(see Appendix), where λ is the spin-orbit coupling constant and Δ is the strength of the orthorhombic component to the crystalline electric field. The splittings are shown in Fig. 6.

In this spectrum, the hyperfine splittings are 38 and 3 Oe for the parallel and perpendicular orientations, respectively. The Fermi contact interaction contribution to these splittings is considerably smaller than that reported for NO₂ and in view of previous arguments which rule against NO₃ and the divalent molecule ions produced by the irradiation of NO₂⁻ and NO₃⁻, it seems likely that this spectrum is due to trapped NO molecules. From the axial symmetry of this spectrum, it is concluded that the molecules are located at either azide-ion or potassium-ion sites with the molecular axis oriented along the crystal *C* axis. The two interstitial sites would not have volumes sufficient to accommodate the NO molecule for such an orientation.

In comparing the hyperfine splittings of this spectrum with those reported for NO trapped in KNO₃,¹⁶ and KCl,¹⁸ a strong correlation is found. In the KNO₃ case, the splittings are 31 and 4.0 Oe, while in the KCl case with the NO molecule located at an interstitial position with its molecular axis oriented along the crystal [100] direction, the splittings are 32.5 and 4.9 Oe. In the case of KNO₃ and KCl, the crystalline electric fields at the

¹⁹ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1951).

²⁰ H. Bethe, *Ann. Physik*, **3**, 133 (1929).

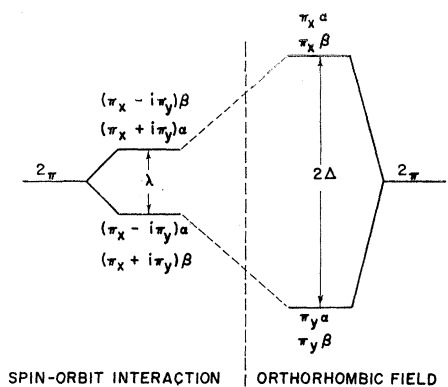


FIG. 6. Splittings of a $^2\pi$ term under pure spin-orbit interaction and under pure orthorhombic crystalline electric field interaction.

sites in question have orthorhombic symmetry. For KN_3 , the normal potassium-ion site has tetragonal symmetry (assuming the internuclear axis of the NO to be parallel to the crystal C axis) while the normal azide-ion site has a predominant tetragonal symmetry with a weak orthorhombic component due to the fact that the four neighboring azide ions are oriented along the crystal $[110]$ direction.

In view of the strong similarities in the hyperfine splittings of these three spectra and in view of the fact that the strengths of the orthorhombic fields in the three structures are undoubtedly different, it is difficult to see how the splitting of a $^2\pi$ term could account for the observed data. The splitting of a $^2\pi$ state by a strong orthorhombic crystalline field, as, for example, at the KNO_3 and KCl sites described in references 16 and 18, respectively, would be expected to produce an anisotropic g tensor with principal values in the neighborhood of the free-electron value. Such asymmetries have been observed and accounted for in the spectrum of the $^2\pi$ state of O_2^- molecule ions trapped at negative-ion sites in alkali halide single crystals with the molecular axis oriented along the crystal $[100]$ direction.²¹ It is expected that the NO molecule would behave at least qualitatively in a manner similar to the O_2^- molecule ion. For a weak orthorhombic crystalline field, as would be expected for the azide-ion site in KN_3 , the perturbation of the $^2\pi$ state would be intermediate to spin-orbit and crystalline electric field interaction. Under such a perturbation, the principal values of the g tensor would exhibit marked departure from the free-electron value. In the limit of pure spin-orbit interaction, as in the case of a free NO gas molecule, the axial g value would vanish. If on the other hand the trapped NO molecules, constrained to fixed orientations by crystalline electric field forces, have a $^2\Sigma$ rather than a $^2\pi$ ground term, then some of the spectral characteristics would seem less anomalous. For example, the similarity in hyperfine splittings and the small g -value departures from the free-electron value would be more in

keeping with an orbitally nondegenerate ground state. Furthermore, the nearly axially symmetric hyperfine splittings in all three spectra and the small but significant g -value departures from the free-electron value would be in keeping with such a state provided it is well isolated. This is not to say that a $^2\Sigma$ assignment for the ground state of a trapped NO molecule, constrained by crystalline forces to a fixed orientation, is free from serious objections. Perhaps the most critical objection that could be raised against such an *ad hoc* assignment is the well established $^2\pi$ term assignment for the ground state of gaseous NO. It is difficult indeed to see how a crystalline field perturbation could produce such an alteration of the molecular electron configuration.

V. SUMMARY

Paramagnetic resonance absorption has been observed in ultraviolet- and x-irradiated single crystals of potassium azide having nitrate and nitrite ion impurities. Two distinct spectra are observed which are associated with the nuclear triplet state of N^{14} . The two spectra are produced by permitting the irradiated crystals to bleach at room temperature for times of the order of a few days. Once produced, the two spectra appear to be quite stable with no noticeable spectral intensity diminution after three years. The defect centers responsible for these two spectra are believed to be irradiation products of nitrate and/or nitrite ion impurities and are tentatively identified as trapped NO_2 and NO molecules. From the axial symmetry of the spectrum assigned to NO_2 and from the partially resolved seven-line multiplet structure in each of the three spectral components, the most likely location of an NO_2 molecule seems to be a potassium-ion vacancy. For NO it is concluded that the molecule cannot be located at either of the two axially symmetric interstitials. The NO molecules are therefore required to be located at either potassium-ion or azide vacancies. No convincing evidence was uncovered which could provide a preference for one of these vacancies over the other.

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APPENDIX

The qualitative behavior of a $^2\pi$ term under the simultaneous perturbation of spin-orbit interaction and an orthorhombic crystalline electric field can be determined by evaluating the matrix elements of these two perturbations in the representation of the four $^2\pi$ functions. The perturbation is given by

$$\mathcal{H}' = \lambda \mathbf{L} \cdot \mathbf{S} + V_{\text{cf}}, \quad (\text{A1})$$

²¹ W. Känzig and M. H. Cohen, Phys. Rev. Letters 3, 509 (1959).

where V_{ef} is an orthorhombic crystalline electric field potential,²⁰ λ is the spin-orbit coupling constant, and \mathbf{L} and \mathbf{S} are the orbital and spin angular momentum operators, respectively. Setting $|1, \frac{1}{2}\rangle = (\pi_x + i\pi_y)\alpha$, $|-1, -\frac{1}{2}\rangle = (\pi_x - i\pi_y)\beta$, etc., where α and β are spin functions, we rewrite Eq. (A1) in its matrix form:

$$\langle M_L, M_S | \mathcal{H}' | M_L', M_S' \rangle = \begin{bmatrix} \frac{1}{2}\lambda & \Delta & 0 & 0 \\ \Delta & -\frac{1}{2}\lambda & 0 & 0 \\ 0 & 0 & -\frac{1}{2}\lambda & \Delta \\ 0 & 0 & \Delta & \frac{1}{2}\lambda \end{bmatrix}, \quad (\text{A2})$$

where $\Delta = \langle \pm 1, \pm \frac{1}{2} | V_{ef} | \mp 1, \pm \frac{1}{2} \rangle$ and where the constant diagonal element $\langle \pm 1, \pm \frac{1}{2} | V_{ef} | \pm 1, \pm \frac{1}{2} \rangle$ has been omitted. The eigenvalues to this matrix are given by Eq. (4), and the four unnormalized eigenfunctions are given by

$$\begin{aligned} \psi_{1,2} &= |1, \pm \frac{1}{2}\rangle \mp \{ \lambda/2\Delta \mp [1 + (\lambda/2\Delta)^2]^{\frac{1}{2}} \} |-1, \pm \frac{1}{2}\rangle, \\ \psi_{3,4} &= |1, \pm \frac{1}{2}\rangle \mp \{ \lambda/2\Delta \pm [1 + (\lambda/2\Delta)^2]^{\frac{1}{2}} \} |-1, \pm \frac{1}{2}\rangle. \end{aligned} \quad (\text{A3})$$

The two extreme cases for these eigenfunctions, see Fig. 6, are obtained by permitting the ratio $\lambda/2\Delta$ to either vanish or become very large.

Spectroscopic splitting factor values for cases corresponding to intermediate values of the ratio $\lambda/2\Delta$ can be obtained by using slightly modified forms of expressions developed by Känzig and Cohen²¹ for the O_2^- problem. For example, the axial component of the g value is given by

$$g_{zz} = g_e - 2 \left[\frac{(\lambda/2)^2}{\Delta^2 + (\lambda/2)^2} \right]^{\frac{1}{2}} L, \quad (\text{A4})$$

where L is a factor close to unity (see reference 21). For the case of NO located at a negative-ion site in KN_3 , the parameter Δ would not be expected to be very large as compared to the spin-orbit coupling constant. Consequently, the g values would be expected to exhibit pronounced departures from the free-electron value. For example, using Eq. (A4) we find that departures of the order of 10% or so would result in the value of g_{zz} for a $\lambda/2\Delta$ ratio of one tenth.

Electron Spin Resonance of Gd^{3+} and Eu^{2+} in Single Crystals of CaO

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Single crystals of CaO doped with Eu^{2+} and Gd^{3+} have been investigated by paramagnetic resonance at X band. Measurements were made at 290, 77, and 4.2°K. The spectra of Eu^{2+} and Gd^{3+} can be described by a cubic spin Hamiltonian. The constants for the spectrum of Gd^{3+} at 290°K are $g = 1.9913 \pm 0.0005$, $b_4 = (+11.6 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}$, $b_6 = (-1.15 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}$. The over-all splitting of the ground state is $(380 \pm 4) \times 10^{-4} \text{ cm}^{-1}$. The constants for the spectrum of Eu^{2+} at 290°K are $g = 1.9914 \pm 0.001$, $b_4 = (+24.0 \pm 0.5) \times 10^{-4} \text{ cm}^{-1}$, $b_6 = (-1.6 \pm 0.5) \times 10^{-4} \text{ cm}^{-1}$, $|A^{151}| = (29.6 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}$, and $|A^{153}| = (13.05 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}$. The over-all splitting of the ground state is $(781 \pm 20) \times 10^{-4} \text{ cm}^{-1}$. The splitting parameters are found to vary only slightly between 290 and 4.2°K.

INTRODUCTION

PARTIAL removal of the eightfold spin degeneracy of $4f^7$, $^8S_{7/2}$ ions by cubic crystalline fields has been a subject of considerable interest in recent years. Low and Rosenburger¹ suggest that the splitting mechanism may be linear in the crystal field potential. An extrapolation of their data indicates that a splitting of about 0.2 cm^{-1} would be expected for Gd^{3+} and Eu^{2+} in CaO. A study of Gd^{3+} - and Eu^{2+} -doped CaO was undertaken to determine whether their suggested mechanism is operative in CaO. The crystal structure of CaO is face-centered cubic with lattice parameter $a = 4.797 \text{ \AA}$.

¹ W. Low and U. Rosenburger, Phys. Rev. **116**, 621 (1959).

EXPERIMENTAL PROCEDURE

Paramagnetic resonance data were obtained using a Varian V-4500 spectrometer. Spectra were taken at room temperature, 77 and 4.2°K. Samples were placed on the side wall of a TE₁₀₂ rectangular cavity resonating at approximately 9.5 kMc/sec. A 12-in. rotating base magnet permitted the study of the angular variation of the spectra. The CaO crystals were obtained from Semi-Elements Inc. Impurities were introduced into the crystals with a concentration of approximately 0.05% by weight. Samples were cleaved into pieces approximately $1 \times 4 \times 4 \text{ mm}$. The orientation of the crystallographic axes was checked by means of x rays.