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# Electron Spin Resonance of Radiation-Induced Defects in Potassium Azide*

D. W. WYLIE,† A. J. SHUSKUS,‡ C. G. YOUNG, AND O. R. GILLIAM
*Department of Physics, University of Connecticut, Storrs, Connecticut*

AND

PAUL W. LEVY
*Brookhaven National Laboratory, Upton, New York*

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Trapped nitrogen atoms and $N_2^-$ molecule ions have been detected in potassium azide ($KN_3$) by electron spin resonance measurements at 77°K following gamma-ray irradiation at this temperature. The nitrogen atom has effective spin $S=\frac{3}{2}$, and each fine structure component shows the hyperfine pattern of a single $N^{14}$ nucleus. The atoms are trapped in two magnetic sites having rhombic symmetry which are equivalent under a 90° rotation about [001]. Choosing $z\|[110]$, $x\|[1\bar{1}0]$, and $y\|[001]$, the results can be fitted to the spin-Hamiltonian, $\mathcal{H}=|\beta|\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}+DS_z^2+E(S_x^2-S_y^2)+A\mathbf{I}\cdot\mathbf{S}$, where $g=2.001\pm0.001$, $D=+0.0143\pm0.0001$ cm$^{-1}$, $E=-0.00199\pm0.00002$ cm$^{-1}$, and $A=0.00051\pm0.00002$ cm$^{-1}$. The other defect, attributed to $N_2^-$, has a spectrum characteristic of a single unpaired electron and a hyperfine pattern corresponding to two equivalent nitrogen nuclei, and is located in two equally populated magnetic sites related by a 90° rotation about [001]. For one site and the same choice of axes, $g_x=2.001\pm0.002$, $g_y=2.001\pm0.001$, and $g_z=1.984\pm0.001$; $A_x=0.0006\pm0.0002$ cm$^{-1}$ and $A_y=A_z=0.00037\pm0.00002$ cm$^{-1}$. The annealing behavior of these defects is related to the growth of the $N_4^-$ molecule ion previously reported.

FUNDAMENTAL to the study of radiation effects in solids is the determination of the various atom configurations which result from the primary radiation-damage event. The energetic recoils produced by, e.g., 1-Mev neutrons, eject roughly $10^3$ atoms from their normal lattice position and except for simple defects on their periphery, the resulting radiation-damage regions are expected to be very complicated. In pseudostable materials, such as the potassium azide ($KN_3$) described here, radiation damage can be formed by purely ionizing radiation, even by ultraviolet light. Clearly, one would like to determine the nature of the damage regions produced by ionization alone. Since they most likely involve only small numbers of atoms, it is expected that they can be completely characterized by electron spin resonance (ESR) and optical measurements. Furthermore, since $N_2$ gas is evolved from heavily irradiated $KN_3$, it is essential to know if only gas molecules are formed during the ionization event, or if other defects are formed simultaneously or as precursors to the gas molecule formation.

An ESR attributed to a single defect consisting of a linear $N_4^-$ molecule ion in potassium azide was previously reported.[1] This $N_4^-$ defect is formed by ultraviolet light or $Co^{60}$ gamma-ray irradiations at room temperature. New ESR measurements on $KN_3$ crystals exposed to $10^6$ r of $Co^{60}$ gamma rays at 77°K and observed prior to warmup show several additional defects. Two of the new defects, described here, are identified as trapped nitrogen atoms and $N_2^-$ molecule ions. The concentration of each of these defects is several times larger than the concentration of the $N_4^-$ defect following gamma-ray irradiations at 77°K. When potassium azide crystals are irradiated with ultraviolet light at 77°K from a high-pressure mercury vapor lamp, the $N_2^-$ and $N_4^-$ molecule ions are easily produced, but the nitrogen atoms are not observed. A comparison of the ultraviolet light and gamma-ray irradiations shows that the ratio of $N_4^-$ to $N_2^-$ is noticeably larger for the ultraviolet light irradiations.

The trapped nitrogen atoms, produced by gamma-ray irradiations, reside in two magnetic sites which are equivalent for 90° rotation of $H_0$ about the $c$ axis. For each site there are three, easily power-saturated, fine structure lines corresponding to an effective spin of $\frac{3}{2}$. The fine structure arises from zero-field splitting of the $^4S_{\frac{3}{2}}$ ground state of atomic nitrogen. The $g$ value is isotropic within experimental error, which signifies negligible spin-orbit interaction as is expected for an $S$ state.

To explain the spectra of atomic nitrogen in nonionic, partially ordered frozen gases, Cole and McConnell[2] have proposed that small zero-field splittings are caused by axially symmetric crystalline fields. In the ionic $KN_3$, however, the crystalline environment of the trapped atoms is observed to be rhombic and the large over-all splitting along [110] is $0.05723\pm0.00005$ cm$^{-1}$. Evidence of trapped nitrogen atoms in x-ray-irradiated sodium azide has been reported by King *et al.*,[3] but with no indication of fine structure. The present authors have observed fine structure of nitrogen atoms in irradiated sodium azide and will report upon it at a later date.

The resonances of the trapped nitrogen atoms are

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† On sabbatical leave from the Department of Physics, University of Maine, Orono, Maine.

‡ Now at the United Aircraft Research Laboratories, East Hartford, Connecticut.

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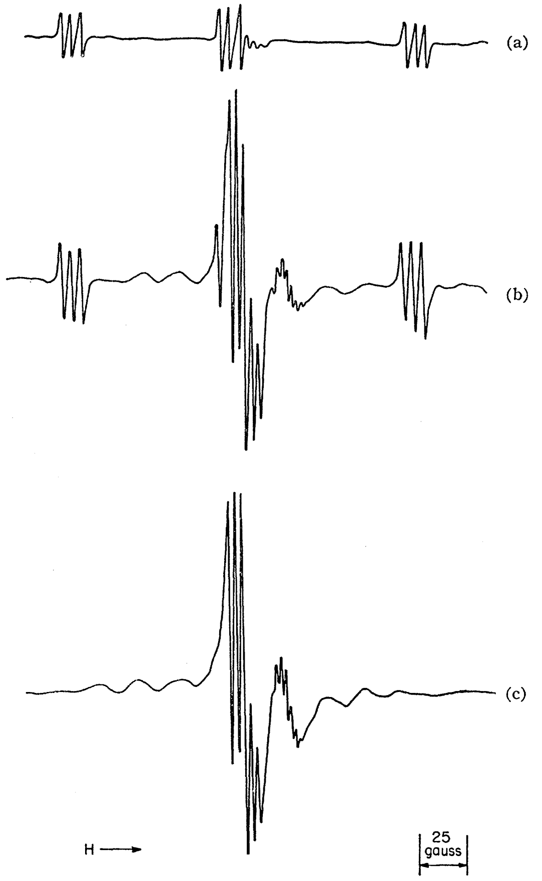

FIG. 1. First derivative of ESR spectra in $KN_3$ following gamma-ray irradiations at 77°K with $H_0$ along [001], recorded at 9.2 kMc/sec with different microwave powers; (a) 0.002 milliwatt, (b) 0.2 milliwatt, (c) 20 milliwatts. (All spectra are not to the same vertical scale.)

shown in Fig. 1(a) for $H_0$ parallel to the $c$ axis, for which orientation the spectra of the two magnetic sites are superposed. Each fine-structure line is split by interaction with the $N^{14}$ nucleus into three equally spaced, equally intense hyperfine lines. This splitting is 5.5±0.2 gauss and is isotropic, which is typical of hyperfine splittings reported for atomic nitrogen in other surroundings.[3,4] The linewidth between inflection points is 2.1±0.2 gauss.

If we choose the $z$ axis along [110], the $x$ axis along [1$\bar{1}$0], and the $y$ axis along [001], the experimental results can be represented by the spin Hamiltonian,

$$\mathcal{H}=|\beta|\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}+DS_z^2+E(S_x^2-S_y^2)+A\mathbf{I}\cdot\mathbf{S},$$

with $S=\frac{3}{2}$, where $g=2.001\pm0.001$, $D=+0.0143\pm0.0001$ cm$^{-1}$, $E=-0.00199\pm0.00002$ cm$^{-1}$, and $A=0.00051\pm0.00002$ cm$^{-1}$.

Since $g$ appears isotropic, the above $g$ value was estimated from the experimental data and was used to compute the magnitudes of $D$ and $E$. The sign of $D$ was determined by measuring the relative intensities of the high-field line to the low-field line at both 77°K and 4.2°K and the sign of $E$ made to match the data. These parameters not only give a good fit along the principal axes but in other directions as well. The computed and the experimental angular variations agree within 1%. At 4.2°K the $g$ value, fine structure splitting, hyperfine splitting, and linewidth agree with the values obtained at 77°K. All observations were made at about 9.2 kMc/sec using a superheterodyne spectrometer.

The paramagnetic center attributed to nitrogen atoms appears stable at 160°K but disappears completely at 196°K. The trapped atoms are not detected following irradiations with ultraviolet light at 77°K. Since a high-energy radiation is required to generate this defect, the trapped atoms could be located interstitially. A site which would exhibit the proper symmetry is an interstitial position between two cations lying parallel to the (001) plane; however, other positions cannot be ruled out, as, e.g., an azide ion vacancy.

The other defect, identified as $N_2^-$, has spectra characteristic of a single unpaired electron associated with a pair of nitrogen nuclei in two equally populated magnetic sites. These sites are equivalent under a 90° rotation of the magnetic field about the $c$ axis. For each magnetic site one would expect five equally spaced hyperfine lines with an intensity ratio 1:2:3:2:1. This intensity ratio is observed for $H_0$ parallel to the $c$ axis. For this orientation the spectra of the two sites coincide, and appear prominently with respect to the $N_4^-$ resonances on the high-field side and with respect to broad resonances of an unidentified defect [Fig. 1(c)]. Since the hyperfine splitting is a maximum for $H_0$ along [110] or [1$\bar{1}$0], the $N_2^-$ molecular axis is known to be in either of these directions. For one magnetic site and the same choice of axes as used to describe the nitrogen atoms, the measured values of the $g$ tensor are: $g_x=2.001\pm0.002$, $g_y=2.001\pm0.001$, and $g_z=1.984\pm0.001$. The corresponding hyperfine splittings are: $A_x=0.0006\pm0.0002$ cm$^{-1}$ and $A_y=A_z=0.00037\pm0.00002$ cm$^{-1}$. Measurements for $H_0$ along the $x$ axis are less accurate since the spectra of $N_2^-$ and $N_4^-$ overlap for this orientation. These measurements are facilitated, however, by the greater abundance of $N_2^-$ defects following the gamma-ray irradiation and by the fact that the $N_4^-$ spectra are well known.

Following irradiations with gamma rays at 77°K, the spectra due to $N_4^-$, $N_2^-$, and nitrogen atoms are all present [Fig. 1(b)]. When the crystal is warmed to 196°K, the spectrum due to the nitrogen atoms disappears while the intensity of the $N_4^-$ increases by a factor of 5 and the intensity of the $N_2^-$ increases by a factor of 2. Further annealing at 196°K shows that the

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[4] C. K. Jen, in *Formation and Trapping of Free Radicals*, edited by Arnold M. Bass and H. P. Broida (Academic Press, Inc., New York, 1960), Chap. 7.

intensity of the $N_4^-$ is increasing while the intensity of the $N_2^-$ is decreasing. The $N_4^-$ reaches its maximum intensity when the $N_2^-$ has just disappeared. When the crystal is now warmed to room temperature for approximately 16 hours, the intensity of the $N_4^-$ spectrum is reduced by one-half. During the annealing studies one of the chromium lines in an oriented sample of $Al_2O_3$ was used as an intensity standard.

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# Paramagnetic Resonance Absorption of Divalent Nickel in $\alpha$-$Al_2O_3$ Single Crystal*

S. A. Marshall, T. T. Kikuchi, and A. R. Reinberg
*Physics Division, Armour Research Foundation, Chicago, Illinois*

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A paramagnetic resonance absorption spectrum has been observed in single crystals of $\alpha$-$Al_2O_3$ having nickel oxide added as an impurity. The spectrum is interpreted as being due to transitions between fine structure states of the divalent nickel ion. Best-fit constants to an axially symmetric spin Hamiltonian are obtained from 4.2°K to 300°K. The spectroscopic splitting factors are found to be nearly constant over this temperature range with average values given by $g_{\parallel}=(2.1957\pm0.0013)$ and $g_{\perp}=(2.1859\pm0.0013)$. The crystal field splitting energy is, on the other hand, found to be temperature dependent following the approximate law $D=-(1.3287+\alpha T^2)$ cm$^{-1}$, where $\alpha=5.2\times10^{-7}$ (°K)$^{-2}$. The average spin-orbit coupling constant over this temperature range is found to be $(-285\pm30)$ cm$^{-1}$.

## I. INTRODUCTION

In recent years, a number of investigations have been reported on the spectra of iron group ions in $\alpha$-$Al_2O_3$. As a host, this structure exhibits some properties which make it favorable for the study of magnetic ions. Briefly, these properties include a moderately high coefficient of thermal conductivity, a relatively low dielectric loss factor and a structure containing anions having zero-spin nuclei. In the $\alpha$-$Al_2O_3$ structure, local cation sites exhibit the trigonal symmetry of a distorted oxygen octahedron with two nonequivalent cation sites per unit cell. For magnetic ions occupying such sites, the crystallographic nonequivalence produces a magnetic nonequivalence when the magnetic ion spin quantum number is equal to or greater than two. For the divalent nickel ion, $S=1$ so that the crystal should exhibit no magnetic nonequivalence from this source.

Of the various magnetic iron group ions, the magnetic spectra of trivalent chromium,[1] iron[2] and vanadium[3,4] along with divalent manganese,[5] cobalt,[6] vanadium[4] and nickel[7] have been observed in this structure. These spectra are observed to exhibit axial symmetry about the threefold axis of the crystal. From this spectral symmetry and from the fact that trivalent iron and divalent manganese, each with spin $S=\frac{5}{2}$, exhibit spectral characteristics strongly suggesting two magnetically nonequivalent sites, it is concluded that sites occupied by the iron group ions are those of the normal trivalent aluminum ions. In a recent report on the trivalent gadolinium ion in $\alpha$-$Al_2O_3$, Geschwind and Remeika reach a similar conclusion and report the additional fact that during the crystal growth process, the gadolinium ion tends to favor one aluminum site over the other.[8] In addition, for the case of divalent ions such as $V^{++}$, $Co^{++}$ and $Mn^{++}$, spectra are reported which tend to suggest no local distortion of an extent sufficient to destroy the trigonal symmetry nor any spectral evidence of localized charge compensation.

In this paper, we wish to report the results of an investigation on divalent nickel ion in $\alpha$-$Al_2O_3$ single crystals. It is felt that these results will be of interest not only because they have to do with yet another iron group ion in this particular structure, but also because of some rather interesting although as yet unexplained spectral behavior.

## II. EXPERIMENTAL PROCEDURE

The magnetic resonance absorption spectrometer used in this investigation is of conventional design making use of superheterodyne detection. Zeeman field was provided by a twelve-inch electromagnet having a $2\frac{1}{2}$ in. pole gap and auxiliary coils for low-frequency field modulation. Microwave power was delivered from a 3 cm wavelength oscillator locked to the specimen cavity.

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