PHYSICAL REVIEW VOLUME 138, NUMBER 2A 19 APRIL 1965

Electron-Spin Resonances in Reactor-Irradiated Aluminum Oxide*

F. T. GAMBLE,† R. H. BARTRAM, C. G. YOUNG,‡ AND O. R. GILLIAM
University of Connecticut, Storrs, Connecticut

AND

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

(Received 30 November 1964)

Three prominent paramagnetic absorption systems have been detected in single crystals of α aluminum oxide (Al_2O_3) following reactor irradiation with and without subsequent low-temperature gamma-ray irradiation. The most prominent system has an asymmetric, slightly anisotropic absorption with $g\approx 2.00$, which appears to result from the superposition of components from several paramagnetic centers. A second system consisting of twelve equally intense lines corresponds to a spin-one center in six inequivalent sites whose z axes are perpendicular to the crystal c axis and nearly parallel to rows of O^{2-} ions. The spin-Hamiltonian parameters for this defect are: $g_z=2.0105\pm0.0020$, $g_x=g_y=2.0190\pm0.0020$, $S=1$, $|D|=0.0710\pm0.0002$ cm^{-1}, and $|E|=0.0025\pm0.0005$ cm^{-1}, where D and E have the same sign. Its spectrum is attributed to an AlO^{3-} molecular ion in a pair of oxygen sites, formed by a replacement collision. The third system is obtained when a reactor-irradiated crystal of Al_2O_3 is gamma-ray irradiated at 77°K and measured prior to warming up. It is a three-line system which saturates with gamma-ray dose but whose saturation level increases with reactor dose. This system corresponds to a spin-$\frac{3}{2}$ center with a symmetry axis parallel to the c axis; its spin-Hamiltonian parameters are: $g_{\parallel}=2.018\pm0.002$, $g_{\perp}=2.011\pm0.002$, $S=\frac{3}{2}$, and $|D|=0.0373\pm0.0002$ cm^{-1}. It is attributed to interstitial O^+ formed from interstitial O^0 by ionization or hole trapping.

INTRODUCTION

A VARIETY of methods have been employed to study the effects of reactor irradiation on α-aluminum oxide. These include optical absorption spectra,[1–5] long-wavelength neutron-scattering cross sections,[6] thermal conductivity,[7] lattice expansion,[8] and electron spin resonance (ESR).[9,10] A recent article describes the ESR results obtained on gamma-ray irradiated Al_2O_3 single crystals.[11] The present paper extends and interprets the earlier ESR measurements on the reactor-irradiated single crystals[9,10]; a discussion of the effects of low-temperature gamma-ray irradiation subsequent to the reactor irradiation is included.

When a single crystal of Al_2O_3 is reactor-irradiated at about 340°K, two resonance systems are observed, both centered about $g=2$. The resonances caused by the reactor irradiation consist of an asymmetric, slightly anisotropic absorption and a system of 12 lines of equal intensity. The angular variation of the latter suggests that they arise from a center with an effective spin of one in six inequivalent sites. Another defect can be observed if the reactor-irradiated sample is gamma-ray irradiated at 77°K and examined by ESR prior to warmup. This paramagnetic center exhibits a three-line fine structure consistent with an effective spin of three-halves. Several additional resonances of lesser intensity are observed which resemble some of the resonances observed following electron bombardment. The paramagnetic centers caused by electron irradiation will be reported in a later publication. The reactor-induced asymmetric resonance and the 12-line system are assumed to result primarily from atomic displacements caused by fast neutrons. The remaining three-line system is attributed to ionization of reactor-induced defects by gamma-ray photons.

CRYSTAL STRUCTURE

A crystal of α-Al_2O_3 may be viewed as a hexagonal close packing of a layer of oxygen ions (O^{2-}) with a layer of aluminum ions (Al^{3+}) in which only two out of the three close-packed sites are occupied. The aluminum ions cause a distortion from the ideal hexagonal close packing, the crystal is actually rhombohedral, and the space group is $D_{3d}{}^6$.[12] The structure can be regarded as an assembly of rhombohedral primitive unit cells with each unit regarded as a lattice point of ten ions. Such a unit assembly, as shown in Fig. 1, consists of two Al_2O_3 "molecules," one rotated 60°

---

* This research was supported by the U. S. Atomic Energy Commission.

† Present address: Department of Physics and Astronomy, Denison University, Granville, Ohio.

‡ Present address: American Optical Company, Southbridge, Massachusetts.

[1] R. A. Hunt and R. H. Schuler, Phys. Rev. **89**, 664 (1953).

[2] P. W. Levy and G. J. Dienes, *Report of the Bristol Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 256.

[3] P. W. Levy, Phys. Rev. **123**, 1226 (1961).

[4] E. W. J. Mitchell, J. D. Rigden, and P. D. Townsend, Phil. Mag. **5**, 1013 (1960).

[5] G. W. Arnold and W. D. Compton, Phys. Rev. Letters **4**, 66 (1960).

[6] J. Antal and A. Goland, Phys. Rev. **112**, 103 (1958).

[7] R. Berman, E. L. Foster, B. Schneidmesser, and S. M. A. Tirmizi, J. Appl. Phys. **31**, 2156 (1960).

[8] D. G. Martin, J. Phys. Chem. Solids **10**, 64 (1955).

[9] C. G. Young, O. R. Gilliam, and P. W. Levy, Bull. Am. Phys. Soc. **6**, 117 (1961).

[10] O. R. Gilliam and C. G. Young, 1962 Conference Radiation Effects on Glass, Rochester, New York (unpublished).

[11] F. T. Gamble, R. H. Bartram, C. G. Young, O. R. Gilliam, and P. W. Levy, Phys. Rev. **134**, A589 (1964).

[12] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948), Vol. II.

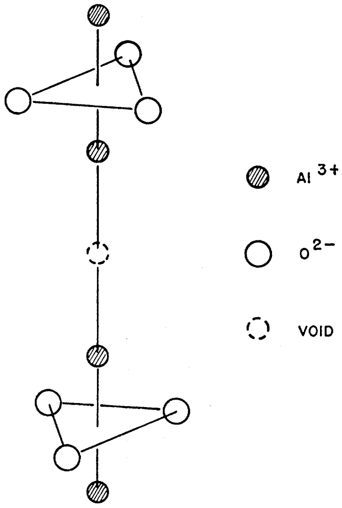

FIG. 1. Unit assembly of ions associated with each lattice point of α-Al_2O_3.

about the c axis with respect to the other. The description in terms of molecules is convenient but should not be taken literally, since the crystal is ionic rather than molecular.[13] The two molecules are separated by an unoccupied interstice of the hcp structure, which forms a natural void in the crystal.

EXPERIMENTAL DETAILS

The samples investigated were α aluminum oxide single crystals grown by the Verneuil process and obtained from the Linde Company. They were cut and polished into rectangles, approximately 0.800 in. by 0.390 in. by 0.040 in., with the crystalline c axis normal to the large surface. The large surfaces were polished to facilitate optical measurements. All of the unirradiated crystals showed prominent ESR spectra of Fe^{3+} and Cr^{3+}, although the impurity content of different crystals varied by as much as a factor of 10. Since impurity analyses on the crystals have not been performed, the presence of other impurities is not known. Estimates by the Linde Company of the impurity concentrations in the starting oxide powders have been published by Gibbs.[14]

The reactor irradiations were made in the Brookhaven National Laboratory (BNL) graphite research reactor at a temperature of approximately 340°K, or, at temperatures less than 220°K in a special "low-temperature" facility. For either irradiation temperature the same defects were observed. The samples received a dose of about 1.7×10^{16} *nvt* of fast neutrons per day of reactor irradiation. Following the reactor irradiations some samples received gamma-ray irradiations at 77°K in calibrated tubular Co^{60} sources at the University of Connecticut or at BNL.

The ESR measurements were made at 9.2 Gc/sec with a superheterodyne paramagnetic-resonance spectrometer using 100-cps magnetic-field modulation. Rectangular TE_{102} cavities were employed into which the samples could be loaded and unloaded at a temperature of 77°K. One of these cavities was designed to facilitate ESR observations between 77°K and room temperature; it is shown in Fig. 2. Typically this cavity was loaded under liquid nitrogen and installed in the brass outer cylinder which was partially filled with liquid nitrogen. The cylinder was vacuum-sealed to the flange on the waveguide by a lead wire "O" ring, and both cavity and cylinder were evacuated while being maintained in liquid nitrogen. The cavity temperature was elevated by passing direct current through the heating coil. The temperature was monitored by a copper-constantin thermocouple mounted on the cavity. Any temperature between 77°K and room temperature could be held to one degree with only slight readjustments of the current after equilibrium had been reached.

An iron-impurity line in an unirradiated aluminum oxide crystal was used for a reference to make relative-intensity measurements. The orientation of this calibrating sample was chosen such that the Fe^{3+} reference line was well separated from the radiation-induced lines. To determine the absolute spin concentration of any defect, the sapphire reference sample was calibrated against both diphenylpicrylhydrazyl and charred dextrose standards. A microwave frequency standard and a nuclear resonance probe were employed to measure precisely the microwave frequency and the magnetic field, respectively. The crystal axes of each sample relative to its external surfaces were determined to accuracies of one-half of a degree by use of an x-ray precession camera.

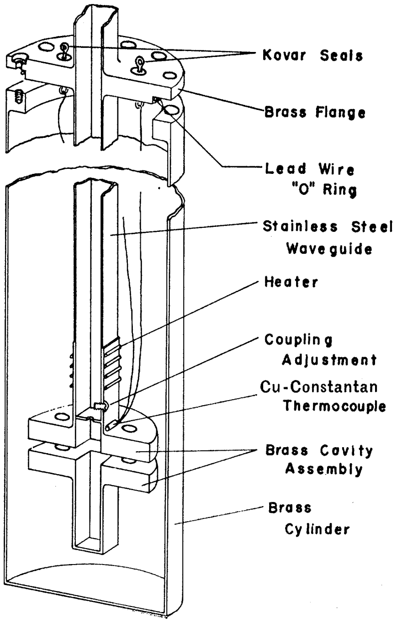

FIG. 2. Variable-temperature cavity which facilitates sample loading at a temperature of 77°K and ESR measurements between 77°K and room temperature.

---

[13] R. Bersohn, J. Chem. Phys. **29**, 326 (1958).

[14] P. Gibbs, in *Kinetics of High Temperature Processes*, edited by W. D. Kingery (John Wiley & Sons, Inc., New York, 1959), p. 26.

EXPERIMENTAL RESULTS

The paramagnetic resonance spectrum shown in Fig. 3 was obtained from a sample which had received a fast-neutron flux of 7×10^{17} nvt below 220°K followed by a 1×10^{6}-*R* Co^{60} gamma-ray dose at 77°K. ESR observations were made prior to warming up. The most prominent of the absorptions is the large central complex absorption labeled A, which hereafter is referred to as the central absorption. The lines of low intensity labeled B are part of a system of 12 equally intense lines. An angular variation study of these lines has shown that they are caused by a spin-one center in six inequivalent sites. The outer lines of a three-line system generated by the 77°K gamma-ray irradiation after the reactor irradiation are labeled by C. These lines are part of a three-line fine structure of a spin-$\frac{3}{2}$ center whose center line is obscured at this orientation by the central reactor-induced absorption.

1. The Central Absorption

As little as 2×10^{15} $(nvt)_{fast}$ of reactor neutron irradiation produces an asymmetric, slightly anisotropic absorption line in α-aluminum oxide. With continued irradiation the integrated central absorption becomes considerably larger than the absorption due to the paramagnetic impurity ions, and it has not appeared to saturate with reactor irradiations up to six weeks. An angular variation study about the crystallographic axes has revealed that the absorption consists of an undetermined number of poorly resolved components varying over 100 to 200 G. The separation between inflection points for the major portion of the absorption, which has an effective g value close to that of the free electron, is about 30 G. The smallness of the angular variation leads one to believe that the absorption arises from defects with effective spin $S=\frac{1}{2}$. The resonances are poorly resolved because of superposition and perhaps because of multiple inequivalent sites. An attempt to resolve the absorption into Gaussian components and, then, from selected defect models to predict the expected angular variations has not been successful.

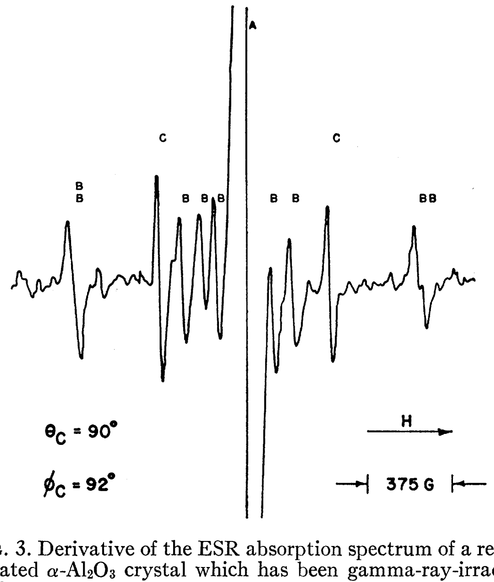

FIG. 3. Derivative of the ESR absorption spectrum of a reactor-irradiated α-Al_2O_3 crystal which has been gamma-ray-irradiated at 77°K and measured prior to warming up. The central absorption, which goes off scale, is labeled by A; the seven lines labeled B are a portion of the 12-line reactor-induced system; and the two outer lines of the three-line system are labeled C. This spectrum corresponds to one orientation with the field H perpendicular to the c axis ($\theta_c=90°$).

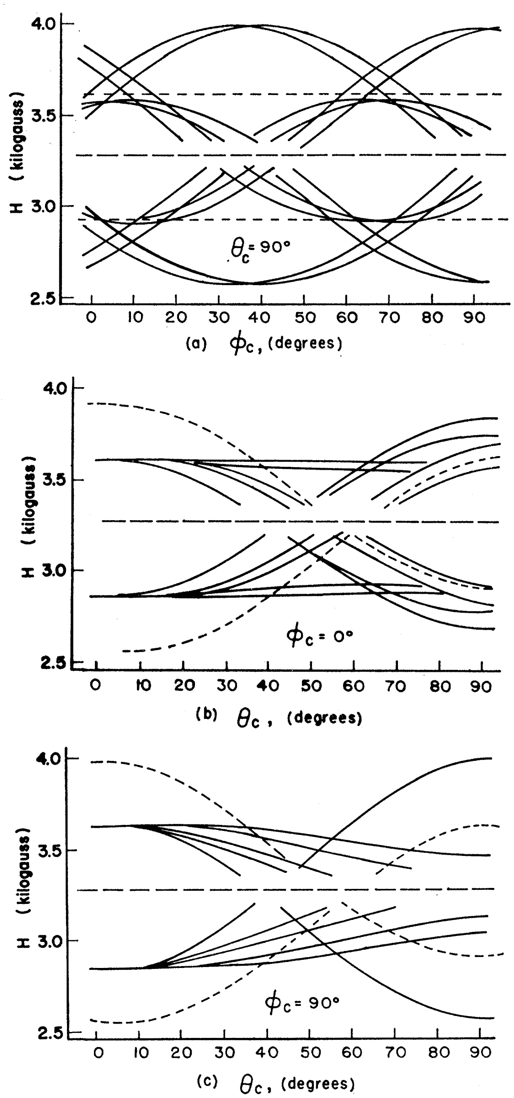

FIG. 4. Angular dependencies of the three paramagnetic systems observed in reactor-irradiated α-Al_2O_3 for rotation of the magnetic field about three orthogonal axes. The solid lines refer to the 12-line system, the short dashed lines refer to the outer lines of the three-line system, and the long-dashed line refers to the central reactor-induced absorption. Here, θ_c specifies the angle H makes with the c axis, and φ_c is the azimuthal angle measured in the basal plane where $\varphi_c=\theta_c=90°$ corresponds approximately to the 100 hexagonal crystal axis. (a) $\theta_c=90°$, (b) $\varphi_c=0°$, and (c) $\varphi_c=90°$.

The paramagnetic center responsible for this resonance is stable at room temperature, but its absorption shows an approximately linear decrease in intensity for step-wise one-hour anneals at temperatures successively higher by 100° intervals from 0 to 500°C. Following the 500°C anneal the line was no longer detected.

2. Spin-One Centers

A fast neutron irradiation of about 10^{16} nvt produces, in addition to the central absorption, a weaker 12-line spectrum of equally intense lines. These lines have a maximum separation of about 1500 G but are centered about the free electron g value; the width of each line is 31 ± 1 G at 77°K and at room temperature. Measurements were made on this system by rotating the external magnetic field in one-degree intervals about three orthogonal axes whose directions were related to external features of the rectangularly shaped sample. One axis was normal to the large surface of the crystal or approximately along the c axis; another was parallel to the large surface and, fortuitously, close to a 100 direction (referred to hexagonal axes); and the third was perpendicular to the first two. The data are represented by the solid-line curves in Fig. 4(a) to (c). These figures show the magnetic fields required for resonances at a fixed frequency as a function of the orientation of the magnetic field with respect to the axes chosen. Here, θ_c corresponds closely to the angle H makes with the c axis and φ_c is an azimuthal angle measured in the basal plane. The direction defined by $\theta_c=\varphi_c=90°$ is close to a 100 direction in the crystal. The long-dashed line refers to the central absorption; the short-dashed curves describe the outer lines of the three-line system.

It was found that the 12-line system corresponds to a defect with spin one in six inequivalent sites. The energy-level system at each site may be described by a spin-Hamiltonian of the form

$$\mathcal{H}=|\beta|\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}+D[S_z^2-\tfrac{1}{3}S(S+1)]+E(S_x^2-S_y^2),\qquad(1)$$

where the components of S and H are referred to the principal magnetic axes (x,y,z) of the site. From the spin Hamiltonian (1), Weger and Low[15] derived an expression for the angular dependence of the energy levels of an ion in a crystalline field with rhombic symmetry in the high-field approximation. From this they determined that the microwave frequency and magnetic field for $\Delta M=\pm1$ transitions are related by the expression

$$\begin{aligned}h\nu=g\beta H+(M-\tfrac{1}{2})\Big[D\Big(\frac{3g_{\parallel}^2}{g^2}\cos^2\theta-1\Big)-3E\Big(\frac{g_{\parallel}^2}{g^2}\cos^2\theta-1\Big)(\cos2\varphi)\Big]-\Big[(D-E\cos2\varphi)^2\Big(\frac{g_{\parallel}g_{\perp}\sin\theta\cos\theta}{g^2}\Big)^2\\+(E\sin2\varphi)^2\Big(\frac{g_{\perp}\sin\theta}{g}\Big)^2\Big]\Big\{\frac{1}{2g\beta H_0}[4S(S+1)-24M(M-1)-9]\Big\}+\Big\{\Big[\frac{Dg_{\perp}^2\sin^2\theta}{g^2}+E\cos2\varphi\Big(1+\frac{g_{\parallel}^2}{g^2}\cos^2\theta\Big)\Big]^2\\+4\Big(\frac{Eg_{\parallel}\cos\theta\sin2\varphi}{g}\Big)^2\Big\}\frac{1}{8g\beta H_0}[2S(S+1)-6M(M-1)-3]\qquad(2)\end{aligned}$$

to terms of second degree in D and E, the axial and rhombic spin-Hamiltonian parameters, respectively. Here, θ is the angle which the magnetic field makes with the magnetic z axis of the individual paramagnetic center, and φ is the angle between the projection of the magnetic-field vector on the xy plane and the x axis. H_0 is defined by

$$H_0=h\nu/g\beta,\qquad(3)$$

where

$$g=(g_{\parallel}^2\cos^2\theta+g_{\perp}^2\sin^2\theta)^{1/2},$$
$$g_{\parallel}=g_z,$$
$$g_{\perp}=\tfrac{1}{2}(g_x+g_y).$$

The magnetic z axes of the centers are all found to lie in the plane normal to the c axis. These axes with respect to the 100 direction in the crystal are listed in Table I. They occur in three closely spaced pairs, separated azimuthally by 120°, with each pair of axes separated by about 6°. The orientations of these axes in the crystal lattice were obtained by comparing ESR data with reciprocal-lattice photographs taken with an x-ray precession camera. Thus it was established that each pair of site z axes is approximately parallel to a row of oxygen ions.

The rhombic component of the crystal field at the defect was too small and the resolution of the lines was inadequate to determine the precise orientation of the

TABLE I. Magnetic z axes for reactor-induced 12-line ESR spectrum in Al_2O_3.

Site	Angle
I	−3°
II	+3°
III	+117°
IV	+123°
V	+237°
VI	+243°

---

[15] W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960), p. 57. The sign of the first second-order term in Low's Eq. (9.7) appears incorrect and has been changed in our Eq. (2).

magnetic x and y axes and to measure g_x and g_y individually. Therefore, it was assumed that $g_x = g_y = g_\perp$ and $g_z = g_{\parallel}$, i.e., axial symmetry, and the value of E was estimated from the deviations from axial symmetry. The spin-Hamiltonian parameters determined for this reactor-induced system of 12 lines are given in Table II.

Table II. Spin-Hamiltonian parameters of reactor-induced 12-line spectrum in Al_2O_3.

$S = 1$
$g_x \approx g_y \approx g_\perp = 2.0190 \pm 0.0020$
$g_z = g_{\parallel} = 2.0105 \pm 0.0020$
$|D| = 2.1284 \pm 0.0020$ Gc/sec $= 0.0710 \pm 0.0002$ cm^{-1}
$|E| \approx 0.075 \pm 0.003$ Gc/sec $= 0.0025 \pm 0.0005$ cm^{-1}

The signs of D and E remain unknown; however, the same sign for each is required.

The presence of the central reactor-induced absorption made it difficult to decide readily between an effective spin of one or a spin of three-halves for this center. However, a comparison of calculations using $S = \frac{3}{2}$ in Eq. (2) and the observed ESR spectra showed that a center line should be easily detectable if the magnetic field H were parallel to the c axis. For this orientation the nature of the second-order terms in Eq. (2) and the expected superposition of the resonance lines from the six inequivalent sites would enhance the detection of the central lines in this system, if such lines existed. No central lines were observed at this orientation. Thus the evidence indicates that a spin of one should be assigned the paramagnetic centers producing the 12-line system.

3. Spin-3/2 Center

When a reactor-irradiated aluminum oxide crystal is gamma-ray irradiated at liquid-nitrogen temperature and ESR measurements are made prior to warmup, a three-line system is observed. A portion of this three-line spectrum is shown in Fig. 3, where it is superimposed on the other two reactor-induced spectra. The linewidths observed are 25±1 G. The angular dependence of the outer two resonance lines is shown in Fig. 4 (a) to (c) by the short-dashed lines. These plots indicate that the magnetic z axis of this center is parallel to the crystal c axis. The long-dashed line represents the central reactor-induced absorption; this absorption at many orientations obscures the central line of the three-line system, which is not indicated in the figures. The three-line system may also be described by the spin Hamiltonian given by Eq. (1) with $E = 0$, i.e., with axial symmetry, and with effective spin $S = \frac{3}{2}$. Likewise, its angular dependence for $\Delta M = \pm 1$ transitions is represented by Eq. (2). The spin-Hamiltonian parameters determined for the three-line system are listed in Table III.

Table III. Spin-Hamiltonian parameters for gamma-ray-induced three-line ESR spectrum in reactor-irradiated Al_2O_3.

$S = \frac{3}{2}$
$g_{\parallel} = 2.018 \pm 0.002$
$g_\perp = 2.011 \pm 0.002$
$|D| = 1.12 \pm 0.002$ Gc/sec $= 0.0373 \pm 0.0002$ cm^{-1}
$E = 0$

For this paramagnetic species, the center line of the spin-$\frac{3}{2}$ fine structure was readily apparent, although only partially resolved, at many orientations of the crystal relative to H, in samples which had received greater than 3×10^{16} nvt fast neutron irradiation followed by a gamma-ray irradiation of 1×10^6R at 77°K. It was observed to grow, anneal, and bleach simultaneously with the two outer lines. Further, a careful check of the angular dependence of all three lines for variations of θ from 0° to 90° indicated second-order deviations in all three lines in close agreement with deviations predicted from use of Eq. 2 with $S = \frac{3}{2}$.

The relative intensity of the three-line spectrum as a function of gamma-ray dose at 77°K is shown in Fig. 5 for a crystal which had received a two-day reactor irradiation. The spectrum reached maximum intensity with a dose of about 2×10^6R. With a three-week reactor-irradiated sample the same dependency on dose was observed, except that the spectrum was more intense. Each data point shown in Fig. 5 represents the average of from two to four comparisons of line intensities with a standard; whereas, the drawn curve is a pure exponential. It is estimated that the intensity measurements were subject to rather large probable errors of ±6% because of instrument variations and because it was necessary to remove the sample from the spectrometer for each dose increment. However, the data points obtained fall, well within this error, on the curve expected for a saturating exponential of the form

$$n = n_0(1 - e^{-f\varphi t}).$$

The symbols in this equation have the following mean-

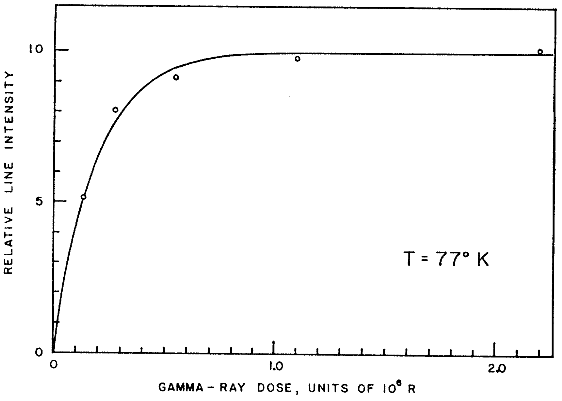

Fig. 5. Typical growth behavior of gamma-ray-induced three-line ESR spectrum in reactor-irradiated Al_2O_3 as a function of gamma-ray dose at 77°K. The experimental points and a pure exponential curve are shown for comparison.

ings: n_0 = the concentration of nonparamagnetic precursors of the paramagnetic centers present when gamma-ray irradiations are started, φ = gamma-ray dose rate, t = total irradiation time, f is the fraction of nonparamagnetic centers converted to paramagnetic centers per unit dose, and n is the concentration of paramagnetic centers present after an irradiation of φt. This is the behavior expected if the reactor irradiation had produced a nonparamagnetic center that was converted to a paramagnetic center by electron or hole trapping during the gamma-ray irradiation.[3] A determination of the constant f yields a value of 0.52 per 10^5 R.

Absolute intensity measurements of the three-line spectrum, made on a sample reactor irradiated for three weeks, showed that the spin concentration was about 5×10^{15} centers per cubic centimeter after exposure to a sufficient gamma-ray dose to reach saturation. In this sample, the center responsible for the 12-line spectrum was present to approximately the same concentration; but the central absorption corresponded to a concentration of about 1.5×10^{16} centers per cc.

The center causing the three-line spectrum was stable at 77°K; however, at a temperature in the vicinity of 180°K the spectrum was observed to anneal exponentially toward zero. This signified that the annealing followed first-order kinetics representing a single process with a unique activation energy. For such a process the governing equation would be of the form

$$dN/dt = -Nse^{-E/kT}, \tag{4}$$

where N is the number of paramagnetic centers, s is a jump frequency, and E is the activation energy.[16] The annealing behavior at two different temperatures was measured to permit a determination of E from the equation

$$E = k\left[\frac{T_1T_2}{T_2-T_1}\right]\ln\left[\frac{(d(\ln N)/dt)|_{T_2}}{(d(\ln N)/dt)|_{T_1}}\right], \tag{5}$$

which is readily obtained from the preceding equation. The ratio of the line intensity N to the initial line intensity N_0 is plotted (log scale) versus time in Fig. 6 for steady annealing temperatures of 178 and 184°K. From the slopes of the curves for these temperatures an activation energy of $E=0.7$ eV was obtained. Most likely the paramagnetic center is losing its charge, i.e., a hole or an electron, simply by thermal agitation.

The spectrum may be regrown by gamma-ray irradiation at 77°K following a room temperature anneal with no detectable change in maximum intensity, which suggests that exposure to purely ionizing irradiation changes the charge state of a defect created by the reactor irradiation. If an unannealed sample is exposed to daylight fluorescent light for 10 h at 77°K, the lines bleach to about one-fourth of their original intensities.

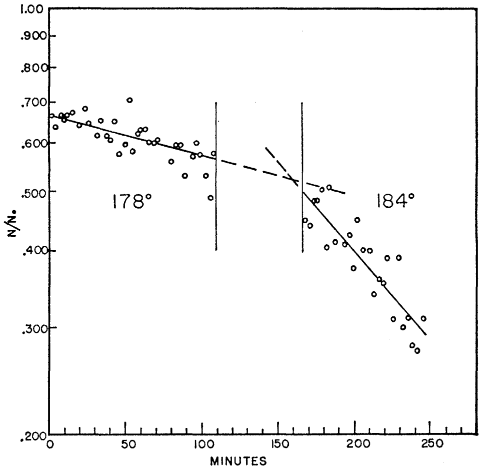

FIG. 6. The annealing characteristics of the gamma-ray-induced three-line ESR spectrum in reactor-irradiated Al_2O_3 for steady annealing temperatures of 178 and 184°K. The ordinate represents the ratio of the line intensity at a time t to the intensity at $t=0$, or N/N_0.

A careful study was made of the impurity resonance lines and the reactor-induced resonance lines during the growth and anneal of the three-line fine structure to determine if there were interrelations among the centers. No significant changes were detected in either the impurity resonance lines or the reactor-induced 12-line system. However, when the three-line spectrum was annealed at 175°K, one component of the central absorption spectrum was observed to increase in intensity.

It was found that during reactor irradiation the Fe^{3+} impurity resonance lines decreased in intensity significantly. To determine whether this change could be related to any of the reactor-induced defects, two Al_2O_3 samples having an order of magnitude-different iron-impurity concentrations were simultaneously reactor-irradiated for two successive two-day periods. The magnitudes of the reactor-induced 12-line spectra and the gamma-ray-induced three-line spectra were compared between the two samples after each irradiation. No significant differences were found in these spectra for the two samples. The Fe^{3+} lines decreased by about 40% for a two-day irradiation. It seems likely that the charge of the iron-impurity ion is changed by reactor irradiation so that the modified center is not observed by ESR.

DISCUSSION

As noted earlier in the paper, the large central absorption appears to be a superposition of many lines, probably due to a number of centers with spins of one-half, although the possibility of a larger effective spin with small zero-field splitting cannot be ruled out.

---

[16] A. W. Overhauser, Phys. Rev. **90**, 393 (1953).

At present there is little basis for further speculation about the nature of these centers.

By contrast with the central absorption, the 12-line spectrum conveys considerable information about a single type of center. The orientations of the site z axes and the fact that the axial component of crystal field greatly exceeds the rhombic component suggest that the center is associated with a pair of adjacent oxygen sites. It is proposed as a tentative model that this center results from a replacement collision in which an aluminum ion displaces a remote oxygen ion and remains in the oxygen site. In the collision, the aluminum captures one electron from the displaced oxygen and then forms an AlO molecule with one of the nearest O^{2-} ions. Presumably, the molecule is formed before the Al^{2+} ion can be ejected from the anion site. Subsequently, this molecule captures three more electrons to form $(AlO)^{3-}$ occupying a pair of adjacent anion sites within the same Al_2O_3 "molecule." The axis of the $(AlO)^{3-}$ molecular ion is nearly, but not precisely, parallel to the original O-O direction, since the aluminum does not remain precisely centered on the anion site; thus a pair of axes separated by 6° corresponds to a pair of sites which differ only in the interchange of the aluminum and oxygen within the $(AlO)^{3-}$ molecular ion. It can be seen from Fig. 1 that this results in 12 inequivalent sites; however, the sites are related in pairs by inversion through the void, so there are only six distinguishable spectra.

The choice of ionization state for the molecule is dictated by the fact that the observed spectrum corresponds to an effective spin of one. Molecular spectra attributed to AlO have been reported by a number of investigators.[17–20] It has been inferred from the molecular spectra that AlO is homologous to BO.[18,19,21] According to Mulliken,[21] the ground configuration of BO is $(K)\ (K)\ (z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)$, and from his correlation diagram for heteronuclear diatomic molecules, the next molecular orbital beyond $x\sigma$, in order of increasing energy, is $v\pi$. Accordingly, a plausible assumption for the ground configuration of $(AlO)^{3-}$ is $(K)\ (K)\ (L)\ (z\sigma)^2\ (y\sigma)^2\ (w\pi)^4\ (x\sigma)^2\ (v\pi)^2$, where the molecular orbitals arise from the $3s$ and $3p$ atomic orbitals of Al and the $2s$ and $2p$ atomic orbitals of O. By Hund's rules the ground term is $^3\Sigma^-$. It is also reasonable to assume that $(AlO)^{3-}$ is stabilized by the crystal field, since the molecule occupies a pair of divalent anion sites.

The absence of resolved hyperfine structure in the 12-line spectrum is made plausible on this model by the fact that the paramagnetic electrons are in π orbitals which preclude contact hyperfine interaction.

The center with spin $\frac{3}{2}$, produced by low-temperature gamma-ray irradiation following reactor irradiation, occupies a site with axial symmetry about the crystal c axis. The sites which exhibit this symmetry are the normal aluminum sites and the natural voids. The absence of resolved hyperfine structure suggests that the center is associated with an oxygen ion, since the large nuclear magnetic moment of Al^{27} would likely give rise to detectable hyperfine structure. The natural voids would be more likely sites for displaced ions. The only oxygen ion with the required spin of three-halves is O^+. Consequently, the three-line spectrum is attributed to interstitial O^+.

The fact that the three-line spectrum saturates in growth with gamma-ray dose, but the saturation level increases with reactor dose, indicates that the gamma rays simply change the charge state of a defect formed by reactor irradiation. This is substantiated by the investigations of gamma-ray irradiated Al_2O_3, in which it was shown that Co^{60} gamma-ray doses as high as 10^7R at 77°K do not cause atomic displacements detectable by ESR[11] and doses as high as 10^9R at room temperature do not create color centers.[3] Thus reactor irradiation must displace oxygens to interstitial sites, where they most likely reside as oxygen atoms O^0. The O^0 has spin one; however, no corresponding ESR spectrum is observed with axial symmetry about the c axis following reactor irradiation. It is postulated that interstitial O^0 is produced by reactor irradiation, but that the zero-field splitting of the spin degeneracy is too large to permit observation of the spectrum with an X-band spectrometer. It is planned to investigate this center further at shorter wavelengths.

SUMMARY

Reactor irradiation of aluminum oxide single crystals gives rise to two ESR spectra. A large, asymmetric, anisotropic absorption is detected which so far remains unidentified. A system of 12 lines has been shown to correspond to a spin-one center in six inequivalent sites with axes nearly along O-O directions. This spectrum is attributed to an $(AlO)^{3-}$ molecular ion formed by replacement collision and occupying a pair of adjacent anion sites. When reactor-irradiated Al_2O_3 is subsequently subjected to low-temperature gamma-ray irradiation, an additional three-line spectrum is developed. This spectrum corresponds to a spin-$\frac{3}{2}$ center with axial symmetry about the c axis, and is attributed to interstitial O^+. By inference, reactor irradiation alone produces interstitial O^0, whose spectrum is not observed because the zero-field splitting is too large.

---

[17] W. C. Pomeroy, Phys. Rev. **29**, 59 (1927).

[18] M. K. Sen, Indian J. Phys. **11**, 251 (1937).

[19] D. Roy, Indian J. Phys. **13**, 231 (1939).

[20] F. P. Coheur and B. Rosen, Mem. Soc. Roy. Sci. Liege **1941**, 405.

[21] R. S. Mulliken, Rev. Mod. Phys. **4**, 1 (1932).