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MASTER

ELECTRON PARAMAGNETIC RESONANCE ABSORPTION STUDIES

OF $(Al_2O_3)_{1-x}(Cr_2O_3)_x$ WITH

CONTROLLED NEUTRON TREATMENTS

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I. INTRODUCTION

Electron paramagnetic resonance (EPR) absorption has long been used to study the internal crystalline (electric) fields of single crystals. The EPR absorption line of a paramagnetic ion placed in a single crystal serves as a sensitive probe of the internal crystalline fields of the crystal. Recent work has suggested another role for the EPR absorption. While the position of resonance of the EPR line is determined by the internal crystalline fields, it is often the variation in the internal crystalline fields caused by imperfections in the single crystal, which determines the width of the EPR line. Thus, from a study of the linewidth of the EPR line, information can be obtained on the imperfections present in single crystals.

This dissertation reports such linewidth studies in single crystals of $(\text{Al}_2\text{O}_3)_{1-x}(\text{Cr}_2\text{O}_3)_x$, with $x = 0.0001\%$ to 0.01% . This crystal system is of interest as it has recently found use in laser and maser systems. Imperfections present in the Al_2O_3 samples may, to a certain extent, affect the performance of these devices. It is therefore significant to investigate these imperfections.

In using the chromium (Cr^{3+}) ion as a probe, it was essential to exclude, as far as possible, linewidth effects which are characteristic of the probe itself. To insure this, crystals of $(\text{Al}_2\text{O}_3)_{1-x}(\text{Cr}_2\text{O}_3)_x$ with very small Cr^{3+} concentrations were investigated. The linewidth obtained in this case is due to the interaction of the Cr^{3+} ions and the surrounding crystalline fields, rather than with other Cr^{3+} ions in the single crystal.

Imperfections in the crystal disturb the crystalline field and produce a dependence of the linewidth on the direction of the magnetic field. Some imperfections are present in the sample initially. Additional imperfections can be introduced by fast neutron irradiation.

In the experiment reported here, the angular variation of the width of the Cr^{3+} EPR line in unirradiated single crystals was measured and compared with the angular variation computed from a strain model, a mosaic model, and a hybrid model. Subsequently, the samples were irradiated with fast neutrons near room temperature. Information concerning the nature of the imperfection produced by the neutron irradiation was obtained by comparing the linewidth variation after fast neutron irradiation with the corresponding linewidth variation before irradiation.

Chapter II gives a brief discussion of the basic EPR theory pertinent to this work, a description of the experimental equipment used, and crystallographic data on the samples. Chapter III and IV report the studies on the unirradiated samples, and the fast neutron irradiated samples, respectively.

II. PRELIMINARY DISCUSSIONS

A. Basic EPR Theory

Electron paramagnetic resonance absorption is a method of observing the magnetic energy level structure of a paramagnetic ion in a magnetic field by inducing magnetic dipole transitions between the magnetic energy levels. Consider a free paramagnetic ion of spin $S=1/2$ located in free space in a magnetic field, H_0 . The interaction of the magnetic field and the spin of the ion is described by the Hamiltonian¹

$$\mathcal{H} = g\beta S_z H_0 \quad (1)$$

where g is the spectroscopic splitting factor, referred to hereafter as the g -value, β is the Bohr magneton ($e\hbar/2mc$), and S_z is the operator for the z component of the spin angular momentum. The g -value in this case would be 2.0023. The energy of the magnetic energy levels of Eq. (1) for $S=1/2$ is given by¹

$$E = \pm(1/2)g\beta H_0. \quad (2)$$

Figure 1 is a plot of Eq. (2), showing the separation of the magnetic energy levels in a magnetic field. The abscissa in Fig. (1) is the magnetic field and the ordinate is the energy of the magnetic energy levels. The energy levels labeled $+1/2$ and $-1/2$ correspond to the levels with the plus and minus sign in Eq. (2), respectively. The difference in energy between the two levels is given by:

$$\Delta E = g\beta H_0 [1/2 - (-1/2)] = g\beta H_0. \quad (3)$$

Fig. 1. The magnetic energy levels of a paramagnetic ion of spin $S=1/2$, located in a magnetic field. The value of the magnetic field increases to the right in the diagram.

To observe the spacing of the energy levels, the paramagnetic ion is subjected to electromagnetic radiation, hereafter referred to as microwaves, of frequency ν . Transitions will take place between the two energy levels via a magnetic dipole interaction if the energy of the microwaves, $h\nu$, is equal to the energy difference of the magnetic energy levels:²

$$\Delta E = g\beta H_0 = h\nu . \quad (4)$$

Equation (4) is called the resonance condition. When this condition is satisfied, power is absorbed by the paramagnetic ions from the microwaves.³ The values of the magnetic field H_0 for a fixed frequency, ν , at which the transitions take place, is called the resonant magnetic field.

The Hamiltonian of Eq. (1) applies to a free paramagnetic ion.

If this free ion is introduced into a diamagnetic single crystal, called hereafter the host crystal, by substitution of the paramagnetic ion for one of the non-paramagnetic ions in the crystal, Eq. (1) is replaced by a more general Hamiltonian⁴

$$\mathcal{H} = \beta \vec{S} \cdot \vec{g} \cdot \vec{H}_0 + \vec{S} \cdot \vec{D} \cdot \vec{S} , \quad (5)$$

where $\vec{g}$ and $\vec{D}$ are second order tensors. The tensors $\vec{g}$ and $\vec{D}$ arise from interactions between the paramagnetic ion and the local crystalline electric field produced by the surrounding host crystal ions.⁴ Equation (5) is called the spin Hamiltonian of the paramagnetic ion in the host crystal.⁵ The separation of the magnetic energy levels of Eq. (5) varies not only with the magnitude of the magnetic field

but also with the direction that the magnetic field makes with the crystallographic axes of the host crystal.⁶ Therefore, the resonant magnetic field will also vary, depending on the direction of the magnetic field. A graph of the angular variation of the resonant magnetic field is called an isofrequency plot. (See for example Fig. 7).

The resonant magnetic field of a collection of paramagnetic ions of the same species does not have an infinitely sharp value as would be inferred from Eq. (4). In particular, paramagnetic ions imbedded in a host crystal exhibit a distribution of resonant magnetic fields. This distribution can be caused by a variety of mechanisms. However, the mechanisms most pertinent to this work are the hyperfine interaction with the paramagnetic nuclei⁷, and imperfections in the lattice of the host crystal. These mechanisms will be explained in the following.

B. Hyperfine Broadening Mechanism

This section will describe the effects of the hyperfine interaction on the resonance condition. An exhaustive treatment of the hyperfine interaction is given in The Principles of Magnetic Resonance, by A. Abragam.⁸

If paramagnetic ions are introduced into a host crystal containing host nuclei with non-zero nuclear spins, an interaction takes place between the nuclear spins and the spins of the paramagnetic ions. This is called the hyperfine interaction. The effect of the

hyperfine interaction can be conveniently described in terms of an effective magnetic field (H_{ef}) at the site of the paramagnetic ion.^{9,10} There are, in general, many nuclear spins surrounding a given paramagnetic ion. The magnitude of H_{ef} is determined, among other things, by the nuclear spin quantum numbers of these neighboring nuclei. For paramagnetic ions at different sites, there will be, in general, different sets of spin quantum numbers for the surrounding nuclei, and thus different magnitudes of the effective magnetic field.

The total magnetic field at a paramagnetic ion will then consist of the external magnetic field and the effective magnetic field. Consequently, the resonance condition will become

$$h\nu = g\beta (H + H_{ef}). \quad (6)$$

Since H_{ef} varies from ion to ion, the value of the external magnetic field, H , necessary to satisfy the resonance condition will also vary from ion to ion. Thus, each paramagnetic ion in the host crystal will have a particular value of H at which resonance occurs. If the number of paramagnetic ions for which the resonance condition is satisfied at a particular value of H is plotted against H , a relatively broad, bell-shaped curve $f(H)$ is obtained, rather than a spike at the (single) resonant magnetic field given by Eq. (4). The recorded EPR absorption line is proportional to the derivative of $f(H)$ (See Chap. II, Sect. D). Therefore, the derivative will be referred to as the EPR line for convenience in the following.

Figure 2 illustrates a typical EPR line. H_0 on the figure is called the center of resonance of the EPR line. The (full) width of the

Fig. 2. An illustration of the EPR line. H_0 is the center of resonance. $2\Delta H$ is the full width and ΔH the half-width of the EPR line.

line, $2\Delta H$, is measured between the two peaks of the EPR line in units of the magnetic field. ΔH is then the half-width of the line.

For the case of hyperfine interactions in a host crystal containing paramagnetic ions in a low concentration, $f(H)$ has been shown to be symmetric about H_0 , and to have a Gaussian shape.^{11,12} Thus the EPR line in this case has the following shape:

$$df(H)/dH = (C)(H-H_0) \exp \left\{ -(H-H_0)^2 / [2(\Delta H)^2] \right\} \quad (7)$$

where C is proportional to the total number of paramagnetic ions, and H_0 is the center of resonance of the line. When a distribution of resonant magnetic fields is caused by the hyperfine interaction, the EPR line is said to be broadened by the hyperfine interaction.

C. Crystal Imperfections

The second major cause of broadening of the EPR lines is imperfections in the lattice of the host crystal. Three types of imperfections will be discussed in the present work: defects which produce strains; charged point defects; and a mosaic structure of the crystal. The effects of these are considered below.

In using Eq. (5) for all of the paramagnetic ions in the crystal, it has been assumed that these ions are all located at identical sites in the host crystal. However, the host crystal may contain varying local strains, in which case the host atoms surrounding the paramagnetic ions vary slightly in position from ion to ion. The values of the $\tilde{D}$ and $\tilde{g}$ tensors in Eq. (5), which determine the resonant magnetic field, depend on the local crystalline

field produced by the surrounding crystal atoms. Consequently, a variation in the positions of these atoms produces a variation in the resonant magnetic field.^{13,14} Thus varying local strains will produce a broadening of the EPR line. This type of broadening will be called strain broadening.

If there are charged point defects distributed throughout the lattice, the magnitude and direction of the electric field produced by them will vary from one paramagnetic ion to another. For those host lattices which lack inversion symmetry at the site of the paramagnetic ion,^{15,16} the application of an electric field causes a shift in the resonant magnetic field of the paramagnetic ion. Consequently, the resonant magnetic fields for these ions will vary, producing a broadening of the EPR line. This type of broadening will be called electric field broadening.

Some apparently single crystals are found to be composed of a large number of microcrystals in the form of a mosaic.^{17,18} These microcrystals can each be considered to be perfect host crystals, but the direction of their crystallographic axes vary slightly from one microcrystal to another. This produces a distribution of the direction of the crystallographic axes with respect to an external magnetic field. If the resonant magnetic field of the paramagnetic ion depends on the angles between the crystallographic axes and the magnetic field, a distribution of the direction of these axes will produce a distribution of resonant magnetic field values for the paramagnetic ions. This type of broadening will be called mosaic broadening.

Any combination of the imperfections discussed above might be present in the host crystal. Therefore, the observed width of the EPR line of the paramagnetic ions is expected to reveal the contribution of the individual broadening mechanisms mentioned above.

D. Experimental Equipment

The basic experimental apparatus used in this work was a Varian V-4500 X-band (8.2kMc/sec to 12.4kMc/sec) electron paramagnetic resonance spectrometer, with a 12 inch rotating magnet. A detailed description of the spectrometer system is given in Varian Associates manuals.^{19,20}

A brief outline of the spectrometer operation will be given in the following, making reference to the simplified block diagram of the spectrometer given in Fig. 3.

Microwaves are produced by the klystron (1) (See Fig. 3) and are propagated through waveguide containing: an isolater (2), variable attenuator (3), and a 20 deci-Bell (dB) coupler (4). The isolater (2) is a unidirectional attenuator which passes (microwave) power traveling toward the microwave bridge (5), but absorbs power traveling in the opposite direction. The variable attenuator (3) regulates the amount of power. The 20 dB coupler (4) allows one one-hundredth of the total power to enter the power meter (6).

The microwave bridge (5) consists of the resistive load (8), the microwave cavity (9), the detector crystal (12), and the four-arm directional coupler, called conveniently the magic T (7). The arms of the magic T (7) have been labeled A, B, C, and D.

Fig. 3. Schematic diagram of the Varian V-4500 EPR spectrometer.

Power from the klystron (1) enters the microwave bridge through arm A. The magic T (7) divides the power equally between arms B and C, with no power entering arm D. The power entering arm C is totally absorbed by the resistive load (8), while power traveling along arm B enters the (microwave) cavity (9). The cavity acts as a tuned circuit which stores microwave energy, producing an intense microwave magnetic field in the region of the sample (10).

Initially, the bridge is adjusted so that the cavity (9) absorbs all the power that enters arm B. When the direct current (D.C.) magnetic field (11) is adjusted so that the resonance condition is satisfied, the paramagnetic ions in the sample absorb power from the microwave field in the cavity. The power absorbed by the paramagnetic ions at a given magnetic field H is proportional to $f(H)$, the number of paramagnetic ions for which the resonance condition is satisfied. This absorption causes power to be reflected from the cavity back along arm B. Under certain conditions, to be described later, this reflected power is proportional to the power absorbed by the paramagnetic ions. The magic T divides this reflected power between arms D and A, no power entering arm C. The power entering arm A is absorbed in the isolator (2). The power entering arm D falls on the detector crystal (12), which produces a (voltage) signal, proportional to the power absorbed by the paramagnetic ions in the cavity.

To facilitate the detection of this signal, the method of field modulation and phase detection was employed. For this purpose, modulation coils (13) are mounted on the outside walls of the cavity in

such a way as to modulate the D.C. magnetic field by a small controllable amount. The modulation frequency employed in the spectrometer is 100 kc/sec. To obtain the magnetic field modulation, the output of a 100 kc/sec crystal oscillator (14) is amplified by a power amplifier (15) and applied to the modulation coils (13). As a consequence of this field modulation, the signal which appears at the detector crystal (12) is proportional to the derivative of $f(H)$. This can be seen from the following discussion. Figure 4 shows a typical plot of the power absorbed by the paramagnetic ions versus the magnetic field, $f(H-H_0)$ versus H . The curve labeled $f(H-H_0)$ shows a typical bell-shaped EPR line. H_0 is the center of resonance. A magnetic field modulation of a small fixed amplitude ΔH and of a fixed frequency (100 kc/sec) is added to the D.C. magnetic field, H . The power absorbed by the paramagnetic ions is consequently modulated at 100 kc/sec by an amount ΔP (See Fig. 4). The amplitude of this power modulation will be approximately equal to

$$\Delta P \approx \Delta H [df(H-H_0)/dH] \quad (8)$$

if ΔH is sufficiently small. The modulated power absorption, ΔP , causes power modulated at 100 kc/sec to be reflected from the cavity. Consequently, a signal proportional to ΔP , modulated at 100 kc/sec, appears at the detector crystal, along with an unmodulated signal proportional to $f(H-H_0)$.

The 100 kc/sec signal at the detector crystal (12) is amplified by the 100 kc/sec amplifier which also blocks the passage of the

Fig. 4. Illustration of the power absorbed by the paramagnetic ions as a function of the magnetic field, showing the effects of field modulation. The curve $f(H-H_0)$ gives the typical variation in the power absorbed as a function of the D.C. magnetic field. A field modulation of amplitude ΔH is applied to the D.C. magnetic field amplitude H at a frequency of 100 kc/sec. As a consequence of this modulation, the power absorbed is modulated by an amount ΔP , also at 100 kc/sec. H_0 is the center of resonance of the EPR line.

unmodulated signal. The modulated signal is phase-detected by the 100 kc/sec phase detector (17). The phase detector produces a D.C. voltage which is proportional to the modulated signal appearing at the crystal detector, and hence also to $df(H-H_0)/dH$. This D.C. signal is used to drive the pen of a chart recorder (18) while the chart is moved forward at a constant speed. To record the signal, the D.C. magnetic field is slowly moved through the resonance at a constant rate, and the recorder traces out the EPR line, proportional to $df(H-H_0)/dH$, on the chart, which can be subsequently calibrated in units of magnetic field. Figure 2, for example, illustrates a typical recorded trace.

The proportionality of the power absorbed by the paramagnetic ions to the power reflected from the cavity depends on the exact matching of the cavity resonance frequency ν_0 , to the frequency of the microwaves, ν . However, as the D.C. magnetic field is swept through the resonance, a shift in the resonant frequency of the cavity will occur. This produces additional reflected power in arm B of the bridge. The magnitude of this power depends on the difference between the cavity frequency and the microwave frequency. To eliminate this additional reflected power, called the dispersion signal, the microwave frequency must be continuously adjusted to match the resonant frequency of the cavity while the magnetic field is being swept through the resonance. The automatic frequency control unit (AFC) (19) is employed to accomplish this.

The AFC consists of a 10 kc/sec oscillator (20), a 10 kc/sec power

amplifier (21), a klystron control unit (22), a 10 kc/sec narrow band amplifier (23), and the 10 kc/sec phase detector (24). The 10 kc/sec oscillator (20) produces an output which is amplified by the 10 kc/sec power amplifier (21) and applied to the klystron control unit (22).

The effect of this applied voltage is to vary the frequency of the klystron by an amount $\Delta\nu$ at 10 kc/sec. Figure 5 shows the effect of this modulation on the power reflected from the cavity. The curve $P(\nu)$ in Fig. 5 illustrates the dependence of the power reflected from the cavity on the klystron frequency. ν_0 is the resonant frequency of the cavity, $\Delta\nu$ is the amplitude of the small frequency modulation. If $\nu \neq \nu_0$, the modulation produces a 10 kc/sec modulation of the reflected power $\Delta P'$. For the two conditions $\nu > \nu_0$ and $\nu < \nu_0$, the phase of the power modulation $\Delta P'$ differs by 180° . If $\nu = \nu_0$, only power modulation at 20 kc/sec appears on the reflected power.

A portion of the reflected power from the cavity falls on the detector crystal (12), producing a 10 kc/sec (voltage) signal proportional to $\Delta P'$, which will be called the AFC signal. This signal is amplified by the 10 kc/sec narrow band amplifier (23), which blocks the passage of the 100 kc/sec EPR signal appearing at the detector crystal. The AFC signal is phase detected by the 10 kc/sec phase detector (24). The output of the phase detector is a D.C. voltage which has one polarity if $\nu < \nu_0$ and the opposite polarity if $\nu > \nu_0$. If $\nu_0 = \nu$, the D.C. voltage is zero because the 10 kc/sec narrow band amplifier (23) blocks the 20 kc/sec AFC signal. This voltage

Fig. 5. The effect of frequency modulation on the power reflected from the cavity. The power reflected from the cavity as a function of frequency is given by $P(\nu)$. A modulation of the frequency by an amount $\Delta\nu$ at 10 kc/sec results in a 10 kc/sec modulation of the reflected power of amplitude $\Delta P'$. The resonance frequency of the cavity is given by ν_0 .

is applied to the klystron control unit in such a way as to shift the klystron frequency toward the cavity frequency until the two are equal. Thus, as the magnetic field passes through the resonance, the cavity resonant frequency ν_0 varies, but the klystron frequency ν is changed by the AFC so that at all times, $\nu_0 = \nu$. As this change in frequency is very small, the EPR lines observed using AFC are considered to be taken at a fixed frequency. As the D.C. magnetic field is swept through the resonance, $P(\nu_0)$ in Fig. 5 varies with the magnetic field. As $\nu_0 = \nu$, this variation is proportional to the curve labeled $f(H-H_0)$ in Fig. 4, if the field modulation is not employed. With the field modulation, $P(\nu_0)$ is modulated at 100 kc/sec. The resulting EPR line produced by the recorder is then proportional to $df(H-H_0)/dH$.

E. Crystallographic Data

The single crystal investigated in this dissertation was $(Al_2O_3)_{1-x}(Cr_2O_3)_x$ with $x = 0.0001\%$ to 0.01% , the chromium (Cr^{3+}) ion being the doping agent in the Al_2O_3 host lattice. This crystal is commonly called ruby.

The Al_2O_3 lattice has the point group symmetry D_{3d} (See Ref. 21). The orthogonal crystallographic axes of the lattice are shown in Fig. 6. The C axis is an axis of three-fold symmetry. The +A axis corresponds to a two-fold axis. The axis labeled M is contained in a mirror plane which also contains the C axis. The Al^{3+} sites in the lattice have only C_3 symmetry pertaining to the C axis.²¹

There are four crystallographically inequivalent Al^{3+} sites in the lattice. The Cr^{3+} ions substitutionally replace at random some

Fig. 6. The crystallographic axes of the Al_2O_3 lattice and the coordinate system to be used in this work.

of the Al^{3+} ions at all four sites with equal probability.¹⁵ The four inequivalent Cr^{3+} sites will be called (a), (b), (c), and (d), for convenience. Each Cr^{3+} site is surrounded by six oxygen ions.^{23,24} If the inversion operation ($\vec{r} \rightarrow -\vec{r}$) is performed on this complex of seven ions, using Cr^{3+} site (a) as the center of inversion, the resulting configuration is identical to the configuration of site (b). This is also the case for the configurations of sites (c) and (d). However, if the inversion operation is performed on site (a), the resulting configuration is not identical to the original configuration of site (a). This is also the case for the sites, (b), (c), and (d).¹⁵

While these sites are crystallographically inequivalent, they may or may not be distinguishable in a given EPR experiment. Assuming a perfect Al_2O_3 lattice, the four Cr^{3+} sites are indistinguishable by means of EPR absorption. However, if the lattice is not perfect, or if external electric fields are applied to the lattice, some of the sites may become distinguishable.¹⁵ This will be discussed in further detail in Chapter IV.

The Cartesian coordinate system, O-xyz, to be employed in this work is also given in Fig. 6. The Cr^{3+} site is taken at O. The x, y, and z axes correspond to the +A, M, and C axes, respectively. The direction of the magnetic field represented by the line $\overline{\text{OH}}$ is given by the angles θ and ϕ .

III. LINEWIDTH STUDIES IN UNIRRADIATED SAMPLES*

A. Introduction

Recent electron paramagnetic resonance (EPR) absorption studies^{26,27} of the Cr^{3+} ion in single crystals of $(\text{Al}_2\text{O}_3)_{1-x}(\text{Cr}_2\text{O}_3)_x$ with x close to 0.03% have indicated that the width of the three EPR lines corresponding to the $(1/2 \rightarrow -1/2)$ and $(3/2 \rightarrow 1/2)$ transitions is approximately 12 gauss, when the external magnetic field is parallel to the crystallographic [111] or C axis of the samples (See Fig. 6). For such small values of x , the spin-spin interactions among the Cr^{3+} ions contribute insignificantly to the linewidth. For example, when x is taken to be 0.001%, the linewidth of the $(3/2 \rightarrow 1/2)$ transition, if broadened solely by the spin-spin interaction, would not be larger than 0.5 gauss.²⁶ Under these circumstances, the hyperfine interactions between the electronic spin of each Cr^{3+} ion and its neighboring Al^{27} nuclei of spin 5/2 and of 100% abundance have to be considered as being responsible for the linewidth. According to Laurance *et. al.*,²⁷ the hyperfine broadening mechanism would lead to a linewidth of 9.7 gauss. This is approximately 81% of the observed width of 12 gauss. Thus the hyperfine broadening mechanism appears to be the major, but not the sole, source of the linewidth for the case of the magnetic field being parallel to the C axis.

The linewidth is expected to vary depending upon the angle θ between the C axis and the magnetic field if the dipolar part of the hyperfine interactions is appreciable. The expected anisotropy of the linewidth may be calculated in terms of the hyperfine coupling constants

* This chapter is based on a publication by the author and Professor Y.W. Kim (See Ref. 25).

measured by Laurance et. al.²⁷ The hyperfine broadening mechanism then would predict a variation of the linewidth between 9.4 gauss and 9.9 gauss [See Eq. (B.14) of Ref. 26], when the samples are rotated over the 90° range of θ about an axis which is perpendicular to the C axis. In the following, the axis of rotation is referred to as the R axis.

However, the experimental results obtained from the samples with x less than 0.01% investigated in the present work indicate that the linewidth varies by approximately a factor of five over the 90° range of θ , and also that the angular dependence of the width is not the same for individual EPR lines. Thus, the hyperfine broadening mechanism alone is not capable of fully accounting for the experimental results.

In order to understand this discrepancy, three different models are considered. In the first, the samples are viewed as being in the form of a mosaic of microcrystals. In the second model, the system is viewed as having random localized strains. The third model is a hybrid of the above two models. The mosaic model is similar in nature to the model employed by Shaltiel and Low¹⁷ for the case of Gd in ThO_2 , and the strain model, to that used by Feher²⁸ to explain the broadening of Mn and Fe absorption lines in MgO.

Elementary theories of the mosaic and strain models are given in the following section. The experimental results and discussions are presented in section C and a conclusion is drawn in the last section.

B. Elementary Theories

Introduction

The magnetic energy level structure of a Cr^{3+} ion in single

crystals of $(Al_2O_3)_{1-x}(Cr_2O_3)_x$ has been conveniently described in terms of an axially symmetric spin Hamiltonian^{26,27,29-31}

$$H = g_{||} \beta S_z H_z + g_{\perp} \beta S_{\perp} H_{\perp} + D[S_z^2 - (1/3)(S)(S+1)] , \quad (9)$$

where the z axis is the axis of symmetry, which is the C axis of the sample, and S stands for an effective spin of 3/2. The two subscripts $||$ and $\perp$ mean "parallel" and "perpendicular" to the z axis, respectively. The values of the constants in Eq. (9) are as follows:

$$g_{||} = 1.9840 , \quad g_{\perp} = 1.9867^{29,30} , \quad \text{and } D = -5.75 \text{ kMc/sec.}^{31} \quad (10)$$

When the resonance condition is established with a fixed microwave frequency ν_0 , and a slowly swept magnetic field, the EPR lines are observed at certain values of the magnetic field, which vary depending upon the value of θ . The curves in Fig. 7 represent an experimental plot of H versus θ for the EPR lines observed from a sample with $x = 0.001\%$ for the value of ν_0 equal to 9.472 kMc/sec. Because of the fixed microwave frequency ν_0 , the curves will be referred to as the isofrequency curves for convenience in the following. The magnetic levels, the resonance transitions and the isofrequency curves are labeled in accordance with the conventions employed by Weber,³² with the proper correction for the sign of D in Eq. (9).

If the sample is crystallographically "perfect", the local C axes passing through the sites of the Cr^{3+} ions are all parallel among themselves, and should make the same angle with the magnetic field. The common direction of the local C axes is then the direction of the C axis of the perfect sample. Also D in Eq. (9) is the same

Fig. 7. The isofrequency curves of the EPR lines of the Cr^{3+} ions in $(\text{Al}_2\text{O}_3)_{1-x}(\text{Cr}_2\text{O}_3)_x$ with $x = 0.001\%$ for the microwave frequency $\nu_0 = 9.472$ kMc/sec. The four energy levels of the ions are labeled, 1, 2, 3, and 4 from the highest level down (see Ref.32). Thus the curve (1-2) corresponds to the transition between the levels 1 and 2. The notations HF and LF are used to distinguish two EPR lines, one at higher field (HF) and the other at lower field (LF), pertaining to a pair of levels. Portions of the curves (1-3), (2-3), and (3-4) are missing for some values of θ , because the corresponding transitions are either forbidden or yield almost unobservable EPR lines.

for all Cr^{3+} ions and the z direction used in Eq. (9) is along the crystallographic C axis. Thus the magnetic levels, and consequently the resonant magnetic field positions of the EPR lines, are coincident for all the Cr^{3+} ions. This means that the width of the EPR lines observed from the perfect sample should be identical to that of the EPR lines pertaining to a single Cr^{3+} ion.* Accordingly, if the local C axes are not all parallel, and/or the value of D in Eq. (9) is not the same for all the Cr^{3+} ions of the sample, the sample may be viewed as being imperfect.

Mosaic Model

As a simple case of the imperfect sample, the sample is viewed as consisting of many perfect microcrystals in a mosaic form. In order to simplify the model, the following assumptions are introduced:

(a) The number of Cr^{3+} ions remains practically constant from one microcrystal to another. (b) The formation of the mosaic is such that, when drawn from a common origin in space, the unit vectors along the C axes of the microcrystals lie within an axially symmetric cone whose aperture angle $2\beta_0$ is very small. (c) The unit vectors are distributed symmetrically about the axis of the cone, and the angular deviation, β , of individual unit vectors from the cone axis may be described in terms of a Gaussian distribution with a suitable standard deviation $\Delta\beta$, which is much smaller than β_0 . The cone axis is then taken to represent the effective C axis of the imperfect sample. Thus, a perfect sample corresponds to the case where β_0 vanishes.

* Since the x value is less than 0.001%, the line broadening due to the spin-spin interactions among the Cr ions is insignificant. Then, the linewidth is very likely to be determined by the hyperfine interactions.

Let the cone axis (representing the effective C axis) be the polar axis of a right-handed coordinate system. Then, a unit vector (representing a local C axis) lying in the cone can be specified in terms of a polar angle β and an azimuthal angle ψ in this frame of reference. According to assumption (c), the probability of the unit vector (β, ψ) lying within a differential solid angle $d\Omega$ in the direction of (β, ψ) may be written as follows:

$$P(\beta) d\Omega = B \exp [-\beta^2/2(\Delta\beta)^2] \sin\beta d\beta d\psi \quad (11)$$

where B is a normalization constant for the Gaussian distribution. Now let the angles that the magnetic field makes with the polar axis and with the unit vector (β, ψ) be θ and θ' respectively, as shown in Fig. 8(a). Since β_0 is assumed very small, the surface formed by the intersection of the cone and a unit sphere centered at O may be taken to be practically flat. The coordinate system shown in Fig. 8(b) may then be used to express $P(\beta)d\Omega$ in terms of $\theta-\theta'$, by using the following approximations:

$$\beta^2 = x^2 + y^2, \quad (12a)$$

$$\psi = \tan^{-1} (y/x), \quad (12b)$$

$$d\Omega = \sin\beta d\beta d\psi = \beta d\beta d\psi = dx dy, \quad (13)$$

$$x = \theta' - \theta, \quad (14)$$

and also using the assumed Gaussian distribution of β :

$$P(\beta)d\Omega = P(x,y)dx dy = B \exp \left\{ -[x^2+y^2]/[2(\Delta\beta)^2] \right\} dx dy, \quad (15)$$

where $\Delta\beta$ is the half-width at maximum slope of the distribution of β .

Thus

$$P(\theta'-\theta)d\theta = P(x)dx = B \exp[-x^2/2(\Delta\beta)^2]dx \int_{-\infty}^{+\infty} \exp[-y^2/2(\Delta\beta)^2] dy, \quad (16)$$

which can be transformed into

Fig. 8. (a) The coordinate system for the mosaic model. The direction of the C axis (OL) of a perfect microcrystal is specified by the angles β and ψ on the unit sphere centered at O. Z is the effective C axis for the sample and H is the direction of the magnetic field. The angle θ is measured between the directions of H and Z, θ' between H and L. The C axes of the microcrystals constituting the sample lie within the cone with an apex angle $2\beta_0$. (b) When β is small, the base of the cone in (a) can be considered to be flat. The coordinates are then given by x and y, with E as the origin. The shaded area corresponds to the differential area having equal values of θ' .

$$P(\theta' - \theta) d\theta' = C \exp [-(\theta' - \theta)^2 / 2(\Delta\beta)^2] d\theta' . \quad (17)$$

The use of the isofrequency curves

$$\theta = f(H) \quad (18)$$

makes it possible to transform $P(\theta' - \theta) d\theta'$ into

$$P(H' - H_E) dH' = C \exp \left\{ -[f(H') - f(H_E)]^2 / [2(\Delta\beta)^2] \right\} (df/dH') dH' , \quad (19)$$

where H_E is the position of resonance for θ .

If the shape of the EPR line E for a single Cr^{3+} ion in a perfect crystal is given by $g(H - H_E)$, the shape of the "composite" line E for the mosaic sample will be given by

$$G(H - H_E) = \int g(H - H') P(H' - H_E) dH' . \quad (20)$$

It is easily seen that G is dependent on the isofrequency curve of the EPR line E. Because of assumption (c), $P(H' - H_E)$ is appreciable only when the difference, h , between H' and H_E is small. Accordingly, $f(H')$ and df/dH' in Eq. (19) may be expanded in powers of h in the vicinity of H_E :

$$H' = H_E + h ; \quad (21)$$

$$f(H') = f(H_E) + [df(H_E)/dH']h + \dots \quad (22)$$

If the derivatives of order higher than 1 are neglected, Eq. (20) can be written as follows:

$$G(H - H_E) = C \int g(H - H_E - h) \exp[-h^2(f')^2 / 2(\Delta\beta)^2] f' dh , \quad (23)$$

where $f' = d\theta/dH$. Since the EPR line E for each microcrystal is primarily broadened by the hyperfine interactions,²⁷ the shape function $g(H - H_E)$

for the line is very likely to be Gaussian.³³ If, then, g is taken to be Gaussian with a half-width Δg at maximum slope, the shape $G(H - H_E)$ of the "composite" E is also a Gaussian, with the full width $2\Delta G$ at maximum slope

$$2\Delta G = 2[(\Delta g)^2 + (f')^{-2}(\Delta \beta)^2]^{1/2}. \quad (24)$$

Experimentally, $2\Delta G$ is measured, and f' obtained from the isofrequency plot for individual EPR lines. If the line is Gaussian, and the value of Δg is available, then Eq. (24) yields the value of $\Delta \beta$, which is a measure of the mosaic model.

Strain Model

As another simple case of the imperfect sample, the sample may be such that D of Eq. (9) varies from site to site of the Cr^{3+} ions, while the variation of the local C axis is insignificant. The small deviation of D from the value of D in the perfect sample may be described in terms of an additional term in the spin Hamiltonian [Eq. (9)];

$$\mathcal{H}' = \sum_{i,j} D_{ij} S_i S_j \quad (25)$$

where the D_{ij} depend on the strain constants at local Cr^{3+} sites.³⁴⁻³⁶

The cartesian components S_i of $\vec{S}$ have the same reference system as used in Eq. (9). When the strain term $\mathcal{H}'$ is treated as a first-order perturbation to Eq. (9), the resonant magnetic field value can be given as

$$H' = H + \sum_{ij} D_{ij} [\langle a | S_i S_j | a \rangle - \langle b | S_i S_j | b \rangle] dH/dv \quad (26)$$

where a and b label the levels of the Cr^{3+} ion between which the transition

takes place and $dH/d\nu$ is the change in magnetic field per change in frequency at the (constant) resonant frequency. The distribution of H' in the vicinity of H is determined by the distribution of the D_{ij} .

Thus, one sees the possibility of a broadening of the line due to local strains.

If, for simplicity, the distributions of the D_{ij} 's are assumed to be all Gaussian and independent of one another, the resulting full width at maximum slope due to strain alone would be given by

$$2\Delta H_S = 2 \left\{ \sum_{ij} \sigma_{ij}^2 [\langle a | S_i S_j | a \rangle - \langle b | S_i S_j | b \rangle]^2 [dH/d\nu]^2 \right\}^{1/2} \quad (27)$$

where the σ_{ij} are the half-widths at maximum slope of the distributions of the D_{ij} in energy units.

The strain broadening and the hyperfine broadening are statistically independent and their effects should be added in the root-mean-square fashion. The full width at maximum slope would then be given by:

$$2\Delta G = 2[(\Delta g)^2 + (\Delta H_S)^2]^{1/2} \quad (28)$$

Hybrid Model

The two preceding models may be combined to form a third model under the following assumptions. Each microcrystal of the mosaic model is now subject to random local strains as in the strain model. A first approximation to the resulting linewidth of such a model would be to treat both mosaic and strain effects as statistically independent.

The resulting full width of the lineshape would be then given by

$$2\Delta G = 2[(\Delta g)^2 + (f')^{-2}(\Delta\beta)^2 + (\Delta H_S)^2]^{1/2} \quad (29)$$

C. Experimental Results and Discussions

Single-crystal boules of $(Al_2O_3)_{1-x}(Cr_2O_3)_x$ with x values being nominally equal to 0.01%, 0.001% and 0.0001% have been purchased from the Linde Company, East Chicago, Indiana. Cubic samples of dimensions 3mm x 3mm x 3mm have been prepared from these boules in such a way that one of the cubic faces is normal to the C axis which has been determined by means of Laue back-scattering x-ray patterns.

EPR absorption studies of these samples have been conducted at room temperature by means of a Varian 4500 EPR spectrometer assembly operated at X-band microwave frequencies. The angular dependence of the EPR lines has been investigated by rotating the samples about R axes with different values of ϕ , perpendicular to the C axis as well as to the magnetic field (See Fig. 6.)

The curves in Fig. 7 represent the isofrequency curves (H versus θ) which have been obtained experimentally from a sample with an x value equal to 0.001%. At $\theta = 0^\circ$, for example, only three lines are observable, and their widths are 11.0, 12.3, and 12.4 gauss for the lines $(1 \rightarrow 3HF)$, $(1 \rightarrow 3LF)$, and $(1 \rightarrow 2)$, respectively. The dependence of the measured width of individual EPR lines on θ is illustrated by the heavy solid curves connecting the vertical bars in Fig. 9. The ordinate and abscissa represent the width and the

Fig. 9. A comparison of the observed and calculated angular dependences of the EPR linewidth. For example, (b) illustrates the comparison for the transition (1-2). The observed angular dependence is indicated by the solid curve joining the "error bars" (for $x = 0.001\%$) and the crosses (for $x = 0.01\%$), while the calculated angular dependence is indicated by the other curves based on the mosaic model with varying $\Delta\beta$, the strain model, and the hybrid model.

angle of rotation, respectively. Over the 90° range of θ , the width varies substantially, and its angular dependence is different for different lines. The shape of individual lines has been found to be approximately Gaussian except for a few orientations. The observed linewidth variation has been found to be virtually independent of the different choice of R axes (independent of ϕ), and crystal boules of different x value. Thus, the width variation seems to be a general property of low Cr-concentration samples. To illustrate the concentration independence, the linewidth data taken on a sample with $x = 0.01\%$ is shown by crosses in Figs. 9(b), (c), and (d).

The linewidth variation of the line $(2 \rightarrow 3LF)$ has not been investigated in the present work. This is because the line overlaps a line belonging to the impurity Fe^{3+} spectrum for almost the entire range of θ , and the overlap is serious enough to make linewidth data for the $(2 \rightarrow 3LF)$ line meaningless.

The value of Δg in Eqs. (24), (28), and (29) has been chosen to be one half of the full width (11.0 gauss) of the line $(1 \rightarrow 3HF)$ at $\theta = 0^\circ$. The following reasons may be cited for choosing this value of Δg . First, $(1/f') = dH/d\theta$ vanishes at $\theta = 0^\circ$ and accordingly the mosaic effect does not contribute to the linewidth. Secondly, the line at this orientation corresponds to the transition $(1/2 \rightarrow -1/2)$ and consequently, $[\langle 1/2 | S_i S_j | 1/2 \rangle - \langle -1/2 | S_i S_j | -1/2 \rangle]$ vanishes for all i, j and thus the strain effect also gives no contribution to the linewidth. However, for the other lines at $\theta = 0^\circ$, which correspond to $(3/2 \rightarrow 1/2)$ transitions, the matrix elements of $S_i S_j$ do not vanish. Therefore the chosen width of 11.0 gauss is expected to be the closest to the width of the line for a perfect sample.

In order to apply Eq. (24), which gives the contribution of the mosaic model alone, the first derivative, $dH/d\theta = (f')^{-1}$ has been evaluated by means of the isofrequency curves $\theta = f(H)$ in Fig. 7. Three values of $\Delta\beta$, 0.08° , 0.10° , and 0.14° have been chosen to compute the angular dependence of the linewidth predicted by Eq. (24). The calculated values are represented by the curves with $\Delta\beta$ values indicated in Fig. 9. Of the three alternative values of $\Delta\beta$, the case of $\Delta\beta = 0.10^\circ$ seems to yield the most optimum fitting to the observed curves.

To evaluate the linewidth variation due to the strains by means of Eqs. (27) and (28), the eigenfunctions of Eq. (9) have been obtained as a function of θ by means of a computer and the matrix elements of $S_i S_j$ evaluated for the appropriate levels represented by the eigenfunctions. The value of dH/dv has been obtained by similar computational method.

Because of the axial symmetry of Eq. (9), and the fact that the value of D_{yy} can be subtracted from all the diagonal elements of D_{ij} without change in the relative spacing of the magnetic levels, the only spin operators that contribute to Eq. (27) are S_x^2 , S_z^2 , and $(S_x S_z + S_z S_x)$. A Gaussian distribution has been assumed for each of D_{xx} , D_{zz} , and $D_{xz} (= D_{zx})$, and the half-widths, σ_{xx} , σ_{zz} , and σ_{xz} , of these distributions have been treated as adjustable parameters. The solid curves labeled "strain" in Fig. 9 represent the calculated linewidth variation obtained by the optimum values of the parameters;

$$\sigma_{xx} = 6.25 \text{ Mc/sec.}, \quad \sigma_{zz} = 2.25 \text{ Mc/sec.}, \quad \sigma_{xz} = 10.6 \text{ Mc/sec.} \quad (30)$$

In using the hybrid model [Eq. (29)], the following optimum value for the parameters were used:

$$\sigma_{xx} = 6.25 \text{ Mc/sec}, \sigma_{zz} = 2.25 \text{ Mc/sec}, \sigma_{xz} = 3.85 \text{ Mc/sec}, \Delta\beta = 0.08^\circ. \quad (31)$$

The linewidth variation computed from Eqs. (27) and (29) with these values of the parameters is illustrated by the curves labeled "hybrid" in Fig. 9.

A survey of Fig. 9 indicates that all of the three proposed models qualitatively predict the observed linewidth variation, and that the strain model is the best of the three. None of the models, however, predicts quantitatively the variation over the entire range of θ . This failure is particularly severe in the region around $\theta = 25^\circ$ for the $(1 \rightarrow 3\text{HF})$ and $(1 \rightarrow 3\text{LF})$ transitions, and around $\theta = 85^\circ$ for the $(2 \rightarrow 3\text{HF})$ transition. Also, the $(3 \rightarrow 4)$ transition shows the anomaly that the peak predicted by all three models is displaced from that of the experimental peak by about 5° . Repeated experimental investigations of the peak region have failed to eliminate the shift of the peaks.*

A few possible causes may be speculated for the lack of quantitative agreement between the theoretical predictions and the experimental results in some angular regions.

* In retrospect, a more satisfactory choice of spin operators would have been $S_x^2 - S_y^2$, S_z^2 , and $S_x S_z + S_z S_x$. However, if these spin operators are used to fit the experimental data of Fig. 9, no noticeable improvement is obtained (See footnote on page 38).

First, two points pertaining to the mosaic model should be re-examined: (i) The formation of the mosaic in the samples might not be "random".¹⁸ If this is the case, the cone in Fig. 8(a) would not be axially symmetric, and accordingly, different choices of the R axis of rotation would yield different linewidth variations. Experimentally, however, no dependence of the linewidth variation on the choice of the R axis has been noticed. (ii) The neglect of the derivatives of $\theta = f(H)$ of order higher than the first might not be proper in obtaining Eq. (23). A discouraging consequence of including the higher order derivatives in Eq. (23) is that the second factor in the integrand becomes non-Gaussian and consequently the shape of G would deviate from the Gaussian shape. Experimentally, however, the observed shape of G is practically Gaussian, except for a few orientations, as mentioned previously. Therefore, it appears that the simple mosaic model used in the present work is not mainly responsible for the quantitative discrepancy between the experimental and calculated results. It is interesting to note here that a mosaic model similar to the present one has been successfully employed by Shaltiel and Low for the case of Gd ions in ThO_2 ,¹⁷ and the value of $\Delta\beta$ based on the former model is very close to that of $\Delta\beta$ based on the present model. There is also an evidence in support of the actual mosaic formation of single crystals of Al_2O_3 ,¹⁸ which would correspond closely to the samples investigated in the present work.

Secondly, it is true that the strains characterized by D_{ij} in Eq. (26) are of a special nature, which would correspond to the case of an axially symmetric distribution of strains at each Cr^{3+} site.

Two types of strains which are a little more general than the one used in the present strain model may be considered: (i) The strains are such that the local C axis is also "tipped" from its direction in a perfect sample. This case is very similar to the hybrid model used in the present work. However, as one can see from Fig. 9, the hybrid model is less successful than the strain model. (ii) The strains are such that the local C axis can no longer be defined. For this case, the spin Hamiltonian itself given by Eq. (9) is inadequate, because the axial symmetry of the D tensor is no longer valid. This type of strain is expected to originate more in samples of Cr-concentrations much larger than 0.01%. So far, however, the spin Hamiltonian given by Eq. (9) has been found to be satisfactory even for samples of larger concentrations.^{31*}

Thirdly, in the case of the strain model, the g values have been taken to remain the same from one Cr³⁺ site to another. Strictly speaking, this is not valid, because a variation of the strain parameters is related to a variation of g value.³⁷ Recently, Scott *et. al.*, have reported on EPR line broadening due to the g-value variation in rare-earth salts.³⁸ This mechanism, however, does not appear to be noticeably effective for the Cr³⁺ ions investigated in the present work (See Appendix A). Nevertheless, possible effects of varying the g values depending on different sites of the ions have been investigated

* In the irradiated samples, to be discussed in Chapter IV, it will be shown that strains are the most likely cause of the additional broadening due to irradiation. When the rms values of the strains are scaled down to match the linewidth at $\theta = 0^\circ$ for the line (1-2) of Fig. 9, the predicted anisotropy is much less pronounced than in Fig. 9. It appears, therefore, that the strains are not primarily responsible for the observed anisotropy in Fig. 9.

by means of a computer. The results of the investigation, however, have indicated that the anisotropy of the linewidth based on the g-value variation is not consistent with the observed anisotropy at all.

Thus, it appears that the quantitative discrepancy between the observed and calculated results in Fig. 9 is not due to the simple nature of the models used in the present work. But some other causes are probably responsible, at least in part, for the discrepancy. In this respect, it is interesting to note that some workers have recently encountered similar situations.^{17,28}

D. Conclusion

The angular dependence of the width of the EPR lines of the samples of $(\text{Al}_2\text{O}_3)_{1-x}(\text{Cr}_2\text{O}_3)_x$ with x less than 0.01% have been investigated by rotating the samples about an axis perpendicular to the C axis of the samples. The observed anisotropy of the width varies from one EPR line to another. The width varies by more than a factor of 5 over the 90° range of the angle of rotation. Such variation of the width is not easily explained in terms of only the hyperfine interactions of Cr^{3+} ions with the neighboring Al^{3+} ions.

To account for the observed linewidth variation, three alternative models have been employed: The mosaic model, the strain model, and the hybrid model. The linewidth variation predicted by each of the models agrees qualitatively with the observed linewidth variation. Quantitatively, however, the models are not satisfactory particularly in some angular regions.

Re-examination of the basic assumptions pertaining to the individual models in reference to the experimental results seem to suggest that the

quantitative discrepancy between the observed and calculated results is not due to the defects of the individual models. It is probably, at least in part, due to some causes which are different in nature from the mechanisms considered in the present work.

IV. LINEWIDTH STUDIES IN IRRADIATED SAMPLES *

A. Introduction

The EPR absorption of the Cr^{3+} ions facilitates studies of the effects of radiation-induced defects on the Cr^{3+} sites. At least some of the radiation defects are expected to become sources of local strain and would disturb the (local crystalline) fields of the Cr^{3+} ions. The disturbed fields would constitute a distribution, which is different from the distribution of the fields before radiation treatments. The new distribution of the fields would then lead to a change in the linewidth of the EPR absorption after irradiation. On the other hand, the original mosaic structure is not expected to be affected significantly, if any, since the radiation induced point defects would not be able to easily change the orientation of the microcrystals in the samples. If some of the radiation defects happen to be electrically charged, they would produce static electric fields of varying intensity at the Cr^{3+} sites. This static electric field interacts with the Cr^{3+} ion and perturbs the EPR energy levels of the ion as pointed out by Royce and Bloembergen.¹⁵ Therefore, the observed EPR spectrum after irradiation would reflect the effects of the strains and/or the electric fields.¹³

The present chapter summarizes the results of a study of the Cr^{3+} resonances in fast neutron irradiated samples. The experimental results are presented in Section B. Theoretical models are given in Section C to account for the observed results. A brief conclusion is drawn in Section D.

* Chapter IV forms the basis of a paper submitted to The Physical Review (1966), by the present author and Professor Y. W. Kim.

B. Experimental Results

Single crystal samples of $(Al_2O_3)_{1-x}(Cr_2O_3)_x$ with x equal to 0.01% and 0.001% with the dimensions 3 mm x 3 mm x 3 mm to 2 mm x 1.5 mm x 1.5 mm have been prepared from the boules used in the experiments reported in Chap. III. The crystallographic C, +A and M axes of the samples²² were determined by means of Laue back scattering x-ray patterns. The width and shape of the EPR absorption lines of the Cr^{3+} ions in these samples have been investigated by rotating the samples about axes perpendicular to both the C-axis of the samples and the direction of the external magnetic field. Figure 6 illustrates the geometry of the rotation. The direction of the magnetic field is specified in terms of two angles, the polar angle θ , and the azimuthal angle ϕ . The axis of rotation R is held perpendicular to both the C axis and the magnetic field.

Subsequently, these samples have been given fast neutron doses between 10^{18} nvt and 10^{19} nvt. The effects of the irradiation have been investigated by comparing the anisotropy of the width of the EPR absorption line of the Cr^{3+} ions before and after the irradiation.

The neutron irradiation has been found to affect the EPR absorption of the Cr^{3+} ions in three aspects. First, after the irradiation, the resonant magnetic field value H of each EPR line is slightly shifted with respect to the resonant field value of the corresponding EPR line before irradiation. For example, in the case of a 1×10^{19} nvt sample, the line (3-4) at $\theta = 90^\circ$ is located at a magnetic field value approximately 8 gauss less than the resonant magnetic field (5,377.9 gauss) of the same line before the irradiation, when the microwave frequency is 9.475 kMc/sec. The maximum shift

is less than 0.2% and the resulting small changes in the constants of the spin Hamiltonian will be neglected in the following. Further discussions of the significance of this shift will be given in Section C. Secondly, the linewidth after irradiation is wider than the corresponding linewidth before irradiation. Furthermore, the linewidth after irradiation is dependent on θ and ϕ while before irradiation it was found to be independent of ϕ (See Chap. III, Sect. C). Figure 10 illustrates the observed anisotropy of the linewidth for the lines; (a) (1-2), (b) (2-3HF), (c) (3-4), (d) (1-3HF), and (e) (1-3LF). The A, B and C curves indicate the dependence of the linewidth on θ , before the irradiation, for $\phi = 0^\circ$ after irradiation, and for $\phi = 30^\circ$ after irradiation, respectively. As for the reasons for choosing $\phi = 0^\circ$ and $\phi = 30^\circ$, refer to the discussions of Fig. 11 below. The line (2-3LF) overlaps with an Fe^{3+} line and its measured width is liable to contain a large amount of error. Accordingly, the anisotropy of the line (2-3LF) is not illustrated in the figure. Figure 11 illustrates typically the dependence of the line (1-2) on ϕ , while θ is kept at 23° . The ϕ -anisotropy exhibits a fairly satisfactory period of 60° , alternately a minimum and a maximum for every 30° . This is also true of the other lines.

Thirdly, the lineshape after the irradiation deviates from the Gaussian shape observed for the line before irradiation (See Chap. III, Sect. C). The deviation is more noticeable as the neutron dosage is increased. It is also noticed that the lineshape for a given line varies depending upon θ and ϕ .

C. Elementary Theories

Introduction

In Chapter III, the anisotropy of the linewidth before irradiation

Fig.10. The observed θ -dependence of the EPR linewidth, for the EPR lines: (a) (1-2), (b) (2-3HF), (c) (3-4), (d) (1-3HF), and (e) (1-3LF). The A-curves refer to a sample before irradiation, where there is no noticeable dependence of the linewidth on the azimuthal angle ϕ . After irradiation, however, the θ -dependence is different in general for different values of ϕ . The B- and C-curves pertain to an irradiated sample (1×10^{19} nvt) and correspond to the cases of $\phi = 0^\circ$ and 30° respectively.

Fig. 11. The observed ϕ -dependence of the linewidth for the line (1-2) at $\theta = 23^\circ$ after irradiation (1×10^{19} nvt).

(i.e., of the A-curves in Fig. 10) was described in terms of the spin Hamiltonian pertaining to a Cr^{3+} ion in a perfect lattice site:

$$\mathcal{H}_0 = \beta g_{\parallel} S_z H_z + \beta g_{\perp} S_{\perp} H_{\perp} + D[S_z^2 - (1/3)S(S+1)] \quad (32)$$

plus a small perturbation

$$\mathcal{H}' = \sum_{ij} D_{ij} S_i S_j \quad (33)$$

caused by local strains and/or mosaic misorientations of the z axis (See Fig. 6). The Gaussian distribution of the values of the D_{ij} and/or the directions of the z axis at various Cr^{3+} sites was taken to be responsible for the Gaussian line shape and the anisotropy of the linewidth.

In the case of the irradiated samples, the effects of radiation-induced defects neighboring a Cr^{3+} site on the local crystalline field at the site are assumed to be effectively describable in terms of an additional small perturbation term, which is denoted as¹⁴

$$\mathcal{H}'' = \sum_{ij} D'_{ij} S_i S_j \quad (34)$$

where each of the indices, i and j, runs through 1, 2, and 3 corresponding to x, y, and z, respectively (See Fig. 6). Then, the lineshape and linewidth after irradiation are to be determined by the combined distribution of D_{ij} and D'_{ij} .

The D'_{ij} can be expressed in terms of the local strain parameters,³⁴⁻³⁶ if the defects are primarily additional sources of strain, or in terms of effective static electric field components at the Cr^{3+} site, if the defects are primarily radiation-induced electric charges.¹⁵

For the case of the strain sources,

$$D'_{ij} = \sum_{kl} G_{ijkl} \epsilon_{kl} \quad (35)$$

or in Voigt notation

$$D'_i = \sum_j G_{ij} \epsilon_j \quad (36)$$

where the ϵ 's in both Eq. (35) and Eq. (36) are the local strain parameters and the Voigt notation in Eq. (36) adopts the convention that the pairs of indices (11), (22), (33), (23), (13), and (12) for the (ij) and (kl) in Eq. (35) should correspond to the single indices (1), (2), (3), (4), (5), and (6) for (i) and (j) in Eq. (36) respectively. The components of the G-tensor have been evaluated by Donoho and Hemphill.³⁴⁻³⁶

For the case of charge sources,

$$D'_{ij} = \sum_k R_{ijk} E_k \quad (37)$$

where the E_k 's are the cartesian components of the effective electric field vector $\vec{E}$ produced at the Cr^{3+} site by the charges. The components of the R-tensor have been evaluated by Royce and Bloembergen.¹⁵ It should be noted here that in Ref. 15, a slightly different form of Eq. (37) is employed.

The distribution of D'_{ij} in Eq. (36) or Eq. (37) is determined by the distribution of ϵ_j or E_k . Since the penetration of the fast neutrons through the sample during the radiation treatment is random in direction, it is expected that the distribution of the radiation-induced defects, whether they are strain sources or charge sources, is also random with regard to both the direction and relative distance to the Cr^{3+} sites. To treat this random case, the following is assumed: First, each strain component or each electric field component possesses a Gaussian distribution:

$$P(\epsilon_i) = 1/[(2\pi)^{1/2} \Delta\epsilon_i] \exp \left\{ -[(1/2)(\epsilon_i/\Delta\epsilon_i)^2] \right\} \quad (38a)$$

$$P(E_i) = 1/[(2\pi)^{1/2} \Delta E_i] \exp \left\{ -[(1/2)(E_i/\Delta E_i)^2] \right\} \quad (38b)$$

where $\Delta\epsilon_i$ and ΔE_i are the square root of the second moment of the ϵ_i and E_i distributions respectively. The probability for a given set of values of the strain components or of the electric field components is taken to be equal to the product of the probabilities for the individual components. In other words, the strain components or the electric field components are considered to be independent of one another. Secondly, the distribution of D'_{ij} is independent of the distribution of D_{ij} . The distributions of D_{ij} and D'_{ij} are both Gaussian.

Thus, an EPR line perturbed by both D_{ij} and D'_{ij} is of Gaussian shape and its half-width ΔH (in units of magnetic field) can be given by the following expression:

$$\Delta H = [(\Delta G)^2 + (\Delta H_i)^2]^{1/2} \quad (39)$$

where ΔG and ΔH_i represent the half-width of the EPR lines due to D_{ij} and D'_{ij} respectively. Detailed discussions of ΔG have been presented in Chap. III (See also the A curves of Fig. 10). In order to compare Eq. (39) with the observed linewidth anisotropy after irradiation, a knowledge of ΔH_i is necessary. Therefore, in the following, ΔH_i will be calculated separately in terms of radiation-induced strain sources and radiation-induced charge sources.

Strain Source Model

Consider the (resonant) frequency pertaining to a pair of energy levels $|a\rangle$ and $|b\rangle$ of a Cr^{3+} ion in the lattice. The perturbation D'_{ij} due to the radiation-induced strain sources results in a shift ν in the frequency after irradiation. The frequency shift ν for a given set of values of the strain parameters, $\epsilon_1 \dots \epsilon_6$, can

be obtained by elementary calculation as follows:

$$\begin{aligned}
 v = & [(1/2)(G_{11}-G_{12})(\epsilon_1-\epsilon_2) \cos 2\phi - (1/2)(G_{11}-G_{12})\epsilon_6 \sin 2\phi \\
 & + (G_{14}\epsilon_4 - G_{25}\epsilon_5) \cos 2\phi - (G_{25}\epsilon_4 + G_{14}\epsilon_5) \sin 2\phi] \langle S_x^2 - S_y^2 \rangle \\
 & + [-G_{14}(\epsilon_1-\epsilon_2) \sin \phi - G_{25}(\epsilon_1-\epsilon_2) \cos \phi - G_{25}\epsilon_6 \sin \phi \\
 & + G_{14}\epsilon_6 \cos \phi - G_{44}\epsilon_4 \sin \phi + G_{44}\epsilon_5 \cos \phi] \langle S_x S_z + S_z S_x \rangle \\
 & + (3/2)[G_{33}\epsilon_3 - (G_{11}+G_{12})(\epsilon_1+\epsilon_2)] \langle S_z^2 \rangle, \quad (40)
 \end{aligned}$$

where $\langle S_x^2 - S_y^2 \rangle$, for example, is an abbreviated notation for $\langle a | S_x^2 - S_y^2 | a \rangle - \langle b | S_x^2 - S_y^2 | b \rangle$. These matrix elements are to be evaluated in the coordinate system of Fig. 6, with the conditions that $\phi = 0^\circ$, and $0 \leq \theta \leq 90^\circ$. This frequency shift is equivalent to a shift, H_i , in the resonant magnetic field, which is given by $H_i = v dH/dv$, where dH/dv is the derivative of the resonant magnetic field with respect to the resonant frequency. Accordingly, the resonant magnetic field H_i has a certain distribution determined by the distributions of the strain parameters. The second moment of the H_i -distribution is the square of the half-width ΔH_i due to the perturbation of D'_{ij} . Thus, ΔH_i is obtained as follows:

$$(\Delta H_i)^2 = (\Delta v)^2 (dH/dv)^2 = (dH/dv)^2 \iiint \iiint v^2 P(\epsilon_1) \dots P(\epsilon_6) d\epsilon_1 \dots d\epsilon_6, \quad (41)$$

where $P(\epsilon_i)$ are given by Eq. (38a). When integrated, Eq. (41) yields two groups of terms: one independent of ϕ and the other depending on ϕ

which is given as follows:

$$\begin{aligned}
 & (\Delta\epsilon_1^2 + \Delta\epsilon_2^2) \sin^2 \phi + \Delta\epsilon_6^2 \cos^2 \phi; \\
 & (\Delta\epsilon_1^2 + \Delta\epsilon_2^2) \cos 2\phi \sin \phi + \Delta\epsilon_6^2 \sin 2\phi \cos \phi; \\
 & (\Delta\epsilon_1^2 - \Delta\epsilon_2^2) \sin \phi; \\
 & (\Delta\epsilon_1^2 + \Delta\epsilon_2^2 - \Delta\epsilon_6^2) \sin \phi \cos \phi; \\
 & \Delta\epsilon_4^2 \cos^2 2\phi + \Delta\epsilon_5^2 \sin^2 2\phi; \text{ and} \\
 & \Delta\epsilon_4^2 \cos 2\phi \sin \phi + \Delta\epsilon_5^2 \cos \phi \sin 2\phi. \quad (42)
 \end{aligned}$$

The Cr^{3+} sites in the Al_2O_3 lattice have three-fold symmetry about the C axis.²¹ For the random distribution of defects considered here, the linewidth predicted by Eq. (41) must also have at least three-fold symmetry about the C axis. In other words, ΔH_1 must be periodic in ϕ with a period of 120° . This condition can be satisfied if it is assumed that:

$$\sqrt{2} \Delta\epsilon_1 = \sqrt{2} \Delta\epsilon_2 = \Delta\epsilon_6; \quad \Delta\epsilon_4 = \Delta\epsilon_5 \quad (43)$$

in Eq. (42). Equation (41) then becomes:

$$\begin{aligned}
 (\Delta H_1)^2 = (dH/dv)^2 \cdot & \left\{ [(1/2)(G_{11}+G_{12})^2 \langle S_x^2 - S_y^2 \rangle^2 + (9/2)(G_{11}+G_{12}) \langle S_z^2 \rangle^2 \right. \\
 & + 2(G_{25}^2 + G_{14}^2) \langle S_x S_z + S_z S_x \rangle^2 \\
 & - 2(G_{11}-G_{12})(G_{14} \sin 3\phi + G_{25} \cos 3\phi) \langle S_x S_z + S_z S_x \rangle \langle S_x^2 - S_y^2 \rangle] \Delta\epsilon_1^2 \\
 & + [(G_{14}^2 + G_{25}^2) \langle S_x^2 - S_y^2 \rangle^2 + G_{44}^2 \langle S_x S_z + S_z S_x \rangle^2 \\
 & - 2 G_{44} \langle S_x S_z + S_z S_x \rangle \langle S_x^2 - S_y^2 \rangle (G_{14} \sin 3\phi + G_{25} \cos 3\phi)] \Delta\epsilon_4^2 \\
 & \left. + (9/4)[G_{33} \langle S_z^2 \rangle^2] \Delta\epsilon_3^2 \right\}. \quad (44)
 \end{aligned}$$

The G-tensor in Eq. (44) differs for different sites of the Cr^{3+} ion in the Al_2O_3 lattice,^{35,36} and ΔH_1 in Eq. (39) is accordingly different for the different sites. Crystallographically,¹⁵ there are four inequivalent sites, which may be grouped into two pairs of sites, the two sites of each pair being related by inversion (See Chap. II, Sect. E). These pairs appear to behave in the same way under the application of uniaxial stress.^{35,36} Therefore, from the point of view of strains, the two pairs constitute two inequivalent sites. The G-tensors pertaining to the two pairs differ in the sign of the G_{25} component. Accordingly, when the sample contains a random distribution of strains, the transition between the state $|a\rangle$ and the state $|b\rangle$ yields two EPR lines corresponding to the two distinct sites of the Cr^{3+} ions. These two lines will possess the same center of resonance but different half widths, ΔH_1 and ΔH_2 , where ΔH_1 and ΔH_2 are given by Eq. (39) for a G-tensor with positive G_{25} and for a G-tensor with negative G_{25} respectively. Thus, these two lines compose the EPR line for the pair of states $|a\rangle$ and $|b\rangle$. Since each of the two lines is assumed to be Gaussian in shape, the composite EPR line will possess the following line shape (of the derivative curve):

$$\begin{aligned} df(H)/dH = (2\pi)^{-1/2} (H-H_0) \left\{ I_1 / (\Delta H_1)^3 \cdot \exp[-(1/2)(H-H_0)^2 / (\Delta H_1)^2] \right. \\ \left. + I_2 / (\Delta H_2)^3 \cdot \exp[-(1/2)(H-H_0)^2 / (\Delta H_2)^2] \right\}, \end{aligned} \quad (45)$$

where I_1 and I_2 are proportional, respectively, to the product of the number of Cr^{3+} ions with the transition probability pertaining to each of the two inequivalent sites. According to Royce and Bloembergen,¹⁵ the two sites are equally populated. The transition probabilities differ insignificantly from one site to the other. Therefore, I_1 and I_2 in Eq. (45) will be taken to be equal to each

other in the following. The half-width, ΔH_{1+2} , of Eq. (45) can be computed graphically, when ΔH_1 and ΔH_2 are known.

If $\Delta H_1 \gg \Delta H_2$, the amplitude of the first term in curly brackets of Eq. (45) will be much smaller than the second. The opposite will be true if $\Delta H_1 \ll \Delta H_2$. Thus the line with the smaller half-width will be most prominent in the derivative curve.

Figure 12 gives a plot of the (full) width, $2\Delta H_1$ and $2\Delta H_2$, as a function of ϕ when $\theta = 23^\circ$ for the line (1-2). It also illustrates the dependence of the width $2\Delta H_{1+2}$ of Eq. (45) on the azimuthal angle ϕ .

ΔH_{1+2} determined in the preceding is expected to account for the observed ϕ -dependence of the line (1-2) for $\theta = 23^\circ$, which is shown in Fig. 11. A comparison of the two figures reveals that the general behavior of ΔH_{1+2} as a function of ϕ is similar to that of the observed width. For example, ΔH_{1+2} exhibits peaks at $\phi = 30^\circ$ and 90° , and there are two peaks at the corresponding angles in Fig. 11. However, $2\Delta H_{1+2}$ at $\phi = 30^\circ$ is approximately 13 gauss larger than $2\Delta H_{1+2}$ at $\phi = 90^\circ$, while the observed widths at the two angles are practically the same. As far as the published value of the G-tensor components are employed,³⁴⁻³⁶ this discrepancy remains, and the cause of the discrepancy is not easily understood. Therefore, an approximation for ΔH_{1+2} has been made as follows:

$$\Delta H_{1+2}(\phi) = (1/2)[\Delta H_1^2(\phi) + \Delta H_2^2(\phi+60^\circ)]^{1/2} \quad \text{if } \Delta H_1(\phi) < \Delta H_2(\phi), \quad (46a)$$

and

$$\Delta H_{1+2}(\phi) = (1/2)[\Delta H_1^2(\phi+60^\circ) + \Delta H_2^2(\phi)]^{1/2} \quad \text{if } \Delta H_1(\phi) > \Delta H_2(\phi). \quad (46b)$$

Fig. 12. The computed ϕ -dependence of the linewidth for the line (1-2) at $\theta = 23^\circ$ after irradiation (1×10^{19} nvt). The computation was made by means of Eqs. (39) and (44) for the case of the strain model. The curves ΔH_1 and ΔH_2 represent the full width of the lines due to the two inequivalent Cr^{3+} sites in the crystalline lattice of the sample. The curve ΔH_{1+2} represents the anisotropy of the composite full width graphically obtained by means of Eq. (45) (See text).

This approximation tends to reduce the difference between two neighboring maxima of the computed ΔH_{1+2} of Eq. (45), and to have little effect on the minima. The approximation given by Eqs. (46a) and (46b) essentially amounts to reducing the value of G_{14} , which will be discussed later.

Charge Source Model

The calculation of ΔH_i in the case of charge sources can be performed in much the same manner starting from Eq. (37) as in the case of strain sources. The shift ν in the resonant frequency due to the radiation-induced electric fields is given by:

$$\begin{aligned} \nu = & [(R_{222} \sin 2\phi - R_{111} \cos 2\phi) \langle S_x^2 - S_y^2 \rangle \\ & + (1/2)(R_{113} \sin \phi - R_{123} \cos \phi) \langle S_x S_z + S_z S_x \rangle] E_1 \\ & + [(R_{222} \cos 2\phi + R_{111} \sin 2\phi) \langle S_x^2 - S_y^2 \rangle \\ & - (1/2)(R_{113} \cos \phi + R_{123} \sin \phi) \langle S_x S_z + S_z S_x \rangle] E_2 \\ & + (3/2) R_{333} \langle S_z^2 \rangle E_3, \end{aligned} \quad (47)$$

where the matrix elements have the same meaning as in Eq. (40).

The corresponding shift H_i in the resonant magnetic field is given by $H_i = \nu dH/d\nu$, as in the case of strains. Therefore, the half-width ΔH_i of the distribution of H_i can be given by the following expression:

$$(\Delta H_i)^2 = (dH/d\nu)^2 \iiint \nu^2 P(E_1) P(E_2) P(E_3) dE_1 dE_2 dE_3 \quad (48)$$

where $P(E_1)$ is given by Eq. (38b).

For reasons mentioned previously, the half-width given by Eq. (47) must be periodic in ϕ with a period of 120° .

This requirement can be satisfied if ΔE_1 is equal to ΔE_2 .

When Eq. (48) is integrated and the periodicity condition is

satisfied, Eq. (48) becomes as follows:

$$\begin{aligned}
 (\Delta H_i)^2 = (\Delta H/dv)^2 \left\{ [(R_{111}^2 + R_{222}^2) \langle S_x^2 - S_y^2 \rangle^2 + (1/4)(R_{113}^2 + R_{123}^2) \langle S_x S_z + S_z S_x \rangle^2 \right. \\
 \left. - (R_{111} R_{113} + R_{222} R_{123}) \langle S_x^2 - S_y^2 \rangle \langle S_x S_z + S_z S_x \rangle \sin 3\phi] \Delta E_1 \right. \\
 \left. + (9/4) R_{333}^2 \langle S_z^2 \rangle^2 \Delta E_3^2 \right\}. \quad (49)
 \end{aligned}$$

The constants in Eq. (49) are the same as in Ref. 15. The x direction in Eq. (49) is the +A crystallographic axis and the notation conforms to Fig. 6. Reference 15 uses a different coordinate system.

Equation (49) is to be used in Eq. (39) in order to calculate the half-width ΔH of the EPR line pertaining to the pair of states $|a\rangle$ and $|b\rangle$. Since ΔE_i of Eq. (49) depends on R_{ijk} , and the R_{ijk} differ for different Cr^{3+} sites, ΔH of Eq. (39) varies depending upon the site of the ions. Thus, it is necessary to determine the number of inequivalent sites of Cr^{3+} with respect to an isotropic distribution of radiation-induced electric fields. (See Chap. II, Section E). The procedure is similar to that employed for the strain source model. According to Royce and Bloembergen,¹⁵ an EPR line located at H_0 splits into two pairs of lines under the influence of an applied electric field. The two lines of each pair are symmetrically located on both sides of H_0 . When the direction of the electric field is reversed, the lines of each pair exchange their positions. Since the distribution of the radiation-induced electric fields is taken to be isotropic in direction and random in magnitude, the distribution would not be able to distinguish between the two lines of each pair. This means

that the two sites of each pair become effectively equivalent. Accordingly, there are two inequivalent pairs of sites. This inequivalence is exhibited by the change of the sign of the R_{222} and R_{123} components of the R-tensor from one pair to the other pair. Thus, the two EPR lines corresponding to the two distinct R-tensors will possess the same center of resonance, but different half widths ΔH_1 and ΔH_2 for ΔH of Eq. (39). The analysis of ΔH_{1+2} of the composite line in terms of ΔH_1 and ΔH_2 can be made in parallel to the corresponding analysis of the strain source model. The peak values of ΔH_{1+2} are approximated in the same way, although it should be noted that the computed peaks of ΔH_{1+2} differ less significantly than in the case of the strain source model.

Because of the nature of the assumption of the random distribution of the radiation-induced charges and effective electric fields, it is reasonable to assume the equality of ΔE_1 and ΔE_3 in Eq. (49) which is to be used in the computation of ΔH_{1+2} . The observed anisotropy of the width is then compared with ΔH_{1+2} .

Comparison with Experimental Results and Discussions

In order to fit the width ΔH_{1+2} to the observed anisotropy of the linewidth, a set of three parameters, $\Delta \epsilon_1$, $\Delta \epsilon_4$ and $\Delta \epsilon_3$, and one parameter ΔE_1 have to be adjusted for the case of strain sources and the case of charge sources, respectively (See Eqs. (39), (44), and (49)).

For the case of strain sources, Fig. 13 illustrates the most satisfactory fit of the full width, $2\Delta H_{1+2}$, to the observed

Fig. 13. Comparison of the observed and computed θ -dependences of the linewidth for the lines: (a) (1-2), (b) (2-3HF), (c) (3-4), (d) (1-3HF), and (e) (1-3LF). The curves 1 and 2 represent the observed θ -dependences at $\phi = 0^\circ$ and 30° , respectively, based on the strain model (See text).

θ -dependence of the width pertaining to the lines: (a) (1-2), (b) (2-3HF), (c) (3-4), (d) (1-3HF), and (e) (1-3LF) for the two cases $\phi = 0^\circ$ and $\phi = 30^\circ$, respectively.* The neutron dosage for this sample is 1×10^{19} nvt. For example, in Fig. 13(a) there are two experimental curves, labeled 1 and 2, corresponding to $\phi = 0^\circ$ and 30° respectively, and there are two calculated curves, labeled 3 and 4, corresponding to the curves 1 and 2 respectively. The values of the parameters in ΔH_{1+2} used for the fitting are given below:

$$\Delta \epsilon_1 = \Delta \epsilon_4 = \Delta \epsilon_3 = 1.8 \times 10^{-4} \quad (50)$$

For the case of charge sources, Fig. 14 illustrates the corresponding fit of the full width, $2\Delta H_{1+2}$, to the observed anisotropy of the linewidth. The values of the parameters used in the fitting are as follows:

$$\Delta E_1 = 240 \text{ Kv/cm} \quad (51)$$

A comparative survey of Figs. 13 and 14 would reveal that the strain source model is more satisfactory than the charge source model. This seems to indicate that the distortion of the local crystalline field is more due to radiation-induced strains than due to radiation-induced charges.

It should be recalled, however, that the successful fit of ΔH_{1+2} to the observed anisotropy of the linewidth is based on two computational approximations made in the theoretical calculations: one on the shape of the individual lines and the other on the peak value of ΔH_{1+2} in its ϕ -dependence. Therefore, further comments on each

* The values of the G-tensor components used to compute ΔH_{1+2} here were taken from Ref. 35. The corresponding values of the same G-tensor published more recently in Ref. 36 appear to be approximately 3/2 times too small to explain the experimental data in that paper.

Fig. 14. Comparison of the observed and computed θ -dependences of the linewidth for the lines: (a) (1-2), (b) (2-3HF), (c) (3-4), (d) (1-3HF), and (e) (1-3LF). The curves 1 and 2 represent the observed θ -dependences for $\phi = 0^\circ$ and 30° respectively, based on the charge source model. (See text).

will be made in the following.

First, although the observed lineshape is not satisfactorily Gaussian, the Gaussian lineshape has been employed in the theoretical considerations in the preceding. This approximation is used solely for the convenience of computing ΔH_{1+2} , but is not without precedence in similar work. For example, E.R. Feher²⁸ has recently employed a similar approximation in dealing with the lineshape of the EPR absorption in Mn^{2+} and Fe^{3+} in MgO .

Secondly, the observed peaks of the linewidth (See Fig. 11, for example) are practically the same, while the corresponding peaks for the computed ΔH_{1+2} (See Fig. 12 for example) have some difference. The approximation used then is to take the square root of the average of the squares of the distinct peaks. The averaging is equivalent to reducing G_{14} . This can be seen, for example, by considering the case illustrated in Fig. 12. The linewidths for $\phi = 30^\circ$ and $\phi = 90^\circ$ can be obtained from Eqs. (39) and (44) as follows:

$$\Delta H_{1+2} = [\Delta G^2 + A^2 \pm G_{14}(G_{11}-G_{12}+G_{44})B^2]^{1/2} \quad (52)$$

where the minus sign is taken for $\phi = 30^\circ$ and the plus sign for $\phi = 90^\circ$. A and B are constants. Using the parameters of Eq. (50) and the values for the G-tensor components in Ref. 35, the predicted linewidth is 79 ± 2 gauss for $\phi = 30^\circ$ and 66 ± 2 gauss for $\phi = 90^\circ$. The observed values for both angles is 70 ± 2 gauss and thus falls between the two theoretical values. If the value of G_{14} were decreased from its quoted value of -15.0 kMc/sec to a value of about -5.0 kMc/sec, the linewidth at $\phi = 30^\circ$ and the linewidth at $\phi = 90^\circ$ would fall within the error bars of the experimental data. Reducing this component of the G-tensor would have minor effects on the predicted linewidth for other

orientations. Perhaps, the value of G_{14} for the samples considered here is much smaller than the G_{14} in Ref. 35.

Shifts in the Resonant Magnetic Field

It has been mentioned in Section B that the resonant magnetic field value of the EPR line shifts by small amounts after irradiation. For example, Table I lists three of the observed shifts for a 1×10^{19} nvt sample. The shift is found to correspond to at most 0.2% of the original magnetic field.

The observed shifts can occur if either the average value of the radiation-induced electric field components or the radiation-induced strain components is not zero. This can be seen from Eq. (47) in the former case, and from Eq. (40) in the latter case.

Since the distribution of the electric field is random, the average values of the electric field components should be zero. This random approximation excludes the charge source model from being responsible for the shift.

In contrast, non-vanishing average values of the strain components have been observed. According to D.G. Martin,³⁹ fast neutron irradiation of Al_2O_3 leads to an expansion of the lattice after the radiation treatment. The expansion appears to take place along the C axis and also uniformly along any direction perpendicular to the C axis. A similar expansion of the lattice is very likely to occur in the samples of the present work, which also employed fast neutron irradiation. For this case, the average values of the strain components should satisfy the following conditions:

$$\bar{\epsilon}_1 = \bar{\epsilon}_2 \neq 0, \bar{\epsilon}_3 \neq 0, \bar{\epsilon}_4 = \bar{\epsilon}_5 = \bar{\epsilon}_6 = 0. \quad (53)$$

TABLE I
SHIFTS IN THE RESONANT MAGNETIC FIELD

(Neutron dose 1×10^{19} nvt; Microwave frequency at 9.475 kmcps).

Line	Angle θ	Observed Shift $\bar{H}_1$ (Gauss)		r -(Eq. (24)) (kmcps)	
		0.01% Cr^{3+}	0.001% Cr^{3+}	0.01% Cr^{3+}	0.001% Cr^{3+}
3-4	90°	$-8.6 \pm .3$	$-8.2 \pm .9$	$0.027 \pm .001$	$0.026 \pm .003$
1-2	90°	$+2.2 \pm .3$	$+2.9 \pm .7$	$0.026 \pm .004$	$0.034 \pm .008$
2-3HF	35°	$-7.5 \pm .4$	$-6.6 \pm .6$	$0.025 \pm .001$	$0.022 \pm .002$

When the above conditions are substituted in Eq. (40), the shift in the resonant magnetic field can be obtained as follows:

$$\bar{H}_i = (3/2)[G_{33}\bar{\epsilon}_3 - 2(G_{11}+G_{12})\bar{\epsilon}_1]\langle S_z^2 \rangle (dH/dv). \quad (54)$$

The quantity

$$r \equiv (3/2)[G_{33}\bar{\epsilon}_3 - 2(G_{11}+G_{12})\bar{\epsilon}_1] \quad (55)$$

from Eq. (54) is theoretically independent of any particular transition line and of the polar coordinates θ and ϕ . That this is indeed so in the present case can be seen, when the observed shifts $\bar{H}_i$ and the known values of $\langle S_z^2 \rangle$ and dH/dv are substituted in Eq. (54). The resulting values of r have been found to remain practically constant. The two columns at the extreme right of Table I show the values of r evaluated for three different transition lines and two different angles. It should be noted here that in Table I the measurement of $\bar{H}_i$ for the 0.001% Cr^{3+} sample is more difficult than for the 0.01% Cr^{3+} sample because of the weaker EPR signals due to the lower concentration of the Cr^{3+} ions in the former case. Accordingly, the values of r for the case of lower Cr^{3+} concentration vary more noticeably than for the case of higher Cr^{3+} concentration.

Unfortunately, the EPR studies of the shifts do not facilitate an evaluation of $\bar{\epsilon}_1$ and $\bar{\epsilon}_3$ separately. However, $(\bar{\epsilon}_3 - \bar{\epsilon}_1)$ appears to increase almost linearly with an increasing fast neutron dosage. This is explained in the following. According to Ref. 35, the differences between G_{33} and $2(G_{11}+G_{12})$ of Eq. (54) is practically negligible, and thus the shift $\bar{H}_i$ may be taken to be proportional to $(\bar{\epsilon}_3 - \bar{\epsilon}_1)$:

$$\bar{H}_i \propto (\bar{\epsilon}_3 - \bar{\epsilon}_1). \quad (56)$$

Since the components of the G-tensor, $\langle S_z^2 \rangle$, and dH/dv are insensitive to a varying neutron dosage, any dependence of the shift on the neutron dosage should be attributed to the dependence of $(\bar{\epsilon}_3 - \bar{\epsilon}_1)$ on the neutron dosage. The curve of Fig. 15 illustrates the observed dependence of the shift on the neutron dosage for the line (3-4) at $\theta = 90^\circ$. The dependence is practically linear. This means that $(\bar{\epsilon}_3 - \bar{\epsilon}_1)$ of Eq. (56) is nearly linear in neutron dosage.

D. Conclusion

Single crystal samples of $(Al_2O_3)_{1-x}(Cr_2O_3)_x$ with $x = 0.01\%$ and 0.001% have been irradiated with fast neutrons for dosages between 10^{18} and 10^{19} nvt near room temperature. The EPR absorption studies of the irradiated samples have yielded two major points of interest: First, the linewidth after irradiation depends on not only the polar angle θ but also on the azimuthal angle ϕ , while it depends only on θ before irradiation. For a given set of values of θ and ϕ , the linewidth after irradiation is substantially larger than that before irradiation. Secondly, the irradiation causes the center of resonance of the individual lines to shift slightly (0.2% at most) relative to that of the corresponding lines before irradiation.

The observed results have been examined in terms of two alternative models: the strain source model and the charge source model, which describe the effect of irradiation on the Cr^{3+} sites in terms of a random Gaussian distribution of radiation-induced strains and radiation-induced static electric fields respectively. The strain source model yields a satisfactory fit to the observed anisotropy of the linewidth and is consistent with the observed shift in the

Fig. 15. The shift in the resonant magnetic field. The data have been taken for the line (3-4) at $\theta = 90^\circ$.

resonant magnetic field. On the other hand, the charge source model yields a less satisfactory fit to the observed anisotropy of the linewidth. In addition, it fails to predict the shift in the resonant magnetic field.

The optimum rms values of the strains are as follows:

$$\Delta\epsilon_1 = \Delta\epsilon_2 = \Delta\epsilon_3 = \Delta\epsilon_4 = \Delta\epsilon_5 = \Delta\epsilon_6/\sqrt{2} = 1.8 \times 10^{-4}.$$

Appendix A: G-Value Variation

An approximate relation between the spin-orbit coupling constant λ and the experimentally measured parameters D , $g_{||}$, and $g_{\perp}$ can be given as follows:³⁷

$$D \approx (1/2)\lambda(g_{||} - g_{\perp}) . \quad (A1)$$

Using the values of Eq. (10),

$$\lambda \approx 4 \times 10^6 \text{ Mc/sec} . \quad (A2)$$

Considering the variation of $g_{||}$ and $g_{\perp}$ to be mutually independent as they are determined by the assumed independent components of D_{ij} , an order of magnitude estimate of the half-width of the variation of either $g_{||}$ or $g_{\perp}$ can be given by

$$\delta g \approx (\delta D / \lambda) \quad (A3)$$

where δD is the half-width of the variation of D .

By using the maximum value of δD (10.6 Mc/sec) from Eq. (30), a value of $\delta g = 0.3 \times 10^{-5}$ is thus obtained. The magnitude of the line broadening due to this value is estimated by

$$\Delta H = (dH/dg)\delta g \quad (A4)$$

The largest value of dH/dg obtained by means of a computer is 3.82×10^3 gauss per unit g , for the line (1-2) at $\theta = 0^\circ$.

Consequently, ΔH is at most 0.01 gauss. This is too small to be significant when compared with the line broadening estimated by using the strain model.

REFERENCES

1. C.P. Slichter, Principles of Magnetic Resonance, (Harper and Row, New York, 1963), Chap. 1, p. 2.
2. S.A. Al'tshuler and B.M. Kozyrev, Electron Paramagnetic Resonance, (Academic Press, New York, 1964), Chap. 1, p. 6.
3. Ibid., Chap. 1, p. 7.
4. W. Low, Solid State Physics, edited by F. Seitz and D. Turnbull, (Academic Press Inc., New York, 1960), Suppl. 2, p. 44.
5. B. Bleaney and K.W.H. Stevens, Repts. Progr. in Phys. 16, 108 (1953).
6. G.E. Pake, Paramagnetic Resonance, (W.A. Benjamin Inc., New York, 1962), Chap. 3, p. 71-75.
7. A. Abragam, The Principles of Nuclear Magnetism, (Oxford at the Clarendon Press, 1961), Chap. 4, p. 97-98.
8. Ibid., Chap. 4.
9. Ibid., Chap. 4, p. 98.
10. N. Laurance, E.C. McIrvine, and J. Lambe, J. Phys. Chem. Solids 23, 515 (1963), see page 519.
11. J.H. Van Vleck, Phys. Rev. 74, 1168 (1948).
12. W.J.C. Grant and M.W.P. Strandberg, Phys. Rev. 135, A727 (1964).
13. R.G. Shulman, B.J. Wyluda, and P.W. Anderson, Phys. Rev. 107, 953 (1957).
14. E.R. Feher and G.D. Watkins, Bull. Am. Phys. Soc. 7, 29 (1962).
15. E.B. Royce and N. Bloembergen, Phys. Rev. 131, 1912 (1963).
16. N. Bloembergen, Science 133, 1363 (1961).
17. D. Shaltiel and W. Low, Phys. Rev. 124, 1062 (1961).
18. D.L. Stephens and W.J. Alford, J. Am. Ceram. Soc. 47, 81 (1964).
19. The NMR-EPR Staff of Varian Associates, V-4502 EPR Spectrometer Systems, (Varian Associates, Publication Number 87-100-074).
20. The NMR-EPR Staff of Varian Associates, NMR and EPR Spectroscopy, (Pergamon Press, Oxford, 1960).
21. R.W.G. Wykoff, Crystal Structures, Second Edition, Vol. 2, (Interscience Publishers Inc., New York, 1963), p. 7.

22. J.B. Wachtman Jr., W.E. Tefft, D.G. Lam Jr., and R.P. Stinchfield, J. Res. Natl. Bur. Std. (U.S.) 64A, 213 (1960).
23. S. Geschwind and J.P. Remeika, Suppl. J. Appl. Phys. 33, 370 (1962).
24. H. Winchell, Bull. Geol. Soc. Am. 57, 295 (1946).
25. R.F. Wenzel and Y.W. Kim, Phys. Rev. 140, A1592 (1965).
26. W.J.C. Grant and M.W.P. Strandberg, Phys. Rev. 135, A715 (1964); 135, A727 (1964).
27. N. Laurance, E.C. McIrvine, and J. Lambe, J. Phys. Chem. Solids 23, 515 (1962).
28. E.R. Feher, Phys. Rev. 136, A145 (1964).
29. A.A. Manenkov and A.M. Prokhorov, Zh. Eksperim. i Teor. Fiz. 28, 762 (1955 [English transl: Soviet Phys. -- JETP 1, 611 (1955)]).
30. M. Zaripov and I. Shamonin, Zh. Eksperim. i Teor. Fiz. 30, 291 (1956 [English transl.: Soviet Phys. JETP 30, 291 (1956)]).
31. J.E. Geusic, Phys. Rev. 102, 1252 (1956).
32. J. Weber, Rev. Mod. Phys. 31, 681 (1959).
33. A.M. Portis, Phys. Rev. 91, 1071 (1953).
34. P.L. Donoho and R.B. Hemphill, in Proceedings of the Eighth International Conference on Low Temperature Physics, edited by R.O. Davies, (Butterworths Scientific Publications Ltd., London, 1963), p. 294.
35. P.L. Donoho, Phys. Rev. 133, A1080 (1964).
36. R.B. Hemphill, P.L. Donoho, and E.D. McDonald, Phys. Rev. 146, 329 (1966).
37. W. Low, in Solid State Physics, edited by F. Seitz and D. Trunbull (Academic Press Inc., New York, 1960), Suppl. 2, p. 82.
38. P.L. Scott, H.J. Stapleton, and C. Wainstein, Phys. Rev. 137, A71 (1965).
39. D.G. Martin, J. Phys. Chem. Solids (G.B.) 10, 64 (1955).

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"Experimental Plasma Flow into a Vacuum Magnetic
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Physical Review, Vol. 119, p. 1187 (1960).

"Linewidth of the Electron Paramagnetic Resonance
of $(Al_2O_3)_{1-x}(Cr_2O_3)_x$ ", R.F. Wenzel and Y.W. Kim,
The Physical Review, Vol. 140, p. A1592 (1965).

"Linewidth of the Electron Paramagnetic Resonance
of Fast Neutron Irradiated $(Al_2O_3)_{1-x}(Cr_2O_3)_x$ ",
by R. F. Wenzel and Y. W. Kim, submitted to The
Physical Review (1966).