invariance  $x \rightarrow ax$ ,  $E \rightarrow E$ ,  $\sigma \rightarrow \sigma$ ,  $\sigma' \rightarrow a^{-2}\sigma'$ . This scale invariance is destroyed when further details of the transports involved are brought in.

Clearly the external field strength  $E_0$  must lie in a rather well-defined range for such solutions. If  $E_0$  is too small, it cannot be raised above the breakdown field by the presence of a more conducting sphere (which even if  $\sigma_1/\sigma_0 \rightarrow \infty$  can at most triple the external field, it is well known). If *E0* is too large there will be a breakdown between the distant sources of the field. If the field should fall during the existence of such a ball, it would disappear quietly, because of the small energies involved; if the field should rise, however, the ball may give way to a high-power discharge.

Thus the nonlinear conduction model is helpful in understanding some of the reported circumstances of ball lightning, and in suggesting further theoretical and experimental work.

PHYSICAL REVIEW VOLUME 135, NUMBER 2A

20 JULY 1964

# Effect of Applied Electric Fields on the Electron Spin Resonance of  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

## JAMES J. KREBS

*U. S. Naval Research Laboratory, Washington, D. C.*  (Received 27 February 1964)

The effect of applied electric fields in broadening the electron spin resonance lines of the isoelectronic ions  $\text{Fe}^{3+}$  and Mn<sup>2+</sup> in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> has been observed. This is interpreted as an unresolved line "splitting" which is linear in the applied field. The change in the spin Hamiltonian *D* parameter with applied field parallel to the *c* axis  $(\partial D/\partial E)$  is 1.00 $\pm$ 0.09 for Fe<sup> $\bar{x}$ </sup> and 1.03 $\pm$ 0.09 for Mn<sup>2+</sup> in units of 10<sup>-5</sup> G cm/V. The existence of this effect implies that these ions replace  $Al^{3+}$  ions substitutionally in the  $\alpha$ -Al<sub>2</sub>O<sub>s</sub> lattice. A simplified calculation indicates that ionic displacement plays an important role in producing the effect in these S-state ions and thatthe resultant relative change in the even component of the axial crystalline field appears to be much larger for Mn<sup>2+</sup> than Fe<sup>3+</sup>.

AS has been pointed out by Bloembergen,<sup>1</sup> if one places a paramagnetic ion in a crystal site which S has been pointed out by Bloembergen,<sup>1</sup> if one lacks inversion symmetry, he can, in general, expect to produce a change in the electron spin resonance (ESR) spectrum upon application of an external electric field. In this paper, the broadening of ESR lines due to the isoelectronic pair of ions  $Fe^{3+}$  and  $Mn^{2+}$  (3d<sup>5</sup>) in  $Al_2O_3$ 



FIG. 1. A portion of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> lattice showing the four types of Al<sup>3+</sup> sites (after Geschwind and Remeika, Ref. 3).

is reported, and the effect is interpreted in terms of an unresolved splitting of the lines.

In the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum) lattice, the Al<sup>3+</sup> ions are located in sites which lack inversion symmetry as is seen in Fig. 1. This representation of the corundum lattice is taken from an article by Geschwind and Remeika<sup>2</sup> as adapted by Artman and Murphy.<sup>3</sup> The Al<sup>3+</sup> ions are surrounded by a greatly distorted octahedral distribution of  $O^{2-}$  ions such that the point symmetry is reduced to  $C_3$  and thus lacks inversion symmetry. As can be seen, however, sites  $a$  and  $f$  in Fig. 1 are related to one another by inversion symmetry, as are sites  $b$  and  $c$ , and all  $Al^{3+}$  sites in the lattice are so related in these two types of pairs.

In ruby, the linear electric field pseudosplitting of certain ESR lines arising from  $Cr^{3+}$  in such sites has been exhibited and measured.<sup>4,5</sup> In actuality, the lines from one type of site merely shift their position while those from the inversion-related site shift by the same amount in the opposite direction. Since it is possible to substitute other iron group transition metal ions into this^ lattice, we considered it would be helpful in elucidating the atomic mechanism to examine the effect

<sup>&</sup>lt;sup>1</sup> N. Bloembergen, Science 133, 1363 (1961).

<sup>&</sup>lt;sup>2</sup> S. Geschwind and J. P. Remeika, Phys. Rev. 122, 757 (1961).  $^{\circ}$  J. O. Artman and J. C. Murphy, J. Chem. Phys. 38, 1544

 $4E.E$ <sup>5</sup> J. O. Artman and J. C. Murphy, Bull. Am. Phys. Soc. 7, 14<br> *Phys.* Soc. 7, 14



FIG. 2. Broadening of the low-field  $Fe^{3+}$  resonance line with the electric field applied parallel to the *c* axis. Note the change in apparent line shape with applied field.

of applied electric fields on the ESR spectra of the isoelectronic pair of ions Fe<sup>3+</sup> and Mn<sup>2+</sup>. These ions have a *<sup>6</sup>S* ground state. This requires a higher order crystal field perturbation to produce a ground-state splitting<sup>6</sup> than is the case for  $\mathrm{Cr}^{3+}$ . As a result, the effect of applied electric fields is expected to be considerably smaller for them than for  $Cr^{3+}$ . This expectation was confirmed experimentally.

The ESR spectra were examined with a Varian X-band spectrometer at room temperature. The  $Al_2O_3$ crystals were grown from a  $PbO-PbF_2$  flux doped with the appropriate impurity. They were alined either by x ray or by making use of the natural crystal faces. Because of the growth habit (platelets with the faces perpendicular to the *c* axis), the samples obtained were only suitable for applying electric fields along the *c* axis. The samples were cut into the form of disks, and the disk faces were coated with evaporated silver electrodes. The crystals were edged with polystyrene dope to lengthen the dielectric breakdown path through the air. Beryllium-copper leaf springs were used to make electrical contact with the samples which were supported by a polystyrene rod at the center of the cylindrical cavity.

Because the observed ESR line splittings were not large enough to produce resolved lines, it was necessary to use other techniques to determine the splitting from the observed line broadening. One of these methods makes use of the increase in the second moment of the line when the line splits. If half of the original line shifts to higher magnetic fields by an amount *a* and half to lower fields by the same amount, the increase in the second moment  $S$  is given by

$$
S-S_0=a^2.\t\t(1)
$$

The line splitting *2a* is thus directly determined by the

second moment increase. Equation (1) is valid for any line shape as long as the second moment can be defined. This excludes Lorentzian lines, of course. The principal problem encountered in using this technique was the fact that the second moment only increased by about 12% for the highest applied fields, and it is difficult to measure second moments to an accuracy of more than 2 or 3%. To achieve even this accuracy, it was necessary to make use of a program which made corrections for base line and line center errors.<sup>7</sup>

Alternatively, one may assume a line shape and calculate the increase in the derivative linewidth when the line splits by an amount *2a.* The relative increases in width *W* for various values of  $2a/W_0$  were calculated for both Lorentzian and Gaussian line shapes and were used to extract the value of the splitting from the observed linewidth increase for a given applied electric field. In practice, it was possible to measure the line widths with an accuracy of  $1-2\%$  while their relative changes were about the same as for the second moment. Since it is the change in these quantities upon application of the electric field which is of interest, this accuracy represented a worthwhile improvement over the second moment method. Furthermore, accurate linewidth measurements were much easier to make.

#### **RESULTS**

For  $Fe^{3+}$  in  $Al_2O_3$ , Fig. 2 shows the line broadening produced by applying an external electric field of 142 kV/cm. The linewidth increases from 10.5 to 13.0 G, and the line shape changes in the expected manner. These data were taken with the magnetic and electric fields parallel to the *c* axis, using the low magnetic field  $-3/2 \leftrightarrow -1/2$  transition. The splitting versus applied field for this line is shown in Fig. 3, where the splittings were determined by the second moment method. As can



FIG. 3. Splitting of the  $-3/2 \leftrightarrow -1/2$  Fe<sup>3+</sup> resonance line as determined by the increase in second moment when the electric field is applied. The electric field is parallel to the *c* axis.

<sup>7</sup> D. J. Kroon, Philips Res. Rept. 15, 501 (1960).

H. Watanabe, Progr. Theoret. Phys. (Kyoto) 18, 405 (1957).



FIG. 4. Line splitting versus applied electric field as determined from the linewidth increase (Fe<sup>3+</sup> in Al<sub>2</sub>O<sub>3</sub>). Two assumed line shapes are shown. The electric and magnetic fields are parallel to the  $c$  axis. The indicated slopes of the straight lines are equal to  $6R<sub>333</sub>$ .

be seen, the scatter of the experimental points is considerable. The behavior of the splitting with applied field for this same line is shown more clearly in the data of Fig. 4, where the splittings are derived from the linewidth increase. The linearity of the splitting with applied field is evident and is in agreement with theory.<sup>1</sup> The figure also illustrates the difference in the derived splitting when a Gaussian or a Lorentzian line shape is assumed. In order to obtain a more accurate value for this splitting constant, a line-shape analysis<sup>8</sup> was made which showed how closely the actual lines approximated the assumed shapes, and appropriate corrections were made. The results for  $Mn^{2+}$  in  $Al_2O_3$  were similar to those for Fe3+ except for a somewhat smaller change in width due to an increased initial ESR linewidth (12.3 G). For  $Mn^{2+}$ , one of the best resolved lines of the electronic spin  $1/2 \leftrightarrow 3/2$  hyperfine set was used for most measurements.

The values obtained by the two methods for both ions are shown in Table I.<sup>9</sup> In this table, the splittings are tabulated in terms of the parameter  $R_{333}$  which appears in the electric field Hamiltonian<sup>4</sup>

$$
3C = \frac{1}{2} \sum_{ijk} R_{ijk} E_i (S_j S_k + S_k S_j), \quad j \leq k, \tag{2}
$$

where  $E_i$  and  $S_i$  are the *i*<sup>th</sup> components of the applied electric field and the electronic spin operator, respectively. Equation (2) is the most general interaction which is linear in the applied field and quadratic in the spin operators. It is worthwhile to point out that the relation between  $2a$  and  $R_{333}$  depends on the transition





considered. Making use of Eq. (2), one finds for the  $1/2 \leftrightarrow 3/2$  transition  $2a = 6R_{333}E_3$ , while for a  $3/2 \leftrightarrow 5/2$ transition  $2a = 12R_{333}E_3$ .

Under  $C_3$  symmetry, the tensor  $R_{ijk}$  has only five independent parameters, and when the electric field is applied parallel to the *c* axis, as was necessary here, only  $R_{333}$  can be determined by experiment.<sup>4</sup> A possible physical origin for such a Hamiltonian was suggested by Rado<sup>10</sup> in his explanation of the magnetoelectric effect in  $Cr_2O_3$ . If we compare the values of  $R_{333}$  obtained by the second moment and linewidth methods, as found in Table I, we see that for both ions the two results are in agreement within experimental error. The somewhat smaller values given by the linewidth method are thought not to reflect a systematic difference. These results give one added confidence in the use of the linewidth method when the line splitting is not resolved. This is convenient since it is considerably easier to apply in practice. As another check on this method, the broadening of the  $1/2 \leftrightarrow 3/2$  low magnetic field Cr<sup>3+</sup> line in  $Al_2O_3$  was examined. The value found for  $R_{333}$ agreed within experimental error with the known value.<sup>4</sup>

In the case of Mn<sup>2+</sup>, it was possible to make measurements on ESR lines from several hyperfine sets. Although the actual amount of splitting for lines from the  $3/2 \leftrightarrow 5/2$  hyperfine set was twice as large as for the  $1/2 \leftrightarrow 3/2$  set, measurements were more difficult because of the increased linewidth and reduced signalto-noise ratio. The results, however, agreed with those shown in Table I. In addition, measurements were made on the  $1/2 \leftrightarrow -1/2$  hyperfine set of Mn<sup>2+</sup> to check for possible changes in the *g* tensor. No change was observed at fields up to 127 kV/cm although the broadening due to a shift of  $3 \times 10^{-4}$  of the initial g value would have been detectable. For the  $Fe^{3+}$  ion, no pure  $1/2 \leftrightarrow -1/2$  transition exists at the X-band frequency used here  $(\sim 9400 \text{ Mc/sec})$ ,<sup>11</sup> and as a result no estimate could be made of the *g* shift although it is expected to be quite small since the experimental *g* value is quite close to the free spin value.

Since only electric field broadening of the ESR lines was observed for the ions considered here, it is necessary to point out certain assumptions made in the interpretation of the data. Thus it was assumed that

<sup>8</sup> R. T. Weidner and C. A. Whitmer, Phys. Rev. 91, 1279 (1953). 9 These values are somewhat different than those reported earlier [Bull. Am. Phys. Soc. 8, 259 (1963)] as a result of additional measurements at higher electric fields.

<sup>10</sup> G. T. Rado, Phys. Rev. Letters 6, 609 (1961).

<sup>11</sup>L. S. Kornienko and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. 40, 1594 (1961) [English transl.: Soviet Phys.—TETP 13, 1120 (1961)].

TABLE II. Crystal radii in octahedral coordination.\*

Ion	Radius $(A)$	
$\rm Gd^{3+} \ Mn^{2+}$ $Cr^{3+}$ $\overline{\text{Fe}}^{3+}$ $A13+$	1.02 0.80 0.69 0.64 0.50	

a L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed., p. 518.

upon application of an electric field the ESR line splits into two parts of equal intensity which retain the same shape and width as the original line. In the case of  $Cr^{3+}$ in  $\overline{A}l_2O_3$ , it has indeed been shown<sup>4</sup> that the linewidth is not altered appreciably when the line is completely split by the electric field. On the other hand, the equal intensity of the two parts would imply that sites related by inversion symmetry are equally populated. In this regard, the observed lack of equality of the intensity of the Gd3+ resonance from two physically equivalent sites in  $\text{Al}_2\text{O}_3$  (such as sites a and b of Fig. 1) should be noted. This has been attributed to a nonequivalence of the two sites during the growth process and is associated with the large size of the  $Gd^{3+}$  ion<sup>2</sup> (Table II). However, the  $Fe^{3+}$  spectrum is known to be normal,<sup>2</sup> and while the complexity of the  $Mn^{2+}$  spectrum when the angle between the magnetic field and the *c* axis is not near 0 or 90° precludes a similar statement concerning this ion, we note that its crystal radius is not greatly different from those of  $Cr^{3+}$  and  $Fe^{3+}$  (Table II). It is therefore expected that the assumption of equality of intensity would be valid for both  $Fe^{3+}$  and  $Mn^{2+}$ . Experimentally, it is possible to resolve this question by measuring the shift in line centroid when the electric field is applied.<sup>4</sup> By this means it was found that for  $b$ oth  $Mn^{2+}$  and  $Fe^{3+}$  the inversion related sites were equally populated to within one part in fourteen.

It should be pointed out that the nonvanishing value of  $R_{333}$  found for these two ions shows conclusively that they are situated in sites which lack inversion symmetry. This finding strongly suggests that the ions enter substitutionally into the  $Al^{3+}$  sites rather than into sites such as *d* and *e* (Fig. 1) which possess inversion symmetry. The axial symmetry of the  $Mn^{2+}$  spectrum indicates that any local charge compensation must lie on the *c* axis.<sup>12</sup> In the case of the crystals used here, no additional impurities have been added to achieve charge compensation. Furthermore, charge compensation by  $Mn^{4+}$  is ruled out since no spectrum due to this ion is seen. While it is possible that a monovalent interstitial or quadrivalent substitutional impurity may be located adjacent to the  $Mn^{2+}$  ion, the ESR spectrum would then indicate that almost every  $Mn^{2+}$  ion is so compensated.

A summary of the "best" electric field effect parameters for Fe<sup>3+</sup> and Mn<sup>2+</sup> is presented in Table III along

with the corresponding  $Cr^{3+}$  values for comparison. These values represent an average of those obtained by the second moment and linewidth methods. For Fe<sup>3+</sup> they include determination on crystals from two different batches, one of which contained Fe<sup>3+</sup> as an unwanted impurity, while for Mn<sup>2+</sup>, results from lines measured in four hyperfine sets are included.

It is of some interest to consider the relative size of the electric field effect for two isoelectronic ions such as we have here. Table III illustrates the fact that within experimental error, the parameter  $R_{333}$  has the same value for both ions and is almost an order of magnitude smaller than for  $Cr^{3+}$ . We can consider  $R_{333}$ as expressing the change in the axial crystal field parameter *D* with applied field *E.* We then find the relation

$$
\frac{3}{2}R_{333} = \partial D/\partial E. \tag{3}
$$

The third column in Table III lists the relative changes  $D^{-1}(\partial D/\partial E)$  with applied electric field. In these terms, we see that  $Mn^{2+}$  and  $Cr^{3+}$  are quite similar in their relative  $D$  changes while the effect for  $Fe<sup>3+</sup>$  is much smaller. This results, of course, from the large *D* value for  $\text{Fe}^{3+}$  (+1796.4 G<sup>11</sup>) as compared to isoelectronic  $Mn^{2+}$  (+208.3 G<sup>12</sup>). This difference in *D* is characteristic of all crystals in which both ions have been examined in sites of axial symmetry. Finally, in the last column of Table III, the relative change in *g* value with applied field is listed.

#### DISCUSSION

Since the theory of the *D* parameter as arising from the even components of the crystalline field potential is not fully understood in the case of  $d^5$  ions,<sup>13</sup> it does not seem profitable at this time to make any detailed calculations based on the odd crystal field components. Such calculations would be required, of course, to make a proper estimate of the change in *D* with applied field which arises via the mixing of odd excited states into the even ground state by the odd components of the crystalline field potential. We therefore content ourselves with some qualitative remarks. Clogston,<sup>14</sup> in explaining the large optical Faraday rotation of the

TABLE III. Summary of the electric field parameters for  $Mn^{2+}$  and  $Fe^{3+}$  in  $Al_2O_3$ .

Ton	$R_{333}$	$D^{-1}(\partial D/\partial E)$	$g^{-1}(\partial g/\partial E)$
	$(10^{-5} \text{ G cm/V})$	$(10^{-9}$ cm/V)	$(10^{-9}$ cm/V)
$Mn^{2+}$	$0.69 + 0.06$	50 +4	< 2.4
$Fe3+$	$0.67 + 0.06$	$5.6 \pm 0.5$	$\cdots$
$\bigcap_{r3^+}$	$6.43 + 0.11$ <sup>a</sup>	$46.6 \pm 0.8$ <sup>a</sup>	$\cdots$

a Taken from Ref. 4 for comparison.

<sup>13</sup> For recent discussions see: W. J. Nicholson and G. Burns, Phys. Rev. 129, 2490 (1963); and A. M. Germanier, D. Gainon, and R. Lacroix, Phys. Letters 2, 105 (1962).

14 A, M. Clogston, J. Appl. Phys. 31, 198S (1960).

<sup>12</sup> W. Low and J. T. Suss, Phys. Rev. 119, 132 (1960).

ferrimagnetic garnets, postulated that the  ${}^6P(3d^44p)$ state of Fe<sup>3+</sup> is depressed from the free-ion value of 190 000 cm<sup>-1</sup> into the neighborhood of 50 000 cm<sup>-1</sup>, based on optical absorption measurements on Fe<sup>3+</sup> in AI2O3. Another possibility considered was that the strong absorption at 50 000 cm<sup>-1</sup> may arise instead from charge transfer states associated with the oxygen ligands. In any case, there are states of predominantly odd parity near 39 000 and 51 000 cm-1 . Such states could contribute to the microwave electric field effect by being mixed into the ground state, as noted above.

It should be pointed out, however, that in the case of  $Cr^{3+}$  in  $Al_2O_{3}$ , detailed calculations<sup>4</sup> indicate that the predominant effect of the applied field is connected with the motion of the  $Cr^{3+}$  ion relative to the surrounding  $O^{2-}$  ions rather than due to the distortion of the Cr<sup>3+</sup> electronic wave function. A molecular orbital calculation for the complex containing the paramagnetic ion<sup>15</sup> was found necessary to predict the proper effect of the ionic motion. In this calculation, it was shown that the sign of *D* and its proper magnitude can be explained by an anisotropic spin-orbit coupling. The change in this anisotropy produced by ionic motion then gives rise to the observed effect.

In the present case, an attempt is made to get some idea of the size of relative change in *D* with electric field within the framework of a crystal field model. This can be done by considering the motion of the ion as producing a change in the even axial component  $V_{ax}$  of the crystalline potential. The *D* parameter may be expressed in the following manner, 6,13

$$
D = D_1 V_{ax} + D_2 V_{ax}^2.
$$
 (4)

The work of Nicholson and Burns<sup>12</sup> suggests that the simple crystal field calculations of Watanabe<sup>6</sup> give the wrong sign for  $D_2$ . In the following, the form of  $(4)$  is taken as valid as suggested by theory, but the signs of *Di* and *D2* are those determined by experiment. This assumption is not arbitrary since it is clear that *D* must vanish in the absence of an axial field, and can in general be expressed in the form of a power series in  $V_{ax}$ . For the small relative ionic displacement *x* produced by available applied electric fields (about  $10^{-12}$  cm for  $10^5 \text{ V/cm}$ ),

$$
V_{\text{ax}} = V_{\text{ax}}{}^{0} + (\partial V_{\text{ax}}/\partial x)_{0}x. \tag{5}
$$

The quantity  $(\partial V_{ax}/\partial x)_0$  is nonvanishing because of the lack of inversion symmetry at the cation site. Otherwise the change would be quadratic in  $x$ . From  $(4)$  and  $(5)$ we obtain

$$
\frac{1}{D}\frac{\partial D}{\partial E} = \frac{1}{V_{\text{ax}}}\left(\frac{\partial V_{\text{ax}}}{\partial x}\right) \left[\frac{D_1 + 2D_2 V_{\text{ax}}^0}{D_1 + D_2 V_{\text{ax}}^0}\right]k\,,\tag{6}
$$

where  $k = \partial x/\partial E$  is the relative ionic motion per unit applied field. If we consider the experimental data for

the relationship between *D* and  $V_{ax}$  as found for Fe<sup>3+</sup> in various crystals by Nicholson and Burns,<sup>13</sup> we conclude that  $D_1$  and  $D_2V_{ax}^0$  have the same sign in  $Al<sub>2</sub>O<sub>3</sub>$ . It follows that the value of the expression in brackets in (6) lies between one and two. It is assumed that the same sign relationship is true for  $Mn^{2+}$ . Further, we expect  $k$  to have roughly the same value for  $Fe^{3+}$ and  $\text{Mn}^{2+}$ . (Although the force on the Mn<sup>2+</sup> ion will be roughly two-thirds that on the Fe<sup>3+</sup> ion, the restoring forces will be correspondingly reduced because of the relaxation of the lattice about the site of the divalent ion.) As was noted in Table III, however, the value of  $D^{-1}(\partial D/\partial E)$  is about 9 times larger for Mn<sup>2+</sup>. It is concluded, therefore, that the quantity  $(V_{ax}^0)^{-1}$  $\times (\partial V_{ax}/\partial x)_0$  is much larger in the case of Mn<sup>2+</sup> if ionic motion is important in giving rise to the electric field effect. Experimentally, it should be possible to obtain the relative sizes of  $V_{ax}^0$  for the two ions from Mossbauer<sup>13</sup> and electron nuclear double resonance measurements of the quadrupole splitting. By thus considering the relative change in *D* rather than the absolute change, the difference in the sensitivity of the two ions to axial crystalline fields (reflected in  $D_1$  and  $D_2$ ) is eliminated for the most part. This difference shows up in the considerably different *D* values of the two ions as noted above.

This technique permits an order of magnitude estimate of the value of  $D^{-1}(\partial D/\partial E)$  due to ionic motion to be made. The work of Laurance and Lambe<sup>16</sup> allows the quantity  $(V_{ax}^0)^{-1} (\partial V_{ax}/\partial x)_0$  to be evaluated at various positions of the ion along the *c* axis of the crystal since they have performed a point-charge calculation of the electric field gradient. In the absence of a molecular orbital calculation, this appears to be the only reasonable way to estimate the relative change in  $V_{ax}$  with motion. The electric field gradient is the leading term in the axial field and is assumed here to be dominant. If we consider the normal  $Al^{3+}$  ion position, we find that  $(V_{ax}^0)^{-1} (\partial V_{ax}/\partial x)_0 = 6.7$  Å<sup>-1</sup>. Furthermore, for an applied field of  $10^5$  V/cm,  $kE\simeq 2.2\times 10^{-4}$  Å for a trivalent ion in  $Al_2O_3$ . Then using (6) we obtain  $D^{-1}(\partial D/\partial E) = (15-30) \times 10^{-4} / 10^5$  V/cm. This is of the same order of magnitude as the experimentally determined values for  $Fe^{3+}$ , especially, and Mn<sup>2+</sup>. If we consider the case of  $Cr^{3+}$ , Kamimura<sup>17</sup> has indicated that the relationship between the trigonal field and *D*  is linear, even including anisotropic spin-orbit effects. The calculations of Lohr and Lipscomb, however, suggest that this is not valid, perhaps because of the importance of the  $Cr^{3+2}T_2(t_2^3)$  state which Kamimura neglected. For a linear dependence, the quantity in brackets in (6) is unity while for the molecular orbital calculation, the corresponding value is 2.5. Then  $D^{-1}(\partial D/\partial E) = (15-38) \times 10^{-9}$  cm/V, which is comparable in magnitude to the measured value. Although

<sup>15</sup> L. L. Lohr, Jr., and W. N. Lipscomb, J. Chem. Phys. 38, 1607 (1963).

<sup>16</sup> N. Laurance and J. Lambe, Phys. Rev. **132,** 1029 (1963).

<sup>17</sup> H. Kamimura, Phys. Rev. **128, 1077 (1962).** 

it has been suggested<sup>3</sup> that the odd components of the axial crystalline field contribute importantly to the value of *D,* the arguments given are no longer considered to be valid.<sup>18</sup> While it is clear that such an oversimplified calculation, based as it is on a point charge model, cannot be expected to give accurate results; it nevertheless indicates that ionic motion probably plays an important role in the microwave electric field effect for  $Fe^{3+}$  and  $Mn^{2+}$  just as for  $Cr^{3+}$ . However, the above discussion does not rule out possible significant contributions from the effect of distortion of the electronic wave function of these S-state ions.

It would be valuable to examine ions which are isoelectronic to the more tractable Cr<sup>3+</sup> ion. These include  $V^{2+}$  and Mn<sup>4+</sup> which have *D* parameters in  $Al_2O_3$  closely similar<sup>16</sup> to that for Cr<sup>3+</sup>. In addition, the effect of

18 J. O. Artman and J. C. Murphy (to be published).

electric fields on the optical spectra of these ions has been studied and interpreted in terms of electronic wave function distortion and ionic displacement.<sup>19</sup> Both of these ions are presently under study in this Laboratory.

## ACKNOWLEDGMENTS

The author would like to express his thanks to V. J. Folen for many illuminating discussions and for his help in x-ray crystal orientation, to R. A. Becker for growing the crystals used, and to the Electron Tubes Shop at the Naval Research Laboratory for their help in fabricating and silvering the samples. I also profited by discussions with J. O. Artman and J. C. Murphy and from the receipt of a copy of M. D. Sturge's manuscript prior to publication.

19 M. D. Sturge, Phys. Rev. 133, A795 (1964).

PHYSICAL REVIEW VOLUME 135, NUMBER 2A 20 JULY 1964

# Coercive Force of Iron Resulting from the Interaction of Domain Boundaries with Large Nonmagnetic Inclusions

WILLIAM D. NIX AND ROBERT A. HUGGINS

*Department of Materials Science, Stanford University, Stanford, California*  (Received 28 February 1964)

The interaction of large inclusions with slowly moving domain boundaries has been quantitatively examined and the contribution made by such inclusions to the coercive force predicted. Several physical models of the interaction between large inclusions and moving Bloch walls were investigated by making calculations of the energy of the closure domain configuration about the inclusions for various positions of the moving domain boundary. By statistically treating a random distribution of inclusions, the coercive force was calculated as a function of the inclusion distribution parameters. Several features of the interactions between spike-shaped closure domains and moving domain boundaries have been elucidated.

# **I. INTRODUCTION**

IT has been shown by many investigators that dislocations, nonmagnetic inclusions, and other chemi-T has been shown by many investigators that discal and physical inhomogeneities influence the properties of bulk ferromagnetic materials. One manner in which imperfections affect the magnetic properties of a material is by acting as impediments or obstacles to the motion of domain boundaries. An analysis of the interaction between domain boundaries and structural imperfections is important in the understanding of irreversible ferromagnetic properties at low and intermediate frequencies.

The particular problem of the determination of the contribution to the coercive force which results from the interaction of domain boundaries with large nonmagnetic inclusions is treated in this paper. It consists of an analysis of the interaction of a moving boundary with the subsidiary domain structure about such inclusions.

One of the first attempts to evaluate the effects of

nonmagnetic inclusions on coercive force was that by Kersten.<sup>1</sup> He supposed that the binding energy between a Bloch wall and a nonmagnetic inclusion is given by the reduction in interfacial energy caused by the intersection of the particle by the domain boundary. It was shown by Néel<sup>2</sup> that when a Bloch wall bisects an inclusion, the reduction in the magnetostatic energy is much greater than the change in Bloch wall energy and is therefore more important in determining the binding energy. Néel<sup>3</sup> also later showed that it is necessary to adopt a realistic statistical model of the particle distribution to be able to compute the coercive force which arises from small inclusions. Dijkstra and Wert,<sup>4</sup> using a simplified form of Néel's statistical model, calculated the coercive force due to inclusions with diameters up to the thickness of a Bloch wall.

<sup>1</sup> M. Kersten, Physik Z. 44, 63 (1943).

<sup>2</sup>L. N6el, Cahiers Phys. 25, 21 (1944).

<sup>3</sup> L. Neel, Ann. Univ. Grenoble 22, 299 (1946).

<sup>4</sup>L. J. Dijkstra and C. Wert, Phys. Rev. 79, 979 (1950).