

## Isotope Effect for Cation Self-Diffusion in CoO Crystals\*

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Diffusion of  $^{60}\text{Co}$  in CoO crystals has been measured in the temperature range from 963 to 1638°C in air by the standard tracer-sectioning technique. The temperature dependence of the diffusion coefficient  $D$  is given by  $D = (5.0 \pm 0.4) \times 10^{-3} e^{-(38390 \pm 230)/RT}$  cm<sup>2</sup>/sec. The isotope effect for cation self-diffusion was determined by simultaneous diffusion of  $^{55}\text{Co}$  and  $^{60}\text{Co}$  tracers in CoO crystals. The strength of the isotope effect, defined by  $E_{60} = [1 - (D_{60}/D_{55})] / [1 - (m_{55}/m_{60})^{1/2}] = \Delta K$  was  $0.582 \pm 0.009$ , independent of temperature in the range from 1081 to 1411°C. This result is consistent with cation self-diffusion by a vacancy mechanism only, and  $\Delta K = 0.746 \pm 0.012$ .

### I. INTRODUCTION

NUMEROUS experiments on diffusion in metal oxides have generally explained the measured diffusion coefficients in terms of the concentration and mobility of the defects that are responsible for the migration of the ionic species in question. The concentration of lattice defects in oxides have, in many cases, been controlled by equilibrating to the partial pressure of a constituent, or by doping. From the dependence of the diffusion coefficient on the ambient partial pressure of one of the constituents (usually oxygen) or on the doping of aliovalent elements, a model can then be formulated. The model, in turn, can be used to deduce the defect structure in the lattice and the diffusion mechanism.

Another approach to the study of the diffusion mechanism is to measure the effect of the isotopic mass on diffusion. This approach has been used successfully for diffusion in metals and in some alkali halides,<sup>1</sup> but has never been attempted in metal oxides. The objective of the present work was to study the diffusion mechanism and some details of the kinetic process for cation self-diffusion in CoO by measuring the relative diffusion coefficients for  $^{55}\text{Co}$  and  $^{60}\text{Co}$  in CoO crystals. CoO is a cation-deficient oxide exhibiting  $p$ -type semiconduction at high temperatures with oxygen pressures near 1 atm. Previous studies have considered the primary non-stoichiometric defect to be a cobalt vacancy. The crystal structure of CoO is of the NaCl type.

### II. CORRELATION FACTORS AND ISOTOPE EFFECT

For random atomic jumps in a cubic crystal, the diffusion coefficient  $D$  is given by

$$D = \frac{1}{6} \Gamma r^2, \quad (1)$$

where  $\Gamma$  is the atomic jump frequency, and  $r$  is the jump distance. If the jump direction of a given atom

depends on the direction of a previous jump, then

$$D = \frac{1}{6} \Gamma r^2 f, \quad (2)$$

where the correlation factor  $f$  takes into account the correlation between the directions of successive atomic jumps. For self-diffusion in a cubic lattice,  $f$  is a numerical factor determined only by the crystal lattice and the diffusion mechanism, and it has been calculated for several diffusion mechanisms in a number of crystal structures.<sup>2,3</sup> Thus, direct measurement of  $f$  may enable a unique determination of the mechanism of diffusion.

For tracer diffusion in solids,  $f$  can be obtained from an accurate measurement of the relative diffusion rates of two different isotopes of the same element. The isotope effect in diffusion has been expressed by Schoen,<sup>4</sup> and later by Tharmalingam and Lidiard,<sup>5</sup> as

$$(1 - D_{\beta}/D_{\alpha}) / (1 - \Gamma_{\beta}/\Gamma_{\alpha}) = f, \quad (3)$$

where the subscripts  $\alpha$  and  $\beta$  pertain to the isotopes with masses  $m_{\alpha}$  and  $m_{\beta}$ , respectively. In those cases in which only one atom undergoes an atomic displacement during the jump process and its jumping motion is not coupled with the surrounding atoms, the ratio of the jump frequencies may be approximated by the simple relation

$$\frac{\Gamma_{\beta}}{\Gamma_{\alpha}} = \left( \frac{m_{\alpha}}{m_{\beta}} \right)^{1/2}. \quad (4)$$

However, if the motion of the jumping atom is coupled with the surrounding atoms, the ratio of the jump frequencies, as given by Mullen,<sup>6</sup> is

$$1 - \frac{\Gamma_{\beta}}{\Gamma_{\alpha}} = \Delta K \left[ 1 - \left( \frac{m_{\alpha}}{m_{\beta}} \right)^{1/2} \right]. \quad (5)$$

Here  $\Delta K$  has the physical meaning of the fraction of the total translational kinetic energy at the saddle

<sup>2</sup> K. Compaan and Y. Haven, *Trans. Faraday Soc.* **52**, 786 (1956); **54**, 1498 (1958).

<sup>3</sup> J. G. Mullen, *Phys. Rev.* **124**, 1723 (1961).

<sup>4</sup> A. H. Schoen, *Phys. Rev. Letters* **1**, 138 (1958).

<sup>5</sup> K. Tharmalingam and A. B. Lidiard, *Phil. Mag.* **4**, 899 (1959).

<sup>6</sup> J. G. Mullen, *Phys. Rev.* **121**, 1649 (1961).

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<sup>1</sup> Among reports, see, for example, N. L. Peterson, *Solid State Phys.* **22**, 409 (1968).

TABLE I. Spectrographic analysis of impurities in a CoO crystal.

Element	Content (wt %)	Element	Content (wt %)
Ag	<0.001	Mo	<0.01
Al	<0.001	Na	<0.01
B	<0.01	Ni	<0.001
Bi	<0.001	Sb	<0.01
Cr	<0.01	Si	<0.005
Fe	<0.01	Sn	<0.005
K	<0.05	Ti	<0.01
Li	<0.001	Zr	<0.01
Mn	<0.001		

point, associated with motion in the direction of the diffusional jump, that belongs to the jumping atom. From Eqs. (3) and (5), the general expression for the isotope effect in diffusion becomes

$$E_{\beta} \equiv \frac{1 - (D_{\beta}/D_{\alpha})}{1 - (m_{\alpha}/m_{\beta})^{1/2}} = f\Delta K, \quad (6)$$

where  $E_{\beta}$  is the strength of the isotope effect. For diffusion mechanisms that involve more than one atom in the jump process, Vineyard<sup>7</sup> has shown that the quantity  $(m_{\alpha}/m_{\beta})^{1/2}$  in Eq. (6) should be replaced by

$$\left[ \frac{(n-1)m + m_{\alpha}}{(n-1)m + m_{\beta}} \right]^{1/2}, \quad (7)$$

where  $n$  is the number of atoms participating in the jump process, and  $m$  is the average mass of the non-tracer atoms.

From the above expressions, one can determine  $E_{\beta} = f\Delta K$  by measuring the relative diffusion coefficients of two isotope of the same element. The measured  $E_{\beta}$  and the allowed values of  $f$  and  $\Delta K$  may permit an unambiguous determination of the diffusion mechanism and thus provide a unique value of  $\Delta K$ .

### III. EXPERIMENTAL

#### A. Materials

CoO crystals were grown by the Verneuil process in an arc-image furnace. The starting material was a "high-purity" grade (>99.999%, according to the supplier) cobalt-oxide powder purchased from Atomergic Chemetals Co., N. Y. The spectrographic analysis of a crystal is shown in Table I.

The isotope <sup>60</sup>Co either was produced by neutron bombardment of a high-purity Co foil in the Argonne CP-5 reactor or was purchased from Nuclear Science Division, International Chemical and Nuclear Corporation, in the form of Co<sup>++</sup> in 0.5 N HCl. Analysis of the isotopes with a multichannel analyzer and a Ge(Li) detector showed no detectable radioactive impurities. The half-life of 5.26 yr for <sup>60</sup>Co, as stated in the literature,<sup>8</sup> was adopted. The isotope <sup>55</sup>Co was

produced by 8-MeV-deuteron bombardment of enriched <sup>54</sup>Fe (>94%) by the nuclear reaction <sup>54</sup>Fe(*d,n*)-<sup>55</sup>Co in the Argonne cyclotron. The <sup>55</sup>Co was chemically separated from the iron target and from a small amount of <sup>52</sup>Mn impurity by ion exchange. The final product of carrier-free <sup>55</sup>Co was in the form of Co<sup>++</sup> in 4 N HCl.

#### B. Procedures

Crystals of approximately 10 by 10 by 3 mm with the large surface area parallel to a {100} crystal plane were cut from a crystal boule. The samples were ground and examined for parallelness and flatness. The finished samples were preannealed in air at the diffusion temperature for a period twice as long as the diffusion annealing time to ensure that the intrinsic defects were in thermodynamic equilibrium.

Two methods were used for depositing a thin layer of the radioactive tracers on the sample surface: (1) <sup>60</sup>Co in the form of Co-metal foil was vapor deposited from a Ta ribbon onto the sample surface, (2) 50 λ of a distilled water solution containing either <sup>60</sup>Co or a mixture of <sup>55</sup>Co and <sup>60</sup>Co in the form of CoSO<sub>4</sub> was dried on the sample surface. The specific activities of both isotopes were high enough so that the thickness of the layer deposited by either method never exceeded 1 μm. Both deposition methods were employed for diffusion of <sup>60</sup>Co and the results were found to be identical within the experimental error. For isotope effect measurements, the drying method was used.

The samples were heated in air in a Pt-40% Rh wire-wound furnace, controlled to ±1°C. The temperature of the sample was measured with a calibrated Pt-(Pt-10% Rh) thermocouple with the hot junction located about 1–2 mm from the samples. For the diffusion anneal at 1638°C, the sample was heated in a Mo wire-wound furnace. The measuring thermocouple in this experiment was a calibrated (Pt-6% Rh)-(Pt-30% Rh) couple.

After the diffusion anneal, a thickness of 6–10 times  $(Dt)^{1/2}$  was ground off the edges of the samples to eliminate edge effects. The samples were sectioned by grinding on 400 emery paper on a precision parallel grinder. The grinding papers were retained for counting and the section weights were determined by weighing the sample between each grinding operation. The thickness of each section was calculated using the weight of the section (determined to ±0.2%) and the area and density of the sample. About 18 sections were taken over an activity drop of two to three decades. For these boundary conditions, the specific activity  $C$  of a radioactive tracer may be expressed as a function of the penetration distance  $X$  by the equation<sup>9</sup>

$$C = M / (\pi Dt)^{1/2} e^{-X^2/4Dt}, \quad (8)$$

where  $M$  is the activity per unit area deposited at  $t=0$

<sup>7</sup> G. H. Vineyard, *J. Phys. Chem. Solids* **3**, 121 (1957).

<sup>8</sup> C. M. Lederer, J. M. Hollander, and I. Perlman, *Table of Isotopes* (John Wiley & Sons, Inc., New York, 1967), 6th ed., p. 21.

<sup>9</sup> J. Crank, *Mathematics of Diffusion* (Oxford University Press, New York, 1956), p. 11.

TABLE II. Diffusion coefficients of  $^{60}\text{Co}$  in CoO in air.

Diffusion temperature (°C)	Diffusion time ( $10^3$ sec)	Diffusion coefficient $D$ ( $\text{cm}^2/\text{sec}$ )	Method of deposition
963	149.40	$(8.009 \pm 0.014) \times 10^{-10}$	a
1034	64.80	$(1.865 \pm 0.028) \times 10^{-9}$	a
1081	32.40	$(3.003 \pm 0.022) \times 10^{-9}$	b
1121	25.20	$(4.860 \pm 0.016) \times 10^{-9}$	a
1121	25.20	$(4.924 \pm 0.036) \times 10^{-9}$	a
1168	14.40	$(6.661 \pm 0.030) \times 10^{-9}$	b
1223	10.83	$(1.223 \pm 0.002) \times 10^{-8}$	a
1237	9.00	$(1.271 \pm 0.011) \times 10^{-8}$	b
1298	3.60	$(2.135 \pm 0.016) \times 10^{-8}$	b
1349	3.60	$(3.305 \pm 0.004) \times 10^{-8}$	a
1411	3.60	$(4.871 \pm 0.022) \times 10^{-8}$	b
1492	3.60	$(8.465 \pm 0.018) \times 10^{-8}$	a
1525	3.60	$(1.129 \pm 0.006) \times 10^{-7}$	a
1525	3.60	$(1.051 \pm 0.007) \times 10^{-7}$	b
1638	1.78	$(1.670 \pm 0.007) \times 10^{-7}$	a

<sup>a</sup> Vapor deposition.

<sup>b</sup> Direct drying as  $\text{CoSO}_4$ .

in the plane  $X=0$  and  $t$  is the diffusion annealing time. The diffusion coefficient can be calculated from the slope of a plot of  $\ln C$  versus  $X^2$ .

For the isotope-effect measurements, both isotopes,  $^{55}\text{Co}$  and  $^{60}\text{Co}$ , were diffused simultaneously in the crystal. The ratio of specific activities ( $C_{55}/C_{60}$ ) as a function of penetration (i.e.,  $C_{60}$ ) can be shown from Eq. (8) to be

$$\ln(C_{55}/C_{60}) = \text{const} - [1 - (D_{60}/D_{55})] \ln C_{60}, \quad (9)$$

where the subscripts 55 and 60 pertain to  $^{55}\text{Co}$  and  $^{60}\text{Co}$ , respectively. Thus, a plot of  $\ln(C_{55}/C_{60})$  versus  $\ln C_{60}$  permits a determination of the relative diffusion coefficient  $1 - (D_{60}/D_{55})$ . In this way, errors arising from the diffusion annealing time, temperature, and sectioning are eliminated.

The ratio of the specific activities ( $C_{55}/C_{60}$ ) was determined at various positions in the sample to within 0.1% by a half-life separation of the  $\gamma$  activities of  $^{55}\text{Co}$  (half-life of 17.49 h) and  $^{60}\text{Co}$  (half-life of 5.26 yr). The decay of the total specific activity  $C_{\text{total}}$  in a section is expressed by

$$C_{\text{total}} = C_{55}e^{-\lambda_{55}\tau} + C_{60}e^{-\lambda_{60}\tau}, \quad (10)$$

where  $\tau$  is the elapsed time from an arbitrary reference time and  $\lambda_{55}$  and  $\lambda_{60}$  are the decay constants. Each of the more than 15 sections per sample was counted about 10 times in a well-type 3 by 3-in. NaI(Tl) crystal scintillation counter over a period of about 7 days. Usually, more than  $10^6$  counts were collected each time to ensure statistical errors of less than  $\pm 0.1\%$ . The total counts were corrected for counter dead time, background, and finite counting time. The specific activities of  $^{55}\text{Co}$  and  $^{60}\text{Co}$  at the reference time were obtained by a least-squares fit of the data to Eq. (10). On each experiment, a sample of the pure  $^{55}\text{Co}$  was

counted over a period of more than ten half-lives to determine the half-life as well as to check the purity of the isotope. The mean value of the half-life determinations for  $^{55}\text{Co}$  was  $17.49 \pm 0.10$  h, compared with the literature values between 17.9 and 18.2 h.<sup>8</sup>

#### IV. RESULTS AND DISCUSSIONS

The penetration of  $^{60}\text{Co}$ , plotted as  $\ln C_{60}$  versus  $X^2$ , is shown in Fig. 1. The diffusion coefficients were calculated from the slopes of the plots and the diffusion annealing times. Since all the penetration plots are straight lines over two to three decades in activity, the calculated diffusion coefficients (Table II) represent bulk diffusion.

The temperature dependence of the diffusion coefficient is shown in Fig. 2. The good agreement between the present data and that previously obtained by Carter and Richardson<sup>10</sup> on polycrystalline samples may be observed in Fig. 2. The temperature dependence for diffusion of  $^{60}\text{Co}$  in CoO in air may be expressed by

$$D = (5.0 \pm 0.4) \times 10^{-3} e^{-(38\,390 \pm 230)/RT} \text{ cm}^2/\text{sec}. \quad (11)$$

Isotope-effect measurements were made at five temperatures from 1081 to 1411°C. The plots of  $\ln(C_{55}/C_{60})$  versus  $\ln C_{60}$  are shown in Fig. 3. The points labeled

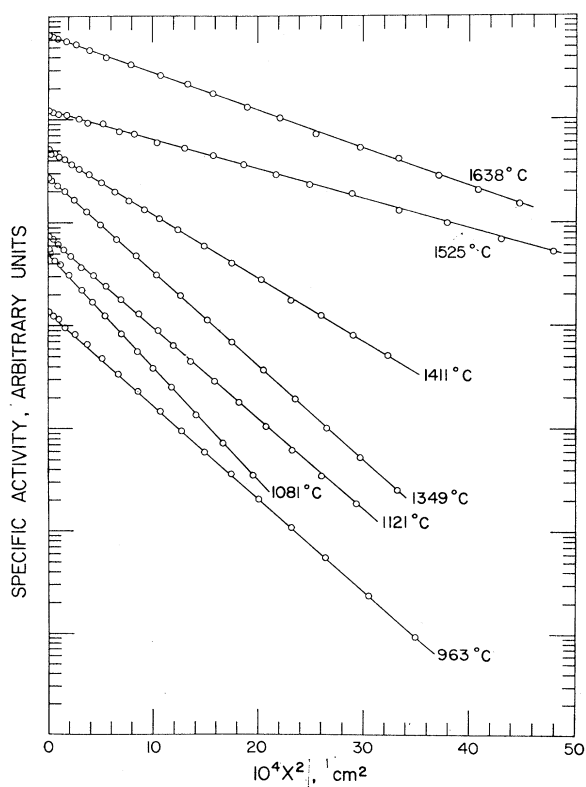


FIG. 1. Log specific activity of  $^{60}\text{Co}$  versus penetration distance squared for the diffusion of  $^{60}\text{Co}$  in CoO in air.

<sup>10</sup> R. E. Carter and F. D. Richardson, J. Metals **6**, 1244 (1954).

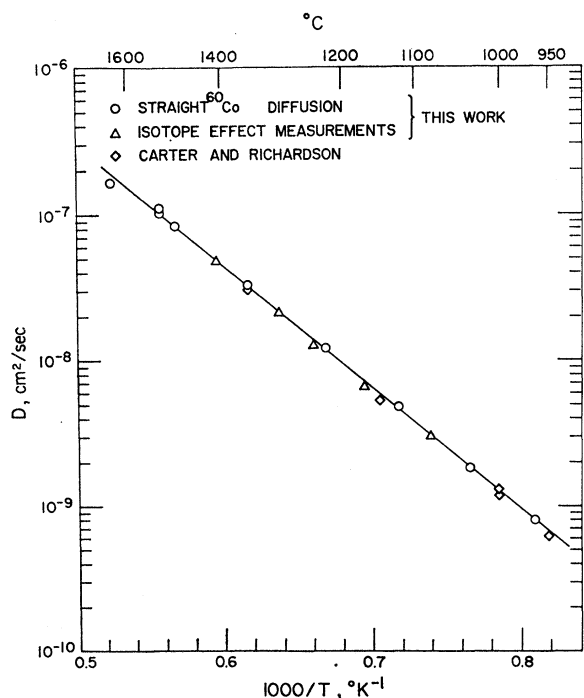


FIG. 2. Log  $D$  versus reciprocal absolute temperature for the diffusion of  $^{60}\text{Co}$  in  $\text{CoO}$  in air.

“null effect” indicate that the measured isotope ratios are not affected by the counting rate. These points were obtained by counting and analyzing, as described above, aliquots of the  $^{55}\text{Co}$  and  $^{60}\text{Co}$  mixture covering the range of activities of the sample sections. The error bar on each point represents the standard error obtained from a least-squares fit of the counting data to Eq. (10). The relative diffusion coefficient,  $1 - (D_{60}/D_{55})$ , at each temperature was obtained by a least-squares fit of the data of Fig. 3 to Eq. (9). Experimental values of  $1 - (D_{60}/D_{55})$  and of  $E_{60}$ , calculated from Eq. (6), are listed in Table III.

It is obvious from Table III that the relative diffusion coefficients are independent of temperature within the experimental error in the range from 1081 to 1411°C.

From Eqs. (6) and (7) we obtain the values of  $\Delta K$  that are needed to make the various diffusion mechanisms consistent with the observed values of  $1 - (D_{60}/D_{55})$  (Table IV).

TABLE III. Relative diffusion coefficient and strength of the isotope effect for  $^{55}\text{Co}$  and  $^{60}\text{Co}$  in  $\text{CoO}$  in air.

Temperature (°C)	Relative diffusion coefficient $1 - (D_{60}/D_{55})$	Isotope effect $E_{60}$
1081	$0.02530 \pm 0.00068$	$0.594 \pm 0.016$
1168	$0.02465 \pm 0.00045$	$0.579 \pm 0.011$
1237	$0.02509 \pm 0.00054$	$0.589 \pm 0.013$
1298	$0.02433 \pm 0.00077$	$0.572 \pm 0.018$
1411	$0.02454 \pm 0.00068$	$0.576 \pm 0.016$
Mean value	$0.02478 \pm 0.00036$	$0.582 \pm 0.009$

TABLE IV. Experimental values of  $\Delta K$  for the various possible mechanisms.

Mechanism	$1 - (\Gamma_{60}/\Gamma_{55})$	$f$	$\Delta K$
Interstitial	0.0426	1.00	0.582
Vacancy	0.0426	0.78	0.746
Vacancy pair	0.0426	$\sim 0.0$	$\gg 1.0$
Interstitialcy:			
collinear	0.0212	0.66	1.77
noncollinear	0.0212	0.96	1.22
Direct exchange	0.0212	1.00	1.17
4-ring exchange	0.0106	1.00	2.34

Since the diffusion coefficient of oxygen in  $\text{CoO}$  has been found<sup>11</sup> to be about four orders of magnitude lower than the diffusion coefficient of Co ions, one would expect the ratio of anion to cation jump frequencies to be very small. Hence, the correlation factor for diffusion by a vacancy pair is estimated to be close to zero.<sup>2,12</sup>

Since  $0 \leq \Delta K \leq 1$ , the only allowed diffusion mechanisms for cation self-diffusion in  $\text{CoO}$  are the interstitial and the vacancy mechanisms. In previous studies,<sup>13</sup> the values of  $\Delta K$  for the interstitial mechanism were consistently close to unity. Therefore, cation self-diffusion in  $\text{CoO}$  is concluded to take place by a vacancy mechanism, with about three-quarters of the translational kinetic energy being carried through the saddle point by the jumping ion.

Since  $\Delta K$  can be as large as unity, one may argue that other mechanisms might also be partially oper-

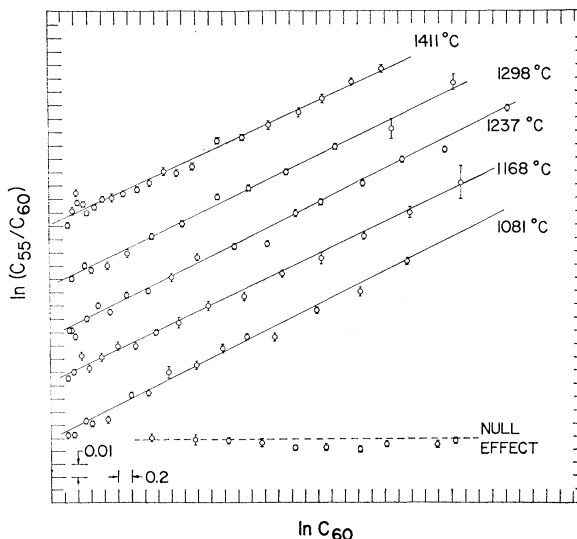


FIG. 3.  $\ln(C_{55}/C_{60})$  versus  $\ln(C_{60})$  for the cation self-diffusion in  $\text{CoO}$  in air;  $\ln(C_{55}/C_{60})$  increases from the bottom to the top and  $\ln(C_{60})$  decreases from the left to the right.

<sup>11</sup> W. K. Chen and R. A. Jackson, *J. Phys. Chem. Solids* **30**, 1309 (1969).

<sup>12</sup> R. E. Howard, *Phys. Rev.* **144**, 650 (1966).

<sup>13</sup> See the references listed in L. W. Barr and A. D. LeClaire, *Proc. Brit. Ceram. Soc.* **1**, 109 (1964).

ating. However, if they are, the experimental results show that their relative contribution to the total diffusion coefficient cannot vary with temperature, because  $1 - (D_{60}/D_{55})$  is temperature-independent. This is not likely for any of the possible second mechanisms. Hence, only one mechanism, the vacancy mechanism, is operating.

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## Ultraviolet Magneto-Optical Properties of Single-Crystal Orthoferrites, Garnets, and Other Ferric Oxide Compounds\*†

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The ultraviolet and visible linear magneto-optical properties of representative ferric oxide compounds were measured by reflection methods between 1.7 and 5.64 eV at room temperature. The experimental technique, based on the complex polar Kerr effect (rotation and ellipticity), was applied to all available single-crystal rare-earth orthoferrites and to representative rare-earth iron garnets, nickel spinel ferrite, and magnetoplumbite. For representative orthoferrites and yttrium iron garnet, the magneto-optical results were reduced, with the aid of additional straight (nonmagnetic) reflectivity data, to obtain the magnetically induced off-diagonal elements of the dielectric tensor. Presentation of the magneto-optical results in the form of the tensor elements facilitates comparison with microscopic theories because of the difference in energy dependence between the tensor elements and the experimental observables. The observed spectra are analyzed in terms of a molecular-orbital theory that elaborates on an earlier calculation by Clogston. For the orthoferrites, explicit calculation of the dielectric-tensor elements has made it possible to identify the most prominent features in the magneto-optical spectra in terms of explicit charge-transfer and crystal-field transitions. The magneto-optical effects in the orthoferrites are approximately the same order of magnitude as in the garnets, although a simple theory would have them an order of magnitude smaller. This is interpreted as evidence for an anisotropic orbital quenching that follows from the low symmetry of the Fe ion in the orthoferrites. Magneto-optical measurements on gallium-substituted europium iron garnet has made it possible to differentiate between the magneto-optical structure that arises from Fe ions on octahedral and tetrahedral sites.

### I. INTRODUCTION

#### A. Motivation and Scope

ALTHOUGH the ferric oxide compounds have been extensively studied, relatively little is known about the wave functions of the electrons that bind them and are responsible for their magnetic character. Much of our present knowledge is restricted to phenomenological constants that describe the material properties without really explaining their origin. The

essential information, a knowledge of the actual wave functions of the magnetic ions, is for the most part lacking. Contribution to this essential knowledge is the objective of the present investigation.

Through the use of optical and magneto-optical (complex polar Kerr effect) reflection techniques, we have made observations of the ultraviolet spectra of bulk, single-crystal ferric oxide compounds.<sup>1,2</sup> The lack of experimental data has for the most part restricted previous workers to speculation on the nature of the highly absorbing transitions which render these materials opaque. The experimental results of the present investigation provide a firm basis for the evaluation of microscopic models and the identification of individual electronic transitions.

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<sup>1</sup> F. J. Kahn, P. S. Pershan, and J. P. Remeika, *Phys. Rev. Letters* **21**, 804 (1968).

<sup>2</sup> F. J. Kahn, P. S. Pershan, and J. P. Remeika, *J. Appl. Phys.* **40**, 1508 (1969).