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Electron Spin Resonance and Optical Fluorescence of the Chromia-Alumina System*

JOSEPH BOHANDY

Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland 20910

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Polycrystalline α-phase Al_2O_3–Cr_2O_3 solid solutions containing 0.01–4.98% Cr have been examined using electron spin resonance (ESR) and optical fluorescence techniques. The *KU*-band ESR spectrum of isolated Cr^{3+} ions in the α-phase material is quantitatively explained using perturbation theory. Arguments against a previous explanation of one of the resonance lines from coupled Cr^{3+} ions are given. The absence of sharp line fluorescence in the presence of the relatively narrow ESR line at $g = 1.98$ in the γ-phase material is further evidence for its assignment to Cr^{5+} ions as opposed to Cr^{3+} ions. Two new fluorescent lines are observed when the γ-phase and α-phase coexist and possible explanations are given.

Introduction

Ruby, which is crystalline dilute solid solution of chromia in α-alumina, has been studied extensively by electron spin resonance (ESR) and by optical techniques. Both isolated Cr^{3+} ions and exchange coupled pairs of Cr^{3+} ions are observed (*1*, *2*).

Many studies of the chromia-alumina system in polycrystalline form have also been made and are summarized in the review article by Poole and MacIver (*3*). O'Reilly and MacIver (*4*) used ESR to study impregnated chromia-alumina catalysts made at 500°C. They also presented a spectrum of polycrystalline ruby, and they stated that plots of ruby resonance fields vs. $\cos\theta$ explain the spectrum. Poole, Kehl, and MacIver (*5*) have reported an ESR study of coprecipitated chromia-alumina catalysts made at 500°, 750°, 900°, and 1400°C. They found a resonance from three different types or phases of chromium ions, viz., a δ resonance, due to isolated Cr^{3+} ions; a γ resonance assigned to Cr^{5+} ions; and two β resonances, β_W and β_N, which were attributed to coupled Cr^{3+} ions. The β_W resonance did not appear in the samples made at 1400°C. At this temperature, the samples are completely converted to the trigonal α-phase of Al_2O_3. More recently, Carman and Kroenke (*6*) reported an ESR study of α-phase chromia-alumina solid solutions containing 0.082–14.70 wt% Cr_2O_3. Their samples were formed at 1350°C and their results differed from those of Poole et al. (*5*) in that two β resonances, designated as β_I and β_N, were observed in the α-phase samples. Furthermore, Poole's β_N resonance was antiferromagnetic and was identified with clumps of α-Cr_2O_3. Carman's β_N resonance was paramagnetic. He attributed β_N to Cr^{3+} ions coupled by a strong electronic exchange interaction and β_I to Cr^{3+} ions coupled by a weak exchange interaction.

There is little doubt that the δ resonances are due to isolated Cr^{3+} ions in the trigonal field of α-Al_2O_3. However, several features of the ESR spectrum are still questionable. First, the α-phase ESR spectrum was not explained quantitatively by Carman. Second, the assignment of the β_I resonance to weakly coupled Cr^{3+} ions is subject to dispute. Third, there is still a question as to whether the γ resonance is due to Cr^{3+} ions or to Cr^{5+} ions. Therefore, the *X*-band ESR measurements have been repeated and extended to *KU*-band frequencies. In addition, optical fluorescence spectra of the polycrystalline chromia-alumina system have been taken at room temperature and at 77°K. Such measurements have not been reported previously to the author's knowledge.

The results of this combined study are (1) a quantitative explanation of the *KU*-band ESR spectrum of isolated Cr^{3+} ions in α-phase Al_2O_3–Cr_2O_3 solid solutions, including several relatively

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strong low field lines; (2) an alternate explanation of the β_I resonance; and (3) the observation of two new fluorescence lines in samples which have not been completely converted to the α-phase.

Experimental Procedure

The chromia–alumina samples were made by preparing mixtures of reagent-grade $AlNH_4(SO_4)_2 \cdot 12H_2O$ containing 0.01–10.0 wt% $CrNH_4(SO_4)_2 \cdot 12H_2O$ and firing at approximately 900°C for 12 hr. The samples were cooled and a portion of the resulting powder was removed. The remaining powders were then heated to 1400°C for 3 hr. X-ray diffraction pictures indicated that the 1400°C samples were homogeneous solid solutions of α-phase Al_2O_3–Cr_2O_3 while the samples made at 900°C contained both α-phase and γ-phase material. Therefore, another sample containing 0.2% Cr was prepared and fired at temperatures from 800°C to 1100°C in 50°C increments. In this way, a series of 0.2% samples ranging from entirely γ-phase material to a mixture of γ-phase and α-phase material was obtained. Atomic absorption and wet chemical analysis of the α-Al_2O_3–Cr_2O_3 solid solutions showed a final Cr content of 0.01–4.98 wt%. The ESR spectra were taken with a standard spectrometer operating at either *X*-band or *KU*-band. The optical fluorescence data were obtained photographically on Kodak Type N plates using a 3-m Jarrell-Ash spectrometer operated in first order and with a dispersion of 5 Å/mm. The samples were illuminated with a 100-W mercury lamp filtered with a $CuSO_4$ solution.

Results and Discussion

Electron Spin Resonance

The *X*-band ESR spectra of α-Al_2O_3–Cr_2O_3 solid solutions are in qualitative agreement with the results of Carman and Kroenke. (*6*) Figure 1 shows a portion of the *X*-band spectrum at room temperature as a function of Cr concentration. One sees the two broad resonances (designated β_I and β_N by Carman) in the 0.55 and 2.14% Cr samples along with the somewhat sharper δ resonance lines attributed to isolated Cr^{3+} ions. The concentration dependence of the δ resonance indicates that they are almost certainly due to isolated Cr^{3+} ions, but a quantitative assignment of the spectrum was not given by Carman and Kroenke. However, van Reijen (*7*) has determined the resonance fields of isolated Cr^{3+} ions in polycrystalline α-Al_2O_3 at *X*-band by diagonalizing the spin-Hamiltonian in the $S = \frac{3}{2}$ manifold. Thus the isolated ion situation at *X*-band is well understood.

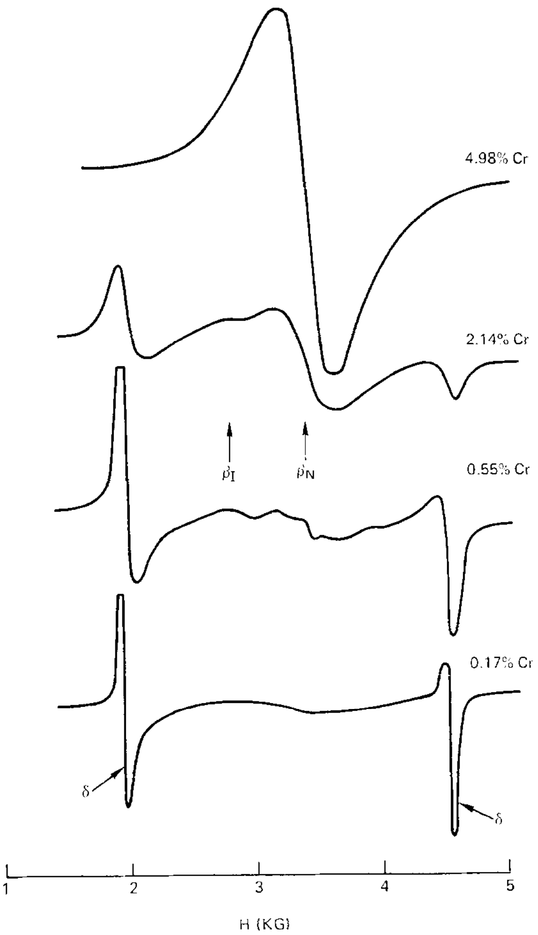

FIG. 1. A portion of the *X*-band ESR spectrum of polycrystalline α-Al_2O_3–Cr_2O_3 solid solutions showing the three types of resonance lines. $T = 300°K$.

Qualitatively, the *KU*-band ESR spectra exhibit the same Cr concentration dependence as at *X*-band.

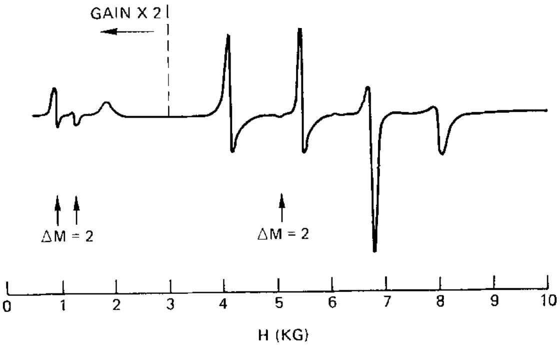

FIG. 2. 16.695 GHz ESR spectrum of a 0.17% Cr sample at room temperature. See Table I for magnetic field values.

Both the number and relative intensities of lines are different, however. Figure 2 shows the 16.695 GHz ESR spectrum of a polycrystalline α-Al_2O_3–Cr_2O_3 sample containing 0.17 wt% Cr. The spectrum can be analyzed in this case without the detailed computer calculation usually necessary to fit polycrystalline ESR spectra by applying the procedure given by Barry (*8*) to the spin-Hamiltonian which describes a crystalline α-Al_2O_3–Cr_2O_3 solid solution, i.e., ruby (*9*). His procedure is as follows. An ESR line will usually occur in polycrystalline ESR spectra at fields which are slowly varying functions of orientation. For the case of axial symmetry one can attempt to fit a polycrystalline ESR spectrum with the stationary values of the second-order perturbation expression for H, the resonance magnetic field, as a function of θ, the angle between H and the unique axis of the crystal. These values are easily obtained and are given by Barry (*8*). They are

$$H_{\mathrm{par}}(\pm\tfrac{3}{2} \leftrightarrow \pm\tfrac{1}{2}) = H_0 \pm 2D, \tag{1}$$

$$H_{\mathrm{per}}(\pm\tfrac{3}{2} \leftrightarrow \pm\tfrac{1}{2}) = H_0 \pm D, \tag{2}$$

$$H_{\mathrm{par}}(+\tfrac{1}{2} \leftrightarrow -\tfrac{1}{2}) = H_0 = \frac{h\nu}{g\beta}, \tag{3}$$

(weak transition)

$$H_{\mathrm{per}}(+\tfrac{1}{2} \leftrightarrow -\tfrac{1}{2}) = H_0 - \frac{0.75D^2}{H_0}, \tag{4}$$

$$H_{42^\circ}(+\tfrac{1}{2} \leftrightarrow -\tfrac{1}{2}) = H_0 + \frac{1.33D^2}{H_0}. \tag{5}$$

The H_{par} transitions will be weaker than the H_{per} transitions because there is only one orientation for which $\theta = 0^\circ$. D, one half the zero-field splitting, is expressed in units of gauss in the above expressions.

Equations (1) to (5) predict a seven-line ESR spectrum while Fig. 2 shows more than seven lines. The additional lines can be explained by extending the procedure of Barry to the "forbidden" $\Delta M = \pm 2$ transitions. These transitions are smaller in intensity than the $\Delta M = \pm 1$ transitions by a factor of the order of $(D/h\nu)^2$. The $\Delta M = 2$ transition fields are (*10*)

$$\begin{aligned} H = \frac{H_0}{2} &- D(M-1)(3\cos^2\theta - 1) \\ &+ \frac{D^2}{H_0}\sin^2\theta\cos^2\theta[4S(S+1) \\ &- 24M(M-2) - 33] \\ &- \frac{D^2}{4H_0}\sin^4\theta[2S(S+1) \\ &- 6M(M-2) - 9]. \end{aligned} \tag{6}$$

The stationary values of (6) are

$$H_{\mathrm{par}}(\pm\tfrac{3}{2} \leftrightarrow \mp\tfrac{1}{2}) = \frac{H_0}{2} \mp D \tag{7}$$

and

$$H_{\mathrm{per}}(\pm\tfrac{3}{2} \leftrightarrow \mp\tfrac{1}{2}) = \frac{H_0}{2} \pm \frac{D}{2} - \frac{0.75D^2}{H_0}. \tag{8}$$

The results are listed in Table I which shows that the *KU*-band ESR spectrum of polycrystalline α-Al_2O_3–Cr_2O_3 solid solutions can be quantitatively explained without a computer fit provided D is sufficiently smaller than the microwave frequency ($D = 5.747$ GHz in ruby.) At *X*-band the low field transitions have a larger intensity relative to the allowed transitions supporting their assignment as $\Delta M = 2$ transitions.

Another questionable point in previous ESR studies is the β_I resonance shown in Fig. 1. Carman has assigned this resonance to Cr^{3+} ions which are weakly coupled by an electronic exchange interaction and has attributed β_N to Cr^{3+} ions coupled by a strong exchange interaction. To eliminate the possibility that β_I results from one of the many other crystallographic phases which are possible in this system or to impurities, a piece of heavily doped (~2 wt% Cr) ruby crystal was crushed and the ESR spectrum recorded as a function of particle size. The essential portion of the resulting spectrum is shown in Fig. 3 where one sees that the β_I resonance is

TABLE I

COMPARISON OF EXPERIMENTAL AND COMPUTED ESR LINE POSITIONS OF 0.17% Cr SAMPLE AT 16.695 GHz

Experimental line positions	$\Delta M = \pm 1$; Eqs. (1)–(5)[a]	$\Delta M = \pm 2$; Eqs. (6) and (7)
Not observable on magnet	10149 G	
8010 G	8080	
6789	6958	
6035	6011	
5437	5477	
5070		5074 G
4139	3942	
Not observed		3506
1850	1873	
1270		1436
934		936

[a] Computed using the spin-Hamiltonian values given in Ref. (9).

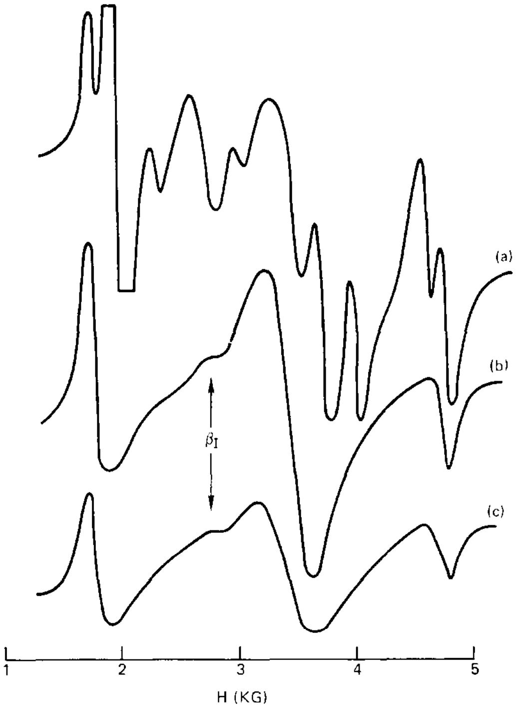

FIG. 3. Comparison of the X-band ESR spectrum of a crushed ruby crystal (~2% Cr) to the 2.14% Cr α-phase sample. (*a*) Particle size approximately 0.05 inch, (*b*) particle size less than 0.006 inch, (*c*) 2.14% Cr α-phase powder.

present in the crushed ruby when the particle size is equal to 0.006 inch. The lower spectrum is included for comparison. Carman's explanation of β_I is believed to be incorrect for the following reason. The spin-Hamiltonian for a pair of ions coupled by an exchange interaction is given by (*11*)

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + JS_1\cdot S_2 + D_e(3S_{1z}S_{2z} - S_1\cdot S_2), \tag{9}$$

where J is the isotropic exchange interaction, D_e includes anisotropic contributions to the exchange interaction plus the anisotropic dipole–dipole interaction, and $\mathcal{H}_1$ and $\mathcal{H}_2$ are spin-Hamiltonians of the isolated Cr^{3+} ions in the axial field of ruby, viz.,

$$\mathcal{H}_i = g\beta H\cdot S_i + D[S_{iz}^2 - \tfrac{1}{3}S_i(S_i + 1)]. \tag{10}$$

Landry, Fournier, and Young (*12*) have shown that when J is larger than the Zeeman term, $g\beta H$, omission of all anisotropic portions of (9) leads to a single ESR line at $g = 2.0$. This is because the allowed $\Delta M_s = \pm 1$ transitions within each manifold of total S all occur at $g = 2.0$. Thus, the assumption of strong isotropic exchange coupling accounts for the strong β_N resonance observed in the samples having a high Cr content. Furthermore, Mollenauer et al. have shown (*13*) that in the case of ruby crystals the J values for the first four nearest neighbor pairs range from 183 to 6.9 cm^{-1} while Statz et al. (*14*) have shown that J is at least 0.5 cm^{-1} out to the eleventh nearest neighbor although a few ESR lines were observed for which J was comparable with D ($D = 0.19$ cm^{-1}). Since the Zeeman energy is 0.3 cm^{-1} at X-band frequencies, we suggest that ESR lines arising from such pairs in α-Al_2O_3–Cr_2O_3 all contribute to β_N and that the β_I resonance is due to Cr^{3+} ions which are coupled by a large anisotropic exchange interaction. The g value for β_I is distinctly lower than that of the β_N resonance.

The γ-phase samples exhibit the relatively narrow (50 G) γ resonance at $g = 1.98$. This line has been attributed to both Cr^{3+} ions and Cr^{5+} ions by various authors (*4*, *15*) with the consensus being for Cr^{5+}. More evidence for Cr^{5+} will be given in the next section.

Optical Fluorescence

The optical fluorescence spectra of the polycrystalline α-phase Al_2O_3–Cr_2O_3 solid solutions were essentially identical to the fluorescence spectrum of crystalline ruby (*1*). At 77°K, only the two R-lines which are due to isolated Cr^{3+} ions are observable in the sample containing 0.01% Cr. All of the more concentrated samples exhibit the R-lines and the numerous exchange-coupled pair lines, the most intense being the two N-lines at 7009 and 7041 Å.

Kaplyanskii et al. (*16*) have reported concentration dependent line shifts in the optical spectrum of ruby crystals containing up to 1.77% Cr. Using the polycrystalline samples, their R-line and N-line measurements have been extended to 4.98 wt% Cr and shifts of other pair lines have been measured. Ruby crystals with this much Cr are extremely difficult, if not impossible, to grow. These results will be presented elsewhere.

Quantitative comparisons between the ESR and optical results could not be made because of the difficulty in comparing optical spectra taken on photographic plates. However, there is a definite correlation. First, the R-line intensity is proportional to the intensity of the δ resonances observed by ESR. Both the R-line and δ ESR intensities increase in the lower Cr concentrations, start decreasing in the 2.14% Cr sample, and are barely visible at 4.98% Cr. Secondly, all of the sharp line fluorescent intensities begin to decrease in the samples containing more than 2% Cr and a corresponding broad-band red emission above 7000 Å is observed. The increase in intensity of this band with Cr concentration correlates with the increase in the β_N ESR signal.

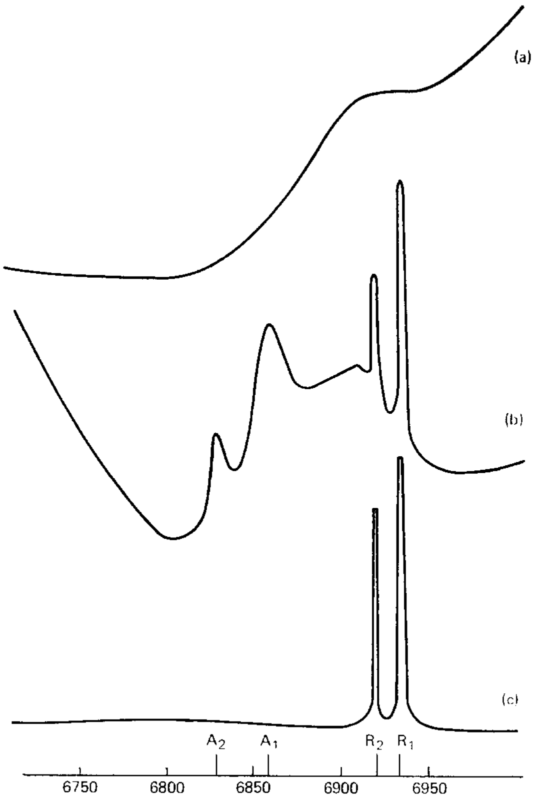

FIG. 4. Change in the fluorescence spectrum of a 0.2% Cr γ-phase Al_2O_3–Cr_2O_3 sample as the calcining temperature is increased. (*a*) 800°C: 16 hr-30 min exposure, (*b*) 950°C: 12 hr-45 min exposure, (*c*) 1400°C: 3 hr-20 sec. exposure.

Fluorescence measurements offer another means of distinguishing between Cr^{3+} and Cr^{5+} in the γ-phase material, the idea being that Cr^{3+} should exhibit an R-line type of fluorescence, even in purely cubic sites (*17*), whereas Cr^{5+} should not. Figure 4(a) shows no sharp line fluorescence at 77°K in the 0.2% Cr γ-phase sample fired at 800°C. The same is true for samples fired at 850° and 900°C. The γ ESR resonance is observed in all of these samples. The absence of fluorescence in the presence of the γ ESR line supports the Cr^{5+} assignment. When the 0.2% Cr γ-phase sample was further heated to 950°C, a trace of the crystallographic α-phase is detected as witnessed by the appearance of the fluorescent R-lines. In addition, two relatively broad lines, referred to as A_2 and A_1, are observed at 6829 and 6862 Å. Figure 4(b) shows A_1, A_2, R_1, and R_2, while in Fig. 4(c) we see that A_1 and A_2 disappear upon complete conversion to the α-phase by heating to 1400°C. It is difficult to interpret A_1 and A_2 because of the limited information. Absorption spectra of the powder in its present state could not be obtained and polarization experiments are meaningless. Since the intensity of A_1 and A_2 increased with Cr concentration (and therefore with R-line intensity), the most obvious possibility was that A_1 and A_2 are analogous to the α-phase R-lines, i.e., ${}^2E_g \rightarrow {}^4A_{2g}$ transitions of Cr^{3+} in a different crystallographic phase of Al_2O_3. However, the fact that A_2 is larger than A_1 at room temperature and smaller than A_1 at 77°K seems to eliminate this possibility. Another possibility is that A_1 and A_2 are magnetic dipole transitions of Cr^{3+} ions in cubic sites of two Al_2O_3 phases because the intensity of A_1 and A_2 is much smaller than that of the α-phase R-lines and there are at least two cubic crystallographic phases of Al_2O_3 which are difficult to distinguish by X-ray analysis. Such Cr^{3+} transitions have been observed in MgO (*17*), for example. Yet another possible origin of the lines is energy transfer from the Cr^{3+} ions in the α-phase to Cr^{3+} ions in the γ-phase followed by subsequent fluorescent emission to the ground state. Experimental support for this is that the existence of A_1 and A_2 depends on the presence of the α-phase material. All of these possible explanations are conjecture and further experimental evidence will be necessary.

Summary and Conclusions

The *KU*-band ESR spectrum of isolated Cr^{3+} ions in polycrystalline α-phase Al_2O_3–Cr_2O_3 solid solutions has been quantitatively explained using perturbation theory. An alternative explanation of the β_I resonance in the concentrated samples is given. Optical fluorescence measurements on both γ-phase and α-phase material have been obtained. The absence of fluorescence lines in pure γ-phase samples which show the γ ESR resonance support its assignment to Cr^{5+} ions. Two new emission lines have been observed in samples which simultaneously contain both γ-phase and α-phase Al_2O_3. The origin of these lines is still uncertain. It is shown that fluorescence measurements can be of great utility in studying phase changes in this type of material.

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