

are moved with respect to one another by changing some parameter (usually magnetic field, electric field, or orientation) of the spin Hamiltonian.

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Observation of Cr^{4+} in $\alpha\text{-Al}_2\text{O}_3$ †

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The paramagnetic resonance spectrum of single crystals of $\alpha\text{-Al}_2\text{O}_3$ containing chromium grown under conditions favoring the stabilization of Cr^{4+} has been observed. Data were taken at X band at liquid-helium temperatures. A single absorption line was observed which is attributed to a $\Delta M = \pm 2$ transition. The crystal-field splitting parameter is inferred from the temperature dependence of the strength of the resonance to be $D \cong +7 \text{ cm}^{-1}$. The spectroscopic splitting factor is $g_{11} = 1.90_{-0.01}^{+0.02}$. A distribution of lower symmetry fields gives rise to an asymmetric line; the range of E values deduced from this asymmetry is $0 \lesssim E \lesssim 0.05 \text{ cm}^{-1}$, where $2E$ is the zero-field doublet splitting. Optical absorption data and radiation effects are presented.

I. INTRODUCTION

THE paramagnetic resonance spectra of iron group ions in the $\alpha\text{-Al}_2\text{O}_3$ host lattice have been the subject of study for some years. The only ion of the $3d^2$ configuration which has received attention is V^{3+} . Optical-absorption measurements on V^{3+} in $\alpha\text{-Al}_2\text{O}_3$ have been made by Pryce and Runciman¹ and spin-resonance studies are reported by Zverev and Prokhorov² and by Lambe and Kikuchi.³ No work has been reported on the isoelectronic species Cr^{4+} in any host lattice. We have performed spin-resonance and optical-absorption measurements on single crystals of $\alpha\text{-Al}_2\text{O}_3$ containing chromium which have been grown under conditions favoring the stabilization of Cr^{4+} , rather than the usual valence state Cr^{3+} (ruby). The crystals, which are bright orange in color and show only a very faint red fluorescence under ultraviolet or green excitation due to a background of Cr^{3+} , bear no visual resemblance to ordinary ruby.

The spin-resonance properties of Cr^{3+} ($S = \frac{3}{2}$) in the axial electric field of $\alpha\text{-Al}_2\text{O}_3$ have been studied extensively.⁴⁻⁶ The crystal-field splitting of 0.38 cm^{-1}

gives rise to a rich and predictable spectrum from Cr^{3+} when resonance measurements are carried out at X-band microwave frequencies. The $S=1$ spin state of Cr^{4+} is readily discernible from such background Cr^{3+} absorptions by its distinctive behavior in regard to number of lines, angular dependence, temperature dependence, and saturation behavior. A paramagnetic resonance-absorption line has been found which is attributable to a system of $S=1$ which we propose is Cr^{4+} .

Optical-absorption measurements have revealed the intense spectra of defect centers rather than the absorptions of the Cr^{4+} ion. The purpose of this paper is to point out the stable existence of the species Cr^{4+} in $\alpha\text{-Al}_2\text{O}_3$ and to describe the spin-resonance properties of this ion.

II. EXPERIMENTAL

The crystals were grown by the Verneuil method. Substitution of tetravalent chromium for trivalent aluminum requires a method of charge compensation. In this case, anionic compensation was used; N^{3-} was substituted for O^{2-} . This substitution can be effected by the incorporation of nitrides in the powder feed.⁷ In order to maximize conversion of Cr^{3+} to Cr^{4+} , the samples were oxidized under one atmosphere of oxygen at 1400°C for approximately 16 h. Because of complications which can be introduced into the spin-resonance spectrum by other transition metal ions, especially iron, great care was taken to prevent impurity contamination. Values of chromium concentration

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¹ M. H. L. Pryce and W. A. Runciman, *Discussions Faraday Soc.* **26**, 34 (1958).

² G. M. Zverev and A. M. Prokhorov, *Zh. Eksperim. i Teor. Fiz.* **34**, 1023 (1958) [translation: *Soviet Phys.—JETP* **7**, 707 (1958)].

³ J. Lambe and C. Kikuchi, *Phys. Rev.* **118**, 71 (1960).

⁴ A. A. Manenkov and A. M. Prokhorov, *Zh. Eksperim. i Teor. Fiz.* **28**, 762 (1955) [translation: *Soviet Phys.—JETP* **1**, 611 (1955)].

⁵ M. M. Zaripov and I. I. Shamonin, *Zh. Eksperim. i Teor. Fiz.* **30**, 291 (1956) [translation: *Soviet Phys.—JETP* **3**, 171 (1956)].

⁶ J. E. Geusic, *Phys. Rev.* **102**, 1252 (1956).

⁷ R. C. Pastor (to be published).

(without regard to valence state) were determined by emission spectroscopy. Typical concentrations were approximately $2 \times 10^{18} \text{ cm}^{-3}$.

The spin-resonance measurements were made at X -band in a 6-in. magnet capable of fields up to 7000 G. Samples were placed in a rectangular cavity in such a position that a component of microwave magnetic field existed both parallel and perpendicular to the static field. Measurements were taken at room temperature, liquid-nitrogen temperature, and liquid-helium temperature. Temperatures below 4.2°K were determined by measuring the vapor pressure over the He bath. The approximate concentration of Cr^{4+} was deduced by taking the difference between total chromium as determined by emission spectroscopy and Cr^{3+} as determined by the relative strength of simultaneous Cr^{3+} spin-resonance absorptions in the sample under consideration and in a sample containing only Cr^{3+} in known amount. The values obtained for the Cr^{4+} concentration, typically $1 \times 10^{18} \text{ cm}^{-3}$, were in agreement with the amount of charge compensator estimated to be incorporated into this material.

The optical-absorption measurements were carried out at room temperature and at liquid-nitrogen temperature in a Beckman DK1A recording spectrophotometer. Path lengths on the order of one centimeter were used. Crystal orientation was established by x-ray methods for both optical absorption and spin resonance measurements.

III. EXPERIMENTAL RESULTS

A. Spin Resonance

In the $\alpha\text{-Al}_2\text{O}_3$ lattice, the cations are located at the center of a slightly distorted octahedron of six oxygen ions. The resulting field of trigonal symmetry leaves a ground-state triplet 3A_2 lowest (see Fig. 1), which is further split by spin-orbit interaction and the axial

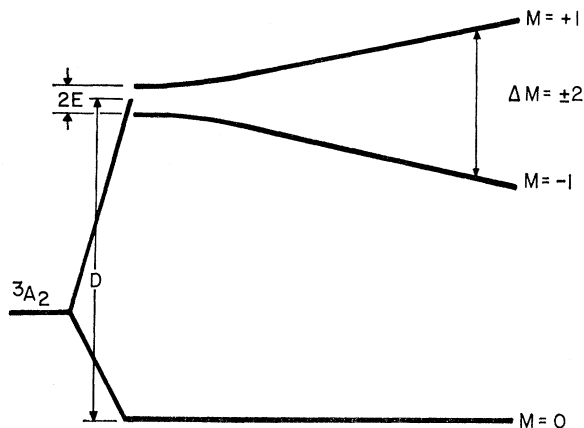


FIG. 1. Ground-state Zeeman energy level diagram for 3A_2 in the axial field of $\alpha\text{-Al}_2\text{O}_3$ plus lower symmetry fields leading to the splitting of the $M=\pm 1$ levels. The relative magnitudes of D , E , and $h\nu$ are not to scale.

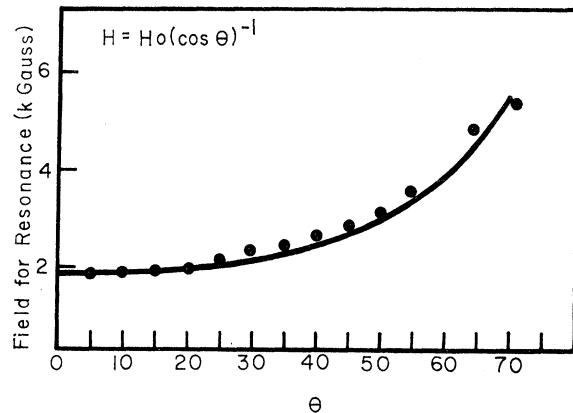


FIG. 2. Angular dependence of the magnetic field for resonance of the $\Delta M=\pm 2$ transition. θ is the angle between the magnetic field and the crystal axis. The points are experimental; the curve is $(\cos\theta)^{-1}$. At 60° the transition is obscured by a Cr^{3+} absorption line.

field into a doublet and a singlet.¹ Fields of lower symmetry mix the $M=\pm 1$ states and give rise to a further splitting ($2E$) of the $M=\pm 1$ doublet.

At liquid-helium temperatures with the crystal axis parallel to the static field, an absorption has been observed at a value of magnetic field appropriate to the transition between the $M=\pm 1$ states of Fig. 1. With the exception of Fe^{3+} background lines,⁸ no other lines not attributable to Cr^{3+} were observed. As the temperature is allowed to increase from 2°K , the intensity of this resonance increases, passing through a maximum at some temperature above 4.2°K . At a still higher temperature the linewidth is observed to increase rapidly until the signal is lost altogether, somewhat below 77°K . Although reliable temperature measurements of the sample were not possible in the range from 4.2 to 77°K , enough data was available below 4.2°K to arrive at an estimate of the splitting D between the singlet ground state and the $M=\pm 1$ levels. These intensity versus temperature measurements indicate that $D=+7 \text{ cm}^{-1}$ to within about 10% .

The observed rapid increase in linewidth with increasing temperature is attributed to the strong temperature dependence of the spin-lattice relaxation time, which apparently becomes less than 10^{-9} sec somewhat below 77°K . Similar behavior has been noted for V^{3+} in $\alpha\text{-Al}_2\text{O}_3$.² No saturation behavior was noted with moderate microwave power (on the order of 0.1 W) at 4.2°K .

The angular dependence of the field for resonance is indicated in Fig. 2. The signal was lost in the region near $\theta=70^\circ$, where θ is the angle between the crystal axis and the static field. The spectrum for $\theta=0^\circ$ is shown in Fig. 3. The line is seen to be steep on the high-field side and to have a long tail on the low-field side.

⁸ L. S. Kornienko and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. **40**, 1594 (1961) [translation: Soviet Phys.—JETP **13**, 1120 (1961)].

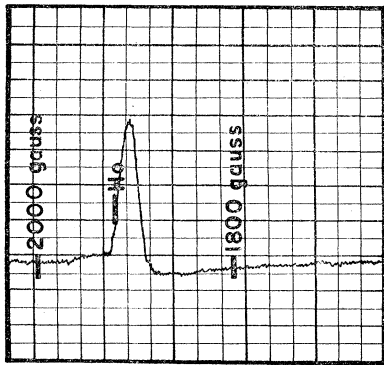


FIG. 3. First derivative presentation of the $\Delta M = \pm 2$ absorption line near 0° orientation. The field indicated was judged to be the approximate field for resonance for the ions situated where $E \approx 0$.

These characteristics do not change with orientation. A similar shaped line has been discussed by Low⁹ for the case of Fe^{2+} in MgO . For our case the shape of the line may be qualitatively explained by assuming a distribution of lower symmetry fields which are responsible for the splitting of the $M = \pm 1$ levels. These distortions of the axial field may arise from the proximity of randomly distributed charge compensator ions or lattice vacancies.

The spin Hamiltonian appropriate to the ground levels of Cr^{4+} is of the form

$$\mathcal{H} = g_{11}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2). \quad (1)$$

The terms have their usual meanings and $S=1$. For our case where $D \gg E$ and $D \gg h\nu$, we need only retain the term containing g_{11} . The separation between the $M = \pm 1$ levels is then closely given by

$$h\nu = 2g_{11}\beta H \cos\theta, \quad (2)$$

where θ is the angle between the crystal axis and the static magnetic field. The agreement with experiment is shown in Fig. 2. The $(\cos\theta)^{-1}$ behavior has been noted for the isoelectronic case of V^{3+} in $\alpha\text{-Al}_2\text{O}_3$ where the initial splitting D is about 10 cm^{-1} .^{2,3} If the term in E is retained, the solution for $\theta=0^\circ$ is given by

$$(h\nu)^2 = (2E)^2 + (2g_{11}\beta H)^2. \quad (3)$$

The spread of E values which gives rise to the asymmetric shape of the absorption curve introduces a difficulty in the establishment of the g value. A detailed analysis of the line shape does not appear warranted. The transition in question ($\Delta M = \pm 2$) is forbidden in the absence of lower symmetry fields. Thus, even if one assumes for example an exponential distribution of E values, the intensity of the absorption must be weighted in a manner to take into account the dependence of the transition probability at a particular site to the magnitude of E . By making use of expression (3) we find a rough spread in E , on the order of $0 \lesssim E \lesssim 0.05 \text{ cm}^{-1}$. The g value, calculated from the

magnetic field indicated in Fig. 3, is $g_{11} = 1.90_{-0.01}^{+0.02}$. For the isoelectronic V^{3+} in $\alpha\text{-Al}_2\text{O}_3$, Zverev and Prokhorov² find $g_{11} = 1.92 \pm 0.01$.

B. Effects of Irradiation on Spin Resonance

The ratio of the spin-resonance signal intensity of Cr^{4+} to Cr^{3+} at 4.2°K was monitored while the sample was subjected to radiation from a high-pressure mercury arc lamp passing through Pyrex Dewars. Several minutes of irradiation were sufficient to convert essentially all of the Cr^{4+} to Cr^{3+} . An additional spin-resonance line appeared near $g=2$ having the characteristic (g value greater than the free-electron value) of a V -center resonance. The integrated intensity of this line did not correlate with the amount of Cr^{4+} to Cr^{3+} conversion. Upon warming to room temperature the resonance from the center disappeared and the Cr^{4+} to Cr^{3+} ratio remained small. Subsequent heating of the sample in oxygen reconverted the Cr^{3+} to Cr^{4+} .

C. Optical Spectra

A portion of the optical-absorption spectrum is shown as A in Fig. 4 for the σ polarization at room temperature. The large band peaking at 4600 \AA is responsible for the intense orange coloration of the sample. A subsidiary broad peak can be observed near 3700 \AA . Curve B represents a correction made by subtracting the calculated absorption due to the Cr^{3+} background. This correction enhances the distinctiveness of the subsidiary peak. The oscillator strength of the entire absorption is calculated to be at least 50 times greater than that of the blue band of Cr^{3+} in $\alpha\text{-Al}_2\text{O}_3$,¹⁰ or the blue band of V^{3+} in MgO .¹¹ The absorptions in the π

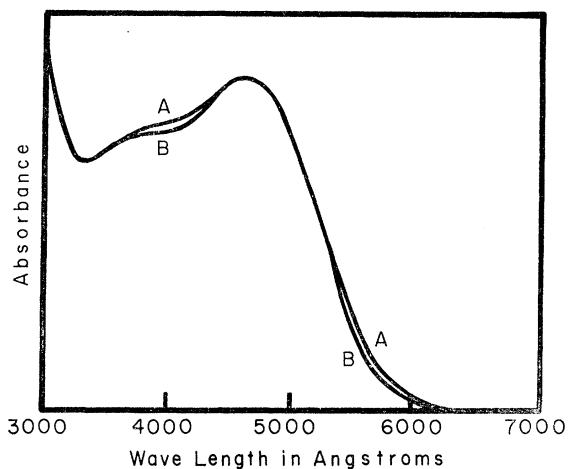


FIG. 4. (A) Optical-absorption spectrum of $\alpha\text{-Al}_2\text{O}_3$ containing Cr^{4+} , σ polarization, room temperature. (B) After correction for calculated Cr^{3+} background absorption.

¹⁰ T. H. Maiman, R. H. Hoskins, I. J. D'Haenens, C. K. Asawa, and V. Evtuhov, *Phys. Rev.* **123**, 1151 (1961).

¹¹ M. D. Sturge, *Phys. Rev.* **130**, 639 (1963).

⁹ W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960), p. 88.

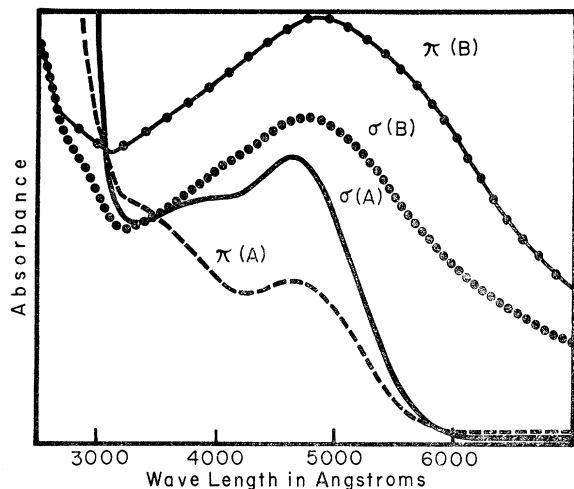


FIG. 5. Optical-absorption spectrum at 77°K of $\alpha\text{-Al}_2\text{O}_3$ containing Cr^{4+} (A) before and (B) after irradiation.

polarization are weaker, meeting the σ bands in the near ultraviolet at 3100 Å. Very weak absorptions were noted at 2900 and 6400 Å in both polarizations.

Spectra taken at 77°K are shown in Fig. 5. The curves labeled (A) show the same general features noted above, with small shifts toward longer wavelengths. After a few minutes of irradiation with the unfiltered light of a high-pressure mercury arc lamp at liquid-nitrogen temperature, the absorptions shown in curves (B) develop. The intensities of the bands as well as the half-widths are seen to have increased. The absorptions have especially increased in the long-wavelength tail, shifting the apparent peaks to still longer wavelengths. (For example, the peak in the π polarization has moved from 4600 to 4800 Å.) In addition, the dichroism has changed sign, and the crystals have taken on a purple hue. No vibrational structure or new absorptions can be seen. After warming to room temperature the samples

quickly bleach out and again exhibit the absorption spectra of (A).

Following the notation of Pryce and Runciman,¹ an assignment of the bands at 4600 and 3700 Å to the Cr^{4+} transitions ${}^3A_2 \rightarrow {}^3A_1$ derived from 3T_2 , and to ${}^3A_2 \rightarrow {}^3A_2$ derived from 3T_1 originally suggested itself since these transitions are most likely to give strong bands with the observed polarization ratios.¹ However, this assignment is not consistent with the experimental facts that coloration induced by irradiation at liquid-nitrogen temperature is reversible, while the irradiation induced conversion of Cr^{4+} to Cr^{3+} is not. In addition, the strength of the absorption bands would imply an unusually large oscillator strength based on the deduced Cr^{4+} concentration. We believe that these absorptions are due to anisotropic color centers associated with the anionic charge compensation mechanism. A further argument for this conclusion is afforded by the fact that we have observed the broad band at 4600 Å in other crystals of $\alpha\text{-Al}_2\text{O}_3$ prepared under similar charge compensation conditions but not containing chromium. A possible model for the blue absorption is afforded by a helium-like doubly charged center. The first ionization energy of such a center imbedded in a medium of optical dielectric constant n_0^2 is $24.6/n_0^4$ eV or $\lambda = 4900$ Å for $\alpha\text{-Al}_2\text{O}_3$ with $n_0 = 1.77$, in reasonable agreement with the observed values.

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