

change would be expected at somewhat lower carrier densities.

The experimental curves are found to decrease more rapidly with increasing temperature than the theoretical ones.

In some samples the experimental values begin to increase again at higher temperatures.

Whether these deviations have real significance or are the result of systematic errors cannot be determined

from the present experiments, especially since the PME effect decreases rapidly with increasing temperature.<sup>10</sup>

#### ACKNOWLEDGMENT

It is a pleasure to acknowledge an informative discussion with W. van Roosbroeck of Bell Telephone Laboratories.

<sup>10</sup> S. Goldstein, H. Mette, and W. W. Gärtner, *J. Phys. Chem. Solids* **8**, 78 (1959).

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### Sharp-Line Fluorescence, Electron Paramagnetic Resonance, and Thermoluminescence of $\text{Mn}^{4+}$ in $\alpha\text{-Al}_2\text{O}_3$

S. GESCHWIND, P. KISLIUK, M. P. KLEIN,\* J. P. REMEIK, AND D. L. WOOD  
Bell Telephone Laboratories, Inc., Murray Hill, New Jersey

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Sharp-line fluorescence, paramagnetic resonance in the ground state, and optical absorption due to  $\text{Mn}^{4+}$  in  $\alpha\text{-Al}_2\text{O}_3$  have been observed (analog of  $\text{Cr}^{3+}$ ). The  $\text{Mn}^{4+}$  valence state is obtained by charge compensation with  $\text{Mg}^{2+}$ . The increased charge of  $\text{Mn}^{4+}$  compared to  $\text{Cr}^{3+}$  results in a stronger crystal field and greater covalency whose effects are clearly seen in both the optical and paramagnetic resonance results. The ground state splitting is  $0.39\text{ cm}^{-1}$ , almost the same as in ruby, while the metastable  ${}^2E$  state splitting is  $80\text{ cm}^{-1}$ . When the crystals are irradiated with ultraviolet ( $<3000\text{ Å}$ ), more than 50% of the ground state of  $\text{Mn}^{4+}$  is depopulated, as long-lived traps are filled which decay via the  ${}^2E$  states through sharp-line thermoluminescence. The possible application to light masers is briefly discussed.

WE have observed sharp-line fluorescence, paramagnetic resonance in the ground state, and optical absorption due to  $\text{Mn}^{4+}$  in  $\alpha\text{-Al}_2\text{O}_3$  (analog of  $\text{Cr}^{3+}$ ). Also, in initial experiments more than 50% of the  $\text{Mn}^{4+}$  ground state has been depopulated by ultraviolet irradiation, filling long-lived traps which decay via the  ${}^2E$  states through sharp-line thermoluminescence. This paper is a preliminary report of our findings whose intent is to draw attention only to the main properties of the system. A more detailed presentation will appear in a subsequent publication.

Single crystals of  $\alpha\text{-Al}_2\text{O}_3\text{-Mn}^{4+}$  were grown from oxide fluxes to which it was found necessary to add  $\text{MgO}$  powder to provide  $\text{Mg}^{2+}$  to charge compensate the  $\text{Mn}^{4+}$  which enters substitutionally into the octahedral  $\text{Al}^{3+}$  site. Similar results were obtained with  $\text{Mg}^{2+}$  compensated crystals grown by the Linde Company by the flame fusion process. The concentration of  $\text{Mn}^{4+}$  in our experiments varied from about 0.1% to 0.001%. While reference may be found in the phosphor literature<sup>1,2</sup> to  $\text{Mn}^{4+}$  in  $\text{Al}_2\text{O}_3$ , the description of the optical and mag-

netic properties has been greatly extended and clarified in this work.

The  $\text{Mn}^{4+}$  ion is isoelectronic with  $\text{Cr}^{3+}$  ( $3d^3$  configuration) and the electronic states of the latter ion

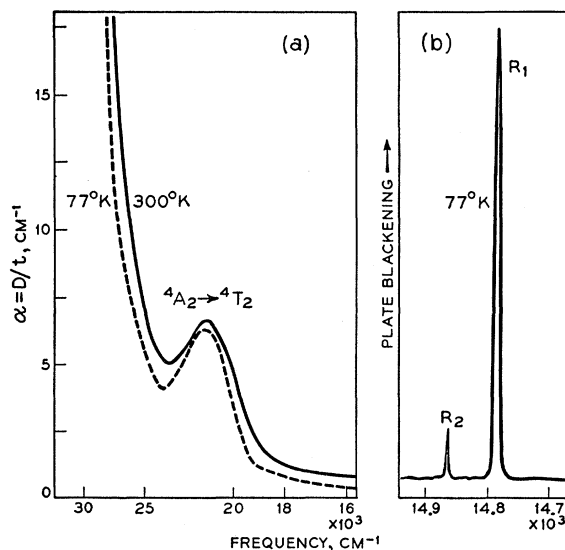


FIG. 1. Absorption (a) and fluorescence (b) spectra of  $\text{Al}_2\text{O}_3\text{-Mn}^{4+}$  grown from flux. Concentration: less than 0.08%  $\text{Mn}^{4+}$  by weight. The curve in (b) is a microphotometer trace giving a nonlinear ordinate.

\* Now at the University of California, Lawrence Radiation Laboratory, P. O. Box 808, Livermore, California.

<sup>1</sup> P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949) who quotes E. Tiede and R. Piwonka, *Chem. Ber.* **64**, 2252 (1931).

<sup>2</sup> F. A. Kröger, *Some Aspects of the Luminescence of Solids* (Elsevier Publishing Company, Inc., Amsterdam, Netherlands, 1948).

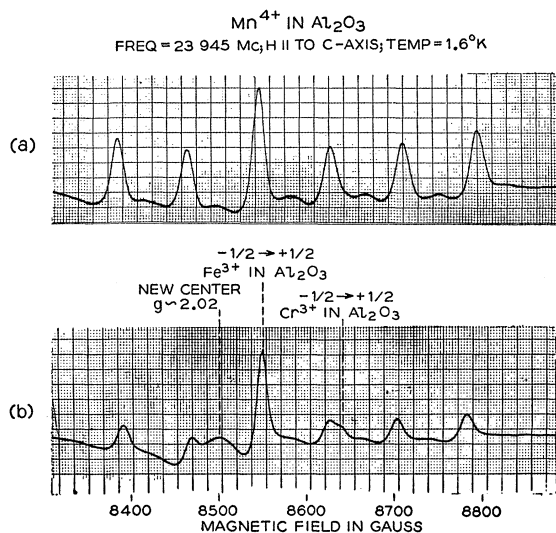


FIG. 2. (a) Electron spin resonance spectrum of  $\text{Mn}^{4+}$  in  $\text{Al}_2\text{O}_3$  at 24 kMc/sec and 1.6°K. The spectrum is also easily seen at room temperature. This particular crystal contains a small amount of  $\text{Fe}^{3+}$  and lesser amounts of  $\text{Cr}^{3+}$  and  $\text{Mn}^{2+}$ . (b) Spectrum after irradiation with ultraviolet. Decrease of  $\text{Mn}^{4+}$  signal relative to  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  is at least 50%. Depopulation of  $\text{Mn}^{4+}$  was also checked relative to  $\text{Cr}^{3+}$  in  $\text{MgO}$  powder shielded in another part of the cavity from irradiating light. Upon warming, the crystals thermoluminesce in the  $R_1$  and  $R_2$  lines and return to their original state. Similar effects are observed at 79°K.

in  $\text{Al}_2\text{O}_3$  (ruby) are well known.<sup>3</sup> It is a well known empirical fact that the strength of the crystal field as well as covalency increases with increased ionic charge.<sup>4</sup> Therefore, due to the increased charge of  $\text{Mn}^{4+}$  compared to  $\text{Cr}^{3+}$ , the crystal field parameter  $Dq$  and the covalency are both larger in  $\text{Mn}^{4+}$ . This causes the  ${}^4A_2 \rightarrow {}^4T_2$  transition to fall at 21 300  $\text{cm}^{-1}$  (see Fig. 1) instead of 18 000  $\text{cm}^{-1}$  as for  $\text{Cr}^{3+}$ , and the charge transfer bands lie at much longer wavelength for  $\text{Mn}^{4+}$ , giving an absorption "edge" near 35 000  $\text{cm}^{-1}$  instead of about 50 000  $\text{cm}^{-1}$  as found for  $\text{Cr}^{3+}$ . The  ${}^4A_2 \rightarrow {}^4T_1$  transition observable for  $\text{Cr}^{3+}$  is, in the case of  $\text{Mn}^{4+}$ , obscured by the charge transfer absorption. The value of  $Dq$  determined from the  ${}^4A_2 \rightarrow {}^4T_2$  transition is about 2170  $\text{cm}^{-1}$  for  $\text{Mn}^{4+}$  compared with 1700  $\text{cm}^{-1}$  for  $\text{Cr}^{3+}$ , and  $B \approx 700 \text{ cm}^{-1}$  for both ions, assuming the relationship  $C=4B$  for these Racah parameters.

The  $R_1$  and  $R_2$  emission lines occur at 14 866  $\text{cm}^{-1}$  and 14 786  $\text{cm}^{-1}$  at 79°K and have lifetimes of 0.8 msec which are essentially independent of temperature. The ratios of the intensities of the  $R_1$  and  $R_2$  lines, measured as a function of temperature from 4.2°K to 295°K correspond to fast thermalization between levels  $82 \pm 5 \text{ cm}^{-1}$  apart, in good agreement with the measured separation of 80  $\text{cm}^{-1}$  between the two lines. Weaker lines due to  $\text{Mn}^{4+}$  were observed in fluorescence at both higher and

lower frequencies. Some of these may be due to sites with different charge compensation, some to pairs of ions, and some to vibrational side-bands, but a complete analysis has not yet been made.

The widths of the  $R_1$  and  $R_2$  lines were about 60  $\text{cm}^{-1}$  at room temperature, but narrowed to about 2  $\text{cm}^{-1}$  at 79°K in the best crystals. It is believed that the 2- $\text{cm}^{-1}$  width is limited by crystal defects or strain as shown by the results with paramagnetic resonance spectra discussed below.

A correlation was observed between the intensity of emission in the  $R_1$ ,  $R_2$  lines and the intensity of the paramagnetic resonance spectrum of  $\text{Mn}^{4+}$ . The electron paramagnetic resonance spectrum was studied at 24 kMc/sec over a range of temperatures from 295°K to 1.6°K. In Fig. 2 is shown the  $-\frac{1}{2} \rightarrow +\frac{1}{2}$  transition of  $\text{Mn}^{4+}$  split into six lines by the hfs interaction with the  $\text{Mn}^{55}$  nucleus ( $I = \frac{5}{2}$ ). The spectrum is adequately described within the accuracy of our measurements by the following spin Hamiltonian

$$\mathcal{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + D[S_z^2 - \frac{1}{3}S(S+1)] + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S}, \quad (1)$$

where  $S = \frac{3}{2}$  and  $I = \frac{5}{2}$ , and the other experimentally determined parameters are listed in Table I. The quadrupole coupling of  $\text{Mn}^{55}$  is small and is neglected and in either case its effect does not appear in the parallel spectrum, and even in the perpendicular spectrum it has a negligible effect insofar as determining the parameters in the spin Hamiltonian listed above. This hfs is essentially the same as that previously observed for  $\text{Mn}^{4+}$  by Mueller<sup>5</sup> in  $\text{SrTiO}_3$  and in  $\text{TiO}_2$  by Andreson,<sup>6</sup> and is in good accord with the core polarization idea of the origin of the hfs.<sup>7</sup> The  $\pm\frac{1}{2} \rightarrow \pm\frac{3}{2}$  transitions were sensitive to crystal strains and were sufficiently broadened in some crystals so that no resolved hfs was seen for these lines except in the more dilute selected crystals. A correlation was made in the strained crystals between the absence of a resolved hfs in the  $\pm\frac{1}{2} \rightarrow \pm\frac{3}{2}$  lines and a broadening of the  $R_1$  and  $R_2$  lines.

The ground state splitting of 11 732 Mc/sec in  $\text{Mn}^{4+}$  is only one percent larger than that of  $\text{Cr}^{3+}$  in  $\text{Al}_2\text{O}_3$ ,

TABLE I. Spin Hamiltonian parameters for  $\text{Mn}^{4+}$  in  $\alpha\text{-Al}_2\text{O}_3$ .

$$\begin{aligned} D &= -0.1957 \pm 0.0001 \text{ cm}^{-1} \\ g_{||} \approx g_{\perp} &= 1.9937 \pm 0.0007 \\ |A_{||}| \approx |A_{\perp}| &= (70.0 \pm 0.5) \times 10^{-4} \text{ cm}^{-1} \end{aligned}$$

<sup>5</sup> K. A. Mueller, Phys. Rev. Letters **2**, 341 (1959).

<sup>6</sup> H. G. Andresen, Phys. Rev. **120**, 1606 (1960); J. Chem. Phys. **35**, 1090 (1961).

<sup>7</sup> According to the ideas concerning exchange polarization of the core by the outer  $d$  electrons, the hyperfine field per unit electron spin should be relatively constant. Since  $A$  measures the hyperfine interaction per unit electron spin,  $A$  for  $\text{Mn}^{4+}$  should be just about the same as for  $\text{Mn}^{2+}$  in  $\text{Al}_2\text{O}_3$  for which  $A = -79 \times 10^{-4} \text{ cm}^{-1}$  [W. Low and J. T. Suess, Phys. Rev. **119**, 132 (1961)], but slightly reduced because of the increased covalency of  $\text{Mn}^{4+}$  compared to  $\text{Mn}^{2+}$  in this bonding. See J. H. Wood and G. W. Pratt, Jr., Phys. Rev. **107**, 995 (1957); V. Heine, Phys. Rev. **107**, 1002 (1957); R. E. Watson and A. J. Freeman, *ibid.* **123**, 2027 (1961).

<sup>3</sup> S. Sugano and Y. Tanabe, J. Phys. Soc. Japan **13**, 880 (1958).

<sup>4</sup> See Table VII in article by D. S. McClure, *Solid-State Physics* (Academic Press Inc., New York, 1959), Vol. 9. For effect of covalency on spin-orbit coupling, see J. Owen, Proc. Roy. Soc. (London) **A227**, 183 (1955).

yet the splitting of the metastable  ${}^2E$  state in  $\text{Mn}^{4+}$  is more than twice as large as  $\text{Cr}^{3+}$ . The splitting of the  ${}^2E$  state is given in lowest order by<sup>3</sup>

$${}^2E(\bar{E}) - {}^2E(\bar{A}_2) \sim \lambda V_{\text{trig}} / ({}^2T_2 - {}^2E), \quad (2)$$

where  $\lambda$  is the spin orbit coupling constant and  $V_{\text{trig}}$  is the interaction energy of the ion with the trigonal part of the crystal field. The position of the  ${}^2T_2$  was not measured as the crystals were too small to observe this weak absorption; however, one would expect the  ${}^2T_2 - {}^2E$  separation to be relatively independent of  $Dq$  according to Sugano and Tanabe.<sup>3</sup> Similarly, although  $\lambda$  for  $\text{Mn}^{4+}$  in the free ion is slightly larger than  $\lambda$  for  $\text{Cr}^{3+}$ , one expects a greater reduction of  $\lambda$  in the crystal for  $\text{Mn}^{4+}$  due to its greater covalency,<sup>4</sup> so that their effective  $\lambda$ 's in the crystal are probably comparable. The increase in the splitting of the  ${}^2E$  state in  $\text{Mn}^{4+}$  compared to  $\text{Cr}^{3+}$  may therefore perhaps be ascribed to a larger  $V_{\text{trig}}$  for the  $\text{Mn}^{4+}$ . This is not inconsistent with the fact that the ground-state splittings are almost the same. For while  $D$  may be expected to vary linearly with  $V_{\text{trig}}$  it may also be expected to go inversely as the second power of  $Dq$ , so that the increase of both may offset each other.<sup>8</sup>

<sup>8</sup> Many excited states contribute to the ground state splitting and with different signs so that it is a fairly complex problem [see S. Sugano and M. Peter, Phys. Rev. **122**, 381 (1961)]. However, if no terms above third order contribute to  $D$ , then one may expect  $D$  to vary as cited above.

When irradiated with ultraviolet ( $< 3300 \text{ \AA}$ ) at  $79^\circ\text{K}$ , the crystals change in color from amber to gray-violet. This color change corresponds to a change in the valence state of  $\text{Mn}^{4+}$  and the filling of traps (as yet unidentified<sup>9</sup>) whose lifetime at  $79^\circ\text{K}$  is greater than 170 hr. On warming, intense sharp line thermoluminescence, corresponding to the  $R$  lines, is observed starting at about  $-70^\circ\text{C}$ , as the traps release their energy. In preliminary experiments with ultraviolet irradiation, we have observed by electron paramagnetic resonance a greater than 50% depopulation of the ground state of  $\text{Mn}^{4+}$  which may be seen in Fig. 2(b). This suggests a way of reducing the pumping power, required in certain cases for observing coherent stimulated emission, utilizing a line which terminates on the ground state. It may be possible in  $\text{Mn}^{4+}$  to depopulate the ground state by storing the ions in the traps and have them idle there, this requiring little power because of the long lifetime of the traps, and then release by some means just a sufficient number to the metastable  ${}^2E$  to overcome the other losses in the optical cavity.

We wish to thank D. Linn, G. Devlin, E. Kelly, and Miss B. Prescott for their experimental assistance; A. M. Clogston, V. Jaccarino, and M. Peter for helpful discussions.

<sup>9</sup> Note added in proof. More recent analysis leads us to believe that the trapping centers are the  $\text{Mg}^{2+}$  ions which capture holes released from the  $\text{Mn}^{4+}$  by the ultraviolet.