

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.¹⁰

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

Sharp-Line Fluorescence, Electron Paramagnetic Resonance, and Thermoluminescence of Mn^{4+} in $\alpha-Al_2O_3$

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Sharp-line fluorescence, paramagnetic resonance in the ground state, and optical absorption due to Mn^{4+} in $\alpha-Al_2O_3$ have been observed (analog of Cr^{3+}). The Mn^{4+} valence state is obtained by charge compensation with Mg^{2+} . The increased charge of Mn^{4+} compared to 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 cm^{-1} , almost the same as in ruby, while the metastable 2E state splitting is 80 cm^{-1} . When the crystals are irradiated with ultraviolet ($<3000\text{ \AA}$), more than 50% of the ground state of 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 Mn^{4+} in $\alpha-Al_2O_3$ (analog of Cr^{3+}). Also, in initial experiments more than 50% of the 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 $\alpha-Al_2O_3+Mn^{4+}$ were grown from oxide fluxes to which it was found necessary to add MgO powder to provide Mg^{2+} to charge compensate the Mn^{4+} which enters substitutionally into the octahedral Al^{3+} site. Similar results were obtained with Mg^{2+} compensated crystals grown by the Linde Company by the flame fusion process. The concentration of Mn^{4+} in our experiments varied from about 0.1% to 0.001%. While reference may be found in the phosphor literature^{1,2} to Mn^{4+} in Al_2O_3 , the description of the optical and mag-

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

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

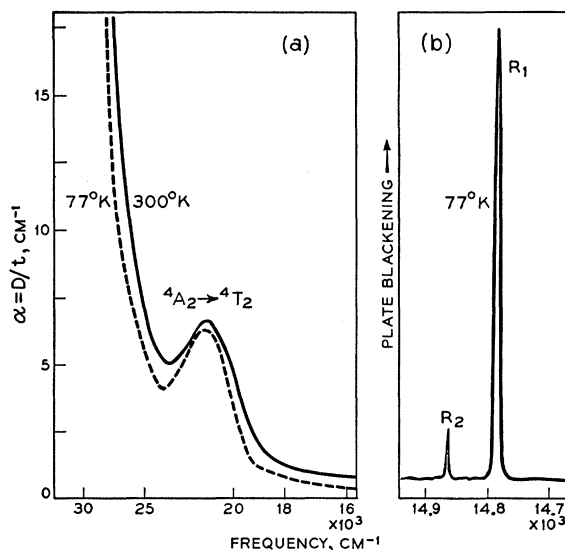


FIG. 1. Absorption (a) and fluorescence (b) spectra of $Al_2O_3+Mn^{4+}$ grown from flux. Concentration: less than 0.08% Mn^{4+} by weight. The curve in (b) is a microphotometer trace giving a nonlinear ordinate.

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

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

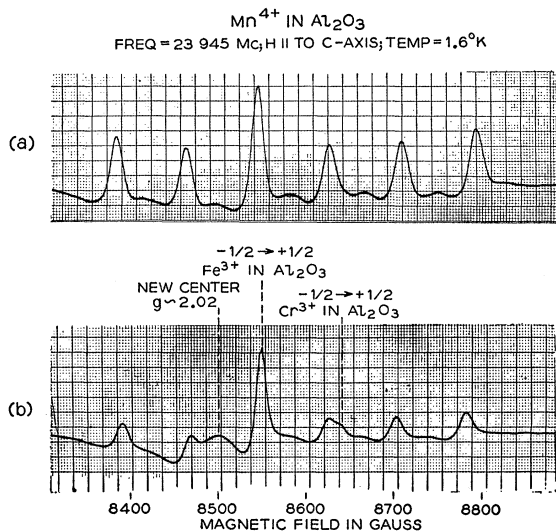


FIG. 2. (a) Electron spin resonance spectrum of Mn^{4+} in Al_2O_3 at 24 kMc/sec and 1.6°K. The spectrum is also easily seen at room temperature. This particular crystal contains a small amount of Fe^{3+} and lesser amounts of Cr^{3+} and Mn^{2+} . (b) Spectrum after irradiation with ultraviolet. Decrease of Mn^{4+} signal relative to Fe^{3+} and Cr^{3+} is at least 50%. Depopulation of Mn^{4+} was also checked relative to Cr^{3+} in 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 Al_2O_3 (ruby) are well known.³ It is a well known empirical fact that the strength of the crystal field as well as covalency increases with increased ionic charge.⁴ Therefore, due to the increased charge of Mn^{4+} compared to Cr^{3+} , the crystal field parameter Dq and the covalency are both larger in Mn^{4+} . This causes the ${}^4A_2 \rightarrow {}^4T_2$ transition to fall at 21 300 cm^{-1} (see Fig. 1) instead of 18 000 cm^{-1} as for Cr^{3+} , and the charge transfer bands lie at much longer wavelength for Mn^{4+} , giving an absorption "edge" near 35 000 cm^{-1} instead of about 50 000 cm^{-1} as found for Cr^{3+} . The ${}^4A_2 \rightarrow {}^4T_1$ transition observable for Cr^{3+} is, in the case of Mn^{4+} , obscured by the charge transfer absorption. The value of Dq determined from the ${}^4A_2 \rightarrow {}^4T_2$ transition is about 2170 cm^{-1} for Mn^{4+} compared with 1700 cm^{-1} for Cr^{3+} , and $B \approx 700$ 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 cm^{-1} and 14 786 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 ± 5 cm^{-1} apart, in good agreement with the measured separation of 80 cm^{-1} between the two lines. Weaker lines due to 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 cm^{-1} at room temperature, but narrowed to about 2 cm^{-1} at 79°K in the best crystals. It is believed that the 2- 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 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 Mn^{4+} split into six lines by the hfs interaction with the 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 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 Mn^{4+} by Mueller⁵ in $SrTiO_3$ and in TiO_2 by Andreson,⁶ and is in good accord with the core polarization idea of the origin of the hfs.⁷ 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 Mn^{4+} is only one percent larger than that of Cr^{3+} in Al_2O_3 ,

TABLE I. Spin Hamiltonian parameters for Mn^{4+} in $\alpha-Al_2O_3$.

$$\begin{aligned} D &= -0.1957 \pm 0.0001 \text{ cm}^{-1} \\ g_{11} \approx g_{\perp} &= 1.9937 \pm 0.0007 \\ |A_{11}| \approx |A_{\perp}| &= (70.0 \pm 0.5) \times 10^{-4} \text{ cm}^{-1} \end{aligned}$$

⁵ K. A. Mueller, Phys. Rev. Letters **2**, 341 (1959).

⁶ H. G. Andreson, Phys. Rev. **120**, 1606 (1960); J. Chem. Phys. **35**, 1090 (1961).

⁷ 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 Mn^{4+} should be just about the same as for Mn^{2+} in Al_2O_3 for which $A = -79 \times 10^{-4}$ cm^{-1} [W. Low and J. T. Suess, Phys. Rev. **119**, 132 (1961)], but slightly reduced because of the increased covalency of Mn^{4+} compared to 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).

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

⁴ 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 Mn^{4+} is more than twice as large as Cr^{3+} . The splitting of the 2E state is given in lowest order by³

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

where λ is the spin orbit coupling constant and V_{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.³ Similarly, although λ for Mn^{4+} in the free ion is slightly larger than λ for Cr^{3+} , one expects a greater reduction of λ in the crystal for Mn^{4+} due to its greater covalency,⁴ so that their effective λ 's in the crystal are probably comparable. The increase in the splitting of the 2E state in Mn^{4+} compared to Cr^{3+} may therefore perhaps be ascribed to a larger V_{trig} for the 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_{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.⁸

⁸ 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°K , the crystals change in color from amber to gray-violet. This color change corresponds to a change in the valence state of Mn^{4+} and the filling of traps (as yet unidentified⁹) whose lifetime at 79°K is greater than 170 hr. On warming, intense sharp line thermoluminescence, corresponding to the R lines, is observed starting at about -70°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 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 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.

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