Paramagnetic Resonance of Chromium in $MgTiO_3$

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The paramagnetic resonance spectrum of Cr^{3+} in single crystals of rhombohedral $MgTiO_3$ was measured at frequencies of 24 kMc/sec and 35 kMc/sec. The results indicate that Cr^{3+} is located at ion sites of trigonal symmetry. The spectrum can be described by an axial spin Hamiltonian with $S=\frac{3}{2}$. The parameters at room temperatures are: $|D|=(15.05\pm0.03)$ kMc/sec, $g_{\parallel}=1.976\pm0.002$, $g_{\perp}=1.981\pm0.002$. Due to the relatively large zero-field splitting, the chemical stability and good mechanical properties, chromium-doped $MgTiO_3$ might be a useful material for solid-state masers.

I. INTRODUCTION

SINCE the first reported operation of a Bloembergen-type solid-state maser,[1] using Cr^{3+} in $K_3Co(CN)_6$, many other materials using either Cr^{3+}, Fe^{3+}, or Gd^{3+} in different host lattices were successfully employed in this type of maser.[2] The broadest application so far found Cr^{3+} in $\alpha-Al_2O_3$ (ruby), due to several desirable features which are connected with the Cr^{3+} ion as well as with the crystallographic, chemical, and mechanical properties of $\alpha-Al_2O_3$. It, therefore, seemed advisable to investigate the electron paramagnetic resonance of Cr^{3+} ions in single crystals of structures similar to that of $\alpha-Al_2O_3$. The first crystal studied in this laboratory was chromium-doped Ga_2O_3, which is known to crystallize in its α phase in the corundum structure, like $\alpha-Al_2O_3$. However, the Verneuil process used for preparing Ga_2O_3 crystals delivered only $\beta-Ga_2O_3$, which is monoclinic.[3] The electron paramagnetic resonance (EPR) spectrum was analyzed and the measured parameters are in good agreement with the results reported by Peter and Schawlow.[4] Since other metal-oxide hosts, crystallizing in the corundum structure,[5] have to be either excluded because of their magnetic properties or because they are not within the experimental range of the flame-fusion technique used, $MgTiO_3$ was selected as host material for Cr^{3+}. $MgTiO_3$ crystallizes in the rhombohedral ilmenite structure, space group $R\bar{3}$[6] which is closely related to the corundum structure.

II. PREPARATION OF SAMPLE

Single crystals of $MgTiO_3$ with a nominal molar concentration of 0.5% Cr_2O_3 were grown in a flame-fusion furnace. The feeding material was prepared by mixing together thoroughly MgO and TiO_2 powder with the appropriate amount of an aqueous solution of chromium alum. The mixture was then sintered for about 70 h at 1100°C. After grinding and passing through a fine wire mesh, the substance was ready for crystal growing. The boule-shaped crystals obtained had an average length of 10 mm, a diameter of 3 mm, and were of blackish appearance, probably due to oxygen deficiency. After proper annealing, the color changed to a greenish hue. In accordance with the rhombohedral crystal structure, Laue back-reflection x-ray pictures taken along the rhombohedral (c) axis showed trigonal symmetry.

III. EXPERIMENTAL RESULTS

The spectrometer employed was of conventional design with bridge, reflection cavity, crystal detection, and automatic frequency control. The rotatable Varian 12-in. electromagnet had additional coils for 200-cps field modulation. Exchange of the microwave part allowed operation at either K band (24 kMc/sec) or Ka band (35 kMc/sec). All measurements were performed at room temperature.

By measuring the absorption lines with the magnetic field H parallel and perpendicular to the rhombohedral axis and also measuring their angular dependence, it was found that the spectrum of Cr^{3+} in $MgTiO_3$ can be explained by the following spin Hamiltonian[7] with $S=\frac{3}{2}$:

$$\mathcal{H}=g_{\parallel}\beta H_z S_z+g_{\perp}\beta(H_x S_x+H_y S_y)+D[S_z^2-\tfrac{1}{3}S(S+1)],$$

$g_{\parallel}$, $g_{\perp}$, D, β, H, and S have their conventional meaning; (x,y,z) is a rectangular coordinate system with z parallel to the rhombohedral axis of the crystal.

The parameters in the spin Hamiltonian were determined to: $|D|=(15.05\pm0.03)$ kMc/sec, $g_{\parallel}=1.976\pm0.002$, $g_{\perp}=1.981\pm0.002$. The energy levels for $H\|c$ and $H\perp c$, calculated from the spin Hamiltonian, are given in Figs. 1(a) and 1(b).

The zero-field splitting $2|D|$ was also determined in a more direct way. By following one transition down to low magnetic fields and extrapolating to zero magnetic field, $2|D|$ was again determined to 30.1 kMc/sec (Fig. 2).

Besides the lines originating from the Cr^{3+} ions,

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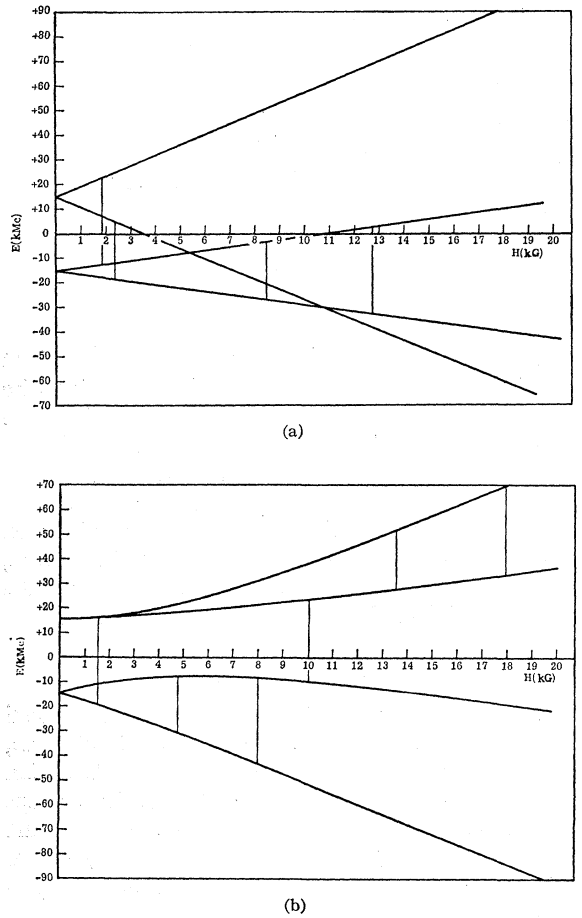

FIG. 1. Energy levels for Cr^{3+} in $MgTiO_3$: (a) $H\|c$, (b) $H\perp c$. The vertical lines indicate measured transitions. The sign of D was not determined. The energy levels are plotted for $+D$. In case of $-D$, the order of the levels is reversed.

additional lines were observed. Most of them can probably be attributed to Fe^{3+} impurities, which were present in the MgO powder used for preparing the crystal.

IV. CONCLUSIONS

The measured EPR spectrum of Cr^{3+} in $MgTiO_3$ indicates that Cr^{3+} ions are located at sites of trigonal symmetry in crystal. The zero-field splitting of 30.1 kMc/sec may be compared with relevant values for Cr^{3+} in different host lattices[2]: $K_3Co(CN)_6$ 5.1 kMc/sec, Al_2O_3 11.4 kMc/sec, TiO_2 43.3 kMc/sec, $Be_3Al_2Si_6O_{18}$ 53.7 kMc/sec, and Y_2O_3 72.3 kMc/sec. Due to its intermediate zero-field splitting, its chemical stability and good mechanical properties, chromium-doped $MgTiO_3$ might be a useful material for solid-state masers operating at frequencies up to about 40 kMc/sec.

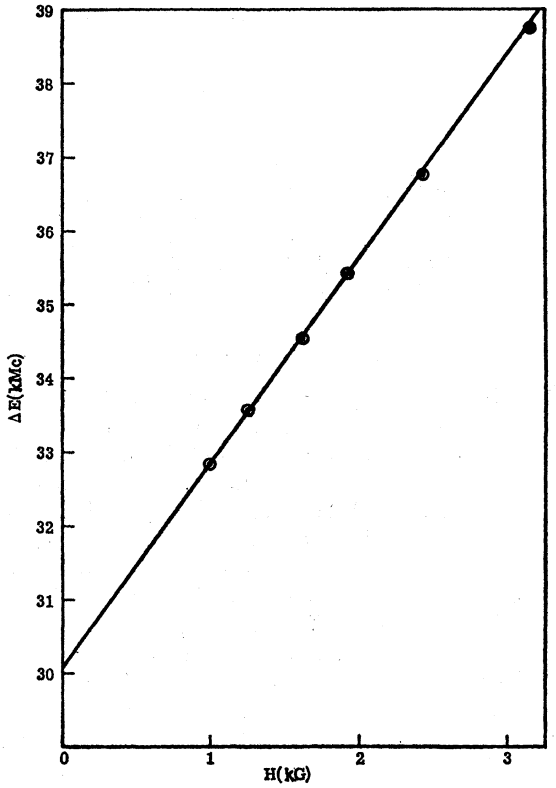

FIG. 2. Determination of $2|D|$ by extrapolation to zero magnetic field. The measured transitions (⊙) occur between the levels $\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$, depending on $\pm D$. The crystal was in the $H\|c$ orientation.

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