

Laue spots was found, though a well-defined strip of reduced reflected intensity appeared on photographs of the region containing the center-line of hillocks. This region shows up on *both* faces of the dendrite after etching as a dense band of etch pits.

It seems to us that the experimental evidence published on dendrite growth directions and relative perfection of faces from both Laboratories can quite well be explained on a basis of a twin nucleation process as described by Bennett and Longini, followed by either extensive or limited overgrowth of further (111) planes according to Billig and Holmes's mechanism. Obviously, with two or more parallel twin planes, the easy directions of nucleation are doubled in number: if existing dendrites are used as seeds, those containing twin

lamellae are thus twice as likely to propagate downwards as those with only one twin plane.

It is hoped that this note will clarify the situation as regards the etch pits on dendritic germanium; there is in fact no difference between the two sets of experimental observations on this point. The need for emphasizing that not all etch pits have facets approximating to {111} form is borne out by the error into which we ourselves had fallen in preparing illustrations from, and describing a specimen which had been etched differently from the majority.

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Paramagnetic Resonance Spectrum of Manganese in Corundum*

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The paramagnetic resonance spectrum of Mn^{2+} in Al_2O_3 was measured at 3 cm. The spectrum can be expressed in a spin Hamiltonian with trigonal symmetry with the following parameters: $g_{11}=2.0017\pm 0.001$, $g_{\perp}=2.000\pm 0.002$, $D=+194.2\pm 1$, $a-F=+21.9\pm 0.6$, $A=-79.6\pm 0.5$, $B=-78.8\pm 0.8$ in units of 10^{-4} cm^{-1} .

INTRODUCTION

THE chromium and iron spectra have been investigated intensively in the trigonal crystal field of aluminum oxide.¹⁻⁴ Recently also the spectrum of trivalent vanadium has been investigated.^{5,6}

It was of interest to see whether divalent ions can be incorporated in the lattice of aluminum oxide and to what extent this may influence the point symmetry. Some investigations in this direction have been made by the Michigan group.⁷ These authors find that V^{3+} can be reduced to divalent V^{2+} in the lattice of Al_2O_3 upon irradiation. Geusic also investigated the spectrum

of divalent cobalt in this lattice.⁸ We wish to report results on divalent manganese in a single crystal of aluminum oxide.^{8a} These results are of interest since they permit a comparison of the magnitude of the initial splitting with that of trivalent iron.

RESULTS

We have investigated the paramagnetic resonance spectrum at 3-cm wavelength and at room temperature, on a single crystal of Al_2O_3 containing manganese.^{8a}

The paramagnetic resonance spectra can be expressed in a simple spin Hamiltonian having the same trigonal symmetry as trivalent iron. This Hamiltonian can conveniently be written as

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + B_2^0O_2^0 + B_4^0O_4^0 + B_4^{*0}O_4^{*0} + B_4^{*4}O_4^{*4} + A(\mathbf{S}\cdot\mathbf{I}), \quad (1)$$

where O_n^m are the following spin operators

$$\begin{aligned} O_2^0 &= 3S_z^2 - S(S+1), \\ O_4^0 &= 35S_z^4 - [30S(S+1) - 25]S_z^2 \\ &\quad - 6S(S+1) + 3S^2(S+1)^2, \\ O_4^4 &= (1/2)(S_+^4 + S_-^4). \end{aligned}$$

⁸ J. E. Geusic, Bull. Am. Phys. Soc. 4, 1260 (1959).

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The starred operators refer to the cubic coordinate system and the unstarred to the trigonal coordinate system.

B_n^m are the crystal field parameters determined from experiment. This Hamiltonian is also written more conveniently as

$$\begin{aligned} \mathcal{H} = & g_{11}\beta\mathbf{H}\cdot\mathbf{S}_z + g_{12}\beta(H_xS_x + H_yS_y) \\ & + D[S_z^2 - (1/3)S(S+1)] + (a/6)[S_x^4 + S_y^4 + S_z^4 \\ & - (1/5)S(S+1)(3S^2 + 3S - 1)] + (1/180)F\{35S_z^4 \\ & - [30S(S+1)]S_z^2 + 25S_z^2 - 6S(S+1) \\ & + 3S^2(S+1)^2\} + A(S_zI_z) + B(S_xI_x + S_yI_y), \quad (2) \end{aligned}$$

with $S = \frac{5}{2}$ and g, β , and S having the usual meaning.

All the thirty lines of the spectrum in which $H\parallel z$ axis and $H\perp z$ axis can be fitted with the following parameters: $g_{11} = 2.0017 \pm 0.001$, $g_{12} = 2.0000 \pm 0.002$, $D = +208.3 \pm 1$ gauss, $a - F = +23.4 \pm 0.6$ gauss, $A = -85.0 \pm 0.5$ gauss, $B = -84.3 \pm 0.8$ gauss. The c axis of this spectrum coincides within three degrees with that of Cr^{3+} , also present in this crystal, and is along the $[111]$ direction. The parameters given here are those measured at 3-cm wavelength and at room temperature. The relative sign of A/D and $(a-F)/D$ was determined from the second-order shifts in this spectrum. Since the sign of A is usually negative for all measured divalent manganese spectra in single crystals, we infer from this that D and $(a-F)$ must both be positive.

DISCUSSIONS

The values of A and B are very similar to those found in MgO .⁹ Unfortunately, we could not determine the cubic field constant separately. The many lines along the $[100]$ direction are too crowded and it is difficult to disentangle the various parameters. At any rate the value of $a-F$ is of the same order as that found for a in MgO (18.65×10^{-4} cm⁻¹).⁹ In hexagonal ZnO the fourth-order correction F has shown to be negative and small¹⁰ (i.e., $D = -216.9 \pm 2.2$, $F = -6.0 \pm 1.5 \times 10^{-4}$ cm⁻¹). It is likely that F is also only a few gauss and probably negative.

It is significant that the divalent manganese can replace the trivalent aluminum in the lattice of Al_2O_3 although the ionic radius of Mn^{2+} is considerably larger. It is also surprising that the trigonal symmetry is preserved. The charge compensation is apparently not in the immediate vicinity of the manganese ion.

Our results should be compared with those of iso-electronic Fe^{3+} .^{3,4} Bogle and Symmons find the following values for Fe^{3+} at room temperature: $g = 2.003$,

$D = 1679 \pm 1$, $|a| = 241 \pm 4$, $a - F = +329 \pm 2$, where D , a , and F are measured in units of cm⁻⁴. Comparing these results we find that the ratio of the two axial splitting parameters for the two ions is 8.6. The signs of the axial splitting parameters are in both cases the same.

The nature of the initial splittings in S -state ions is not too well understood at present. According to Watanabe¹¹ and Hutchison *et al.*,¹² the magnitude and sign of the axial splitting parameter D is caused in the main by two types of interaction, one within the d^5 configuration in which the axial potential V_{AX} is quadratic and is of the form $V_{LS}V_{AX}V_{AX}V_{LS}$, and one connecting different configurations such as $3d^4 4s$ and is of the form $V_{SS}V_{AX}$. Here V_{LS} and V_{SS} signify the spin-orbit and spin-spin interactions, respectively. Other interactions involving the spin-orbit coupling to a higher power contribute presumably only little since the spin-orbit coupling for d^5 is relatively small. These two interactions according to Watanabe are of opposite sign. A detailed correlation of the results on trivalent iron and divalent manganese must involve an evaluation of these matrix elements. Such a comparison, however, may be difficult, because of a number of possible differences of behavior of these two ions in the lattice of Al_2O_3 . First of all, the Coulomb interactions between the divalent manganese and the surroundings is smaller and the ionic radius is larger. This may in part reduce the initial splitting. On the other hand, the charge compensation for Mn^{2+} may lie along the z axis and therefore increase the axial potential V_{AX} . Some evidence for this is obtained from the isoelectronic spectra of V^{2+} and Cr^{3+} in Al_2O_3 . There it is found that D is nearly twice as large for V^{2+} compared with Cr^{3+} . However, the nature of the initial splitting in the d^3 configuration is different from that of the d^5 configuration. There most of the relevant mechanisms leading to the initial splitting seem to be linearly dependent on V_{AX} .

We are now engaged in a search of the spectrum of Mn^{3+} . This spectrum is of some interest in that it should throw some light on the role of the Jahn-Teller effect on d^4 configurations in a trigonal field.

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