the T_1 center has not been done, but it seems clear that with hydrolysis, the formation proceeds in time as Gd^{3+}-$F_i^- \rightarrow T_2 \rightarrow T_1$, indicating that the T_1 center is particularly stable. This stability might account for part of the apparent increase in the concentration of dissolved Gd^{3+}. A study of these formation kinetics would be interesting in its own right and this work indicates that ITC would be a valuable experimental tool in such a study.

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V_{Al} and V^- Centers in MgO†

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The center produced by ionizing radiation which has been generally accepted to be the intrinsic V^- center in nominally pure MgO is shown to be actually associated with an aluminum impurity. A stable center with identical g values is produced by irradiation with energetic particles and its properties are compatible with the intrinsic V^- center.

During the course of previous work in this laboratory on trapped-hole centers affiliated with the alkali impurities in the alkaline-earth oxides,[1-3] it became obvious that, in order to understand better the nature of these centers, it would be necessary to explore further the environment of the V^- center in MgO. The ESR properties of the V^- center (previous notations: H_1, V_1 centers) were first investigated by Wertz *et al.*[4-6] and their results showed that the center, which can be produced in as-grown crystals by a short exposure to ionizing radiation, possessed tetragonal symmetry about a ⟨100⟩ direction with $g_\parallel = 2.0032$ and $g_\perp = 2.0385$. They proposed a model of a hole trapped on an oxygen ion, forming an O^- ion adjacent to an Mg-ion vacancy. Related centers such as the V_F, V_{OH}, and V_{OD}, where an F^-, OH^-, or OD^- ion replaces the O^{2-} ion adjacent to the positive-ion vacancy and opposite to the O^- ion, may also be produced by ionizing radiation, and these centers have been studied by both ESR[7,8] and electron-nuclear double-resonance (ENDOR)[8-10] techniques. Those ENDOR results unequivocally identified the axial interactions of the fluorine, hydrogen, and deuterium nuclei in these related centers, but shed little light on the detailed structure of the defects. In particular, no information about the nearest-neighbor magnesium interactions was reported. The relative concentrations of these centers are

found to be dependent upon both the sample and its thermal treatment. All these defects are relatively unstable at room temperature as a result of thermal leakage of the trapped holes from the defects.

The purpose of this communication is to provide conclusive evidence that the center which has been generally accepted to be the V^- center in nominally pure as-grown MgO is actually associated with a diamagnetic trivalent aluminum ion, and it is therefore a charge-compensated center, which we shall hereafter call the V_{Al} center, rather than an intrinsic V^- defect. The strong sample dependence observed for the relative concentrations is thus merely a manifestation of the relative purity of the MgO crystals used. This claim is based on an extensive survey utilizing ESR, ENDOR, and thermal-stability measurements of the defects in crystals obtained from various major suppliers: Muscle Shoals (MS), Norton, General Electric, W. & C. Spicer, Ltd., and Oak Ridge National Laboratory (ORNL). The total impurity content of crystals from the first two sources is roughly 1000 ppm, while for the others, 100 ppm or less.

Figure 1 illustrates the ESR spectrum obtained from an ORNL-grown crystal containing V_{OH}, V_F, and V_{Al} centers for $\vec{H}$ oriented at 90° to the defect axis. Since all V-type centers have essentially the same $g_\parallel$, the 90° orientation affords the greatest discrimination between the various g values. The values quoted in the literature[11,12] are $g_\perp = 2.0396$, 2.0388, and 2.0385, for the V_{OH}, V_F, and V_{Al}, respectively, and values we determined for these centers agree extremely well with these numbers. The linewidth of the center

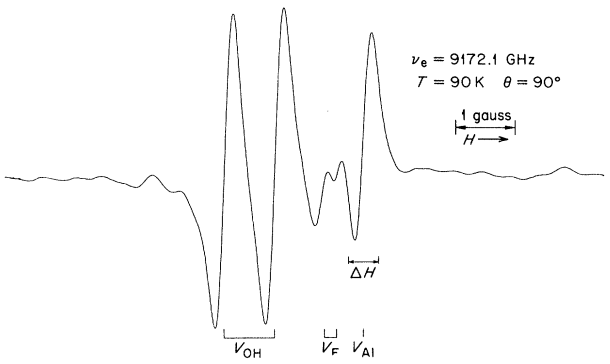

FIG. 1. ESR spectrum for a γ-irradiated ORNL-grown MgO crystal with $\vec{H}$ perpendicular to the defect axis. The interval labeled ΔH beneath the V_{Al} center depicts the portion of the line for which aluminum ENDOR was observed [Fig. 2(b)].

at $g_\perp = 2.0385$ was 0.3 G immediately after irradiation. The horizontal arrow at the bottom of Fig. 1 refers to the region where ENDOR of an aluminum impurity was observed (Fig. 2). An $S = \frac{1}{2}$, $I = \frac{5}{2}$ Hamiltonian with principal axes for both the magnetic hyperfine and electric quadrupole interactions parallel to a ⟨100⟩ direction describes the observed spectra, with the relevant parameters $A_\parallel = \pm 0.176 \pm 0.005$ MHz, $A_\perp = \mp 0.073 \pm 0.005$ MHz, and $P = \mp 0.552 \pm 0.005$ MHz. The hyperfine interaction can be expressed in terms of its isotropic and anisotropic components as $a = \pm 0.010$ MHz and $b = \pm 0.0835$ MHz, respectively. (This aluminum ENDOR signal has also been independently observed by Garrison and DuVarney[13] in a W. & C. Spicer, Ltd., crystal.) The aluminum ENDOR spectrum was associated with the ESR signal with the characteristic 0.3-G linewidth (at $\theta = 90°$) in every crystal of the 100-ppm total impurity group that we studied (to date, eight crystals, several each from General Electric, W. & C. Spicer, Ltd., and ORNL). Since our experimental g values agree to within ± 0.001 of the published values,[12] it is not possible that we were probing the center ($g_\perp = 2.0390$) reported by Wertz and Auzins,[14] which they called the V_a and which would occur at a different region of the spectrum. (It would lie, in any case, between the V_{OH} and V_F centers in a spectrum such as that shown in Fig. 1.) The stability of the center discussed here, with a characteristic half-life of <10 h at room temperature,[15] is more consistent with an essentially neutral V_{Al} center, viz., an Al^{3+} charge-compensated V^- center, than with the previously postulated intrinsic V^- center, in which the paramagnetic hole is expected to be trapped in a much deeper potential well.

As further proof that aluminum is the charge compensator for the Mg vacancy in as-grown crystals, we have found a dramatic increase in both the ESR and aluminum ENDOR signals when the crystals were diffused with aluminum-oxide powder at 1875 K or doped with Al_2O_3 in the growth process. Indeed, it is interesting to note that in the first report on this center Wertz and Auzins originally postulated a trivalent metal ion as a charge compensator for the Mg vacancy,[4] although in later work, the model was changed to require no charge compensation.[11,12] Such charge compensation should be possible in lattice sites somewhat removed from the trapped hole as well. If one examines the many weak ESR lines occurring on either side of the strong V_{Al} resonance, one finds many lines which clearly are not symmetric

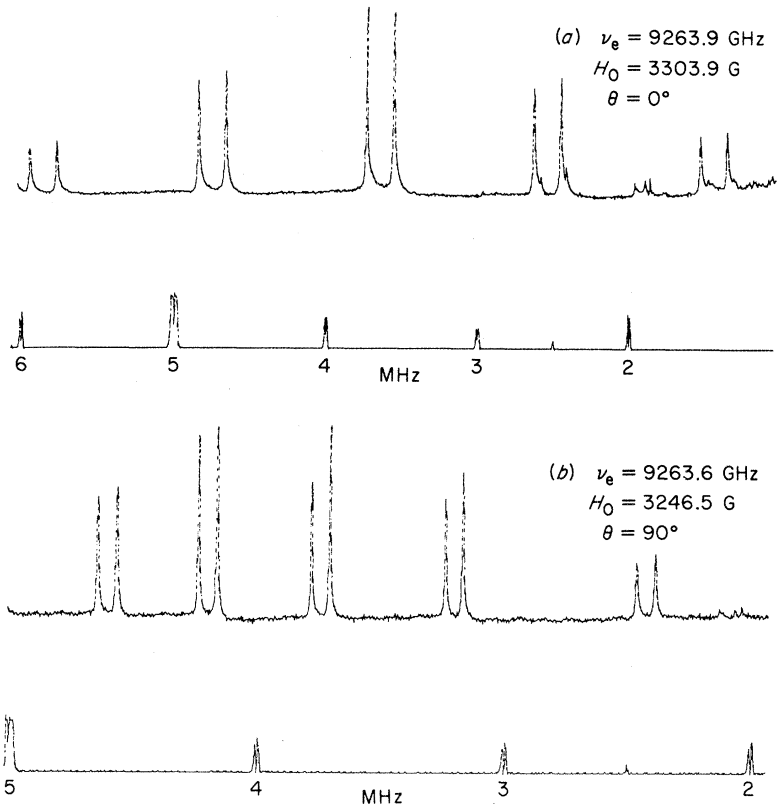

FIG. 2. Aluminum ENDOR spectrum obtained when the V_{Al} ESR line is saturated. (a) H parallel to the defect axis, $\theta = 0°$; (b) H perpendicular to the defect axis, $\theta = 90°$.

to it (as would be the case for interactions with ^{25}Mg nearest neighbors). An ENDOR survey through these weak lines, having different $g_\perp$ values than the main V_{Al} line, reveals a large number of other ^{27}Al hyperfine interactions, with smaller magnetic hyperfine and electric quadrupole terms, which may be due to Al^{3+} charge compensators in other (relatively improbable) positions.

In the case of γ-irradiated MS and Norton crystals, which are very impure, ESR signals were also found at $g_\perp = 2.0385$, but with larger linewidths (0.5–0.6 G). The fact that this center is very unstable (decay half-life of 2 h at room temperature for crystal MS-16[15]) is not reconcilable with the stable intrinsic V^- center. A negatively charged V^- center would not be expected to decay by electron capture because of Coulomb repulsion. In fact, weak Al ENDOR signals were seen in the MS crystal, and there were indications of weak Al signals in the Norton crystal. Because of the large impurity content in these crystals, the ESR saturation behavior was different, preventing us from deducing whether the ESR line was a composite of several different charge compensating impurities or totally due to aluminum.

There is reason to suspect[16] that the stable, intrinsic V^- center may also exist in crystals which were subjected to knock-on damage caused by energetic particles, such as neutrons or 2-MeV electrons. Our suspicion that this is an intrinsic center is based on the following observations. Firstly, its concentration has not decayed appreciably at room temperature over a period of 2 years following prolonged electron irradiation, although any V_{Al} centers would have decayed. Secondly, the concentration of V-type centers induced by unlimited ionizing radiation followed a normal radiation-damage growth curve upon irradiation with 2.0-MeV electrons. The ESR spectrum exhibited the same g values as the V_{Al} center within experimental accuracy, had a linewidth of 0.3 G at $\theta = 90°$, and was slightly more difficult to saturate at 4.2 K. We are presently studying both the ESR and ENDOR of this spectrum to determine the detailed structure of this center.[16] There was no aluminum ENDOR

signal observable on this stable defect or on any of the weak lines associated with it. When, however, these electron-irradiated crystals were given a short ionizing γ irradiation, we observed an increase in the ESR signal and an aluminum ENDOR signal indicating that V_{Al} centers had been rejuvenated. Therefore, in a single sample, the ENDOR spectrum clearly distinguishes two different centers with the same g values. This distinction between two species, both having the same g values, the V_{Al} and the stable V-type center, serves to explain the observations that the defects having $g_\perp = 2.0385$ are sometimes stable in electron-irradiated[17] and neutron-irradiated[18] crystals and that these defects can trap an extra hole to form the $S=1$ center (previous notations: H_2, W, V_2) at reduced temperatures.[11]

The remarkable coincidence of these $g_\perp$ values for the V_{Al}, stable V-type, and the (perhaps different) V-type center in the MS and Norton crystals has been carefully verified by observing the ESR at 90 K of pairs of different crystals glued together. In no case was there a splitting observable at $\theta = 90°$. Thus, except for saturation behavior at 4.2 K and the small linewidth differences, one can distinguish between these centers by means of the ENDOR spectra they produce.

Aluminum is usually present as an impurity in MgO, and we have shown that the presence of the V_{Al} center is a general phenomenon in many crystals from various sources. It is clear from the evidence presented here that this unstable center, which is produced by ionizing radiation, is not the V^- center. From the small aluminum hyperfine interaction, we propose the following structure for the defect designated V_{Al}: a linear array of O^-–Mg-vacancy–O^{2-}–Al^{3+}.

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