EPR and optical studies of γ-irradiated MgO:Ga

G. E. Holmberg
Department of Physics,
University of Connecticut, Storrs, Connecticut 06268

K. H. Lee and J. H. Crawford, Jr.
Department of Physics and Astronomy,
University of North Carolina, Chapel Hill, North Carolina 27514
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EPR lines which appear when MgO:Ga is γ-irradiated at room temperature have been assigned to Ga^{2+} ions in substitutional cation sites. For ^{69}Ga at 77 K, we have $g = 1.996 \pm 0.0005$ and $A = 8.563 \pm 0.008$ GHz. Optical absorption bands at 370 and 300 nm in γ-irradiated MgO:Ga have been attributed to Ga^{2+} and Ga^{1+}, respectively, as a result of bleaching and annealing experiments.

I. INTRODUCTION

Four new EPR lines appear between 5.3 and 11 kG at X band when MgO:Ga is subjected to γ irradiation at room temperature. We assign these lines to Ga^{2+} ions in substitutional cation sites. Ga^{2+} has previously been observed by EPR in ZnS:Ga under 450-nm optical irradiation at low temperatures by Räuber and Schneider[1]; the gallium center decayed rapidly at 77 K when the irradiation was discontinued but was partly frozen in at 4.2 K. Ga^{2+} centers are stable at room temperature in MgO for the order of days. The Fermi-contact interaction of Ga^{2+} in MgO has a temperature dependence which is similar to that of the isoelectronic Cu^0 and the analogous Ag^0 center in alkali chlorides.[2-7] We also observe optical-absorption bands which correlate with the production and decay of Ga^{2+} EPR lines. We attribute a 370 nm band to Ga^{2+} and a 300 nm band to Ga^{1+}.

II. EXPERIMENTAL METHODS

The samples used in this study were cleaved from MgO:Ga crystals grown at Oak Ridge National Laboratory. The samples were exposed to ^{137}Ce γ irradiation at room temperature. The number of Ga^{2+} centers saturated at about $5 \times 10^{18}/cm^3$ after a dose of 3×10^4 rad. Data were taken at X band between room temperature and 70 K. A Varian V-4502 EPR spectrometer was used for the measurements, with the exception of the 70 K measurement where a Bruker ER-420 spectrometer was used. A variable temperature accessory manufactured by Oxford Instruments was used for the measurement at 70 K.

Optical absorption was measured using a Cary 14R spectrometer; and optical bleaching was accomplished with light from a 150-W xenon short-arc discharge lamp which was dispersed by a Bausch and Lomb high-intensity monochromator.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Ga^{2+} has a $^2S_{1/2}$ ground state due to a $4s^1$ electron. There is a strong hyperfine interaction with its $I = \frac{3}{2}$ nucleus which splits the ground-state energy in zero field. The ground-state paramagnetic behavior can be described by the spin Hamiltonian

$$H = g\mu_B \vec{H}\cdot\vec{S} + A\vec{I}\cdot\vec{S} - g_n\mu_N\vec{H}\cdot\vec{I} \ , \tag{1}$$

where

$$A = (\tfrac{8}{3}\pi) g\mu_B g_n \mu_N |\psi(0)|^2 \tag{2}$$

and $I = \frac{3}{2}$. The energy levels for this ground state are described by the Breit-Rabi formula. A graph of ground-state energy as a function of magnetic field is shown in Fig. 1. Transitions are observed between

$$(F=1,\ M_F=-1) \leftrightarrow (F=2,\ M_F=-2)$$

and

$$(F=2,\ M_F=-2) \leftrightarrow (F=2,\ M_F=-1) \ .$$

The latter transition is shown in Fig. 2 for ^{69}Ga at 70 K. Variable temperature accessory data is shown because 77 K data was subject to noise from liquid-nitrogen bubbles. The values of g and A for the two isotopes are given in Table I. Watanabe has shown

TABLE I. Spin-Hamiltonian parameters for Ga^{2+} in MgO.

T (K)	Isotope	g	A (GHz)
RT	^{69}Ga	1.999 ± 0.001	8.31 ± 0.001
RT	^{71}Ga	2.000 ± 0.001	10.58 ± 0.001
77	^{69}Ga	1.9996 ± 0.0005	8.563 ± 0.008
77	^{71}Ga	1.9999 ± 0.0005	10.894 ± 0.008

that a positive g shift results from a partial electron transfer through spin-orbit interaction from ligand ions to the s-state ion.[8] The g value for Ga^{2+} in MgO shows a small negative shift of about -0.0025 from the free-electronic g value. A negative g shift is consistent with a more ionic and less covalent host crystal structure, in agreement with an observation by Hausmann and Schreiber,[9] who reported the g shift for Sn^{3+} $(5s)^1$ in ZnO to be -0.0145 as opposed to positive g shifts measured by others for Sn^{3+} in the more covalent ZnS, ZnSe, and ZnTe lattices.

The ratio of the Fermi contact interactions at 77 K of the two isotopes is 0.7860, which agrees within experimental error with the ratio of the nuclear moments of the isotopes, 0.7870148, as measured by NMR.[10] Measurements at X band between 9.0 and 9.4 GHz gave consistent results so it was not necessary to measure in another microwave band for further proof that the observed lines were indeed from Ga^{2+}.

Each of the observed lines (see Fig. 2) had an intense, isotropic central line with a width of about 1 G; this is consistent with a Ga^{2+} ion in a substitutional site. Each central line was flanked by less intense satellite lines whose positions varied with magnetic field angle. Angular satellite lines were also observed in ZnS:Ga by Räuber and Schneider.[1] ZnS can be grown with a twinned cubic structure, but the incorporation of impurities enhances the formation of hexagonal and higher polytype domains. They suggested that the angular dependent lines might arise from centers in noncubic domains of the ZnS crystal. However, MgO has only the cubic structure, so satellite lines in this case have another cause. It is believed that they result from superhyperfine interactions with the 10%-abundant ^{25}Mg nuclei in nearest or next-nearest cation locations. Raizman and Suss[11] have observed a transferred superhyperfine interaction between an Ir^{2+} ion and a next-nearest neighbor ^{25}Mg ion via an O^{2-} ion. However, a Jahn-Teller distortion enhanced the interaction in their case; interactions with ^{25}Mg ions located in directions perpendicular to the Jahn-Teller distortion axis were not resolved with EPR.

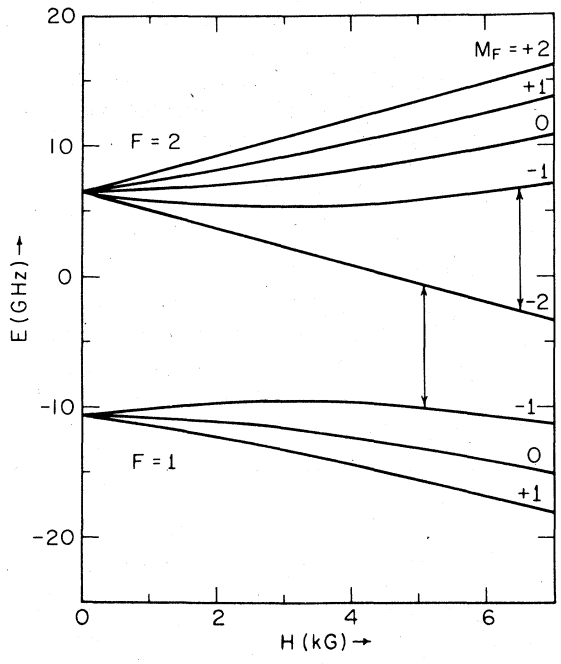

FIG. 1. Energy levels as a function of magnetic field for $^{69}Ga^{2+}$ in MgO at 77 K. X-band transitions are shown for 9.4 GHz.

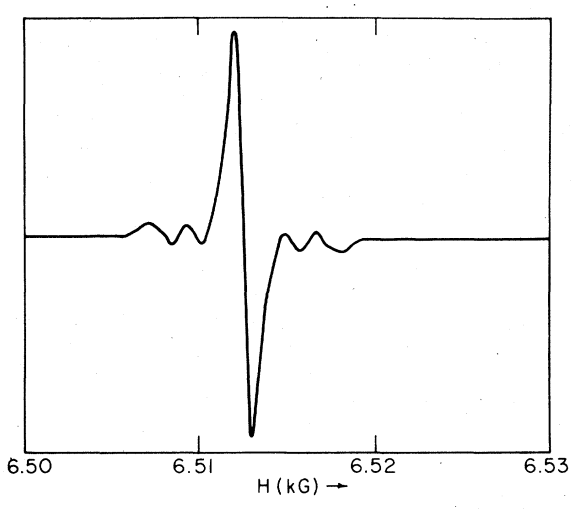

FIG. 2. $^{69}Ga^{2+}$ EPR line at 70 K. Transition is $(F=2, M_F=-2) \rightarrow (F=2, M_F=-1)$ for a microwave frequency of 9.4 GHz. $\vec{H} \| [100]$.

Although there is no Jahn-Teller distortion for MgO:Ga, it is quite possible that the O^{2-} ion is instrumental in transferring the Ga^{2+} spin density to ^{25}Mg ions in next-nearest cation sites. A transfer via an intervening Cl^- ion was observed by Holmberg *et al.*[12] for the Ag^0 center in KCl and NaCl. The spin-density transfer increased for the smaller NaCl lattice, and the MgO lattice is even more compact. Experiments are planned in the near future to investigate the MgO:Ga^{2+} satellite lines in order to test this hypothesis.

The Fermi contact interaction for Ga^{2+} in MgO is temperature dependent, as shown in Table I. Similar behavior has been observed for Cu^0 and Ag^0 centers in alkali chloride crystals[2,7]; these centers also have $^2S_{1/2}$ ground states, and Cu^0 is isoelectronic to Ga^{2+}. The Fermi contact interaction for Cu^0 in both NaCl and LiCl exhibited a linear decrease of about 0.05%/K as the temperature was increased from 77 K to 150 or 200 K.[7] From the data of Table I, Ga^{2+} in MgO decreases by 0.013%/K between 77 K and room temperature, under the assumption that the change is linear. Baranov *et al.* attributed the temperature dependence for Cu^0 to: (a) an alteration of the distance to the neighboring anions caused by local vibrations due to the presence of impurity ions (The anharmonicity of these vibrations, in particular, would lead to a temperature-dependent local lattice expansion), and harmonic vibrations of the stabilized atom and surrounding ions; and possibly (b) the production of an admixture of excited electronic states (e.g., $3d^9 4s^2$) caused by interaction of the atom with lattice vibrations.[7] It is curious that none of the studies of ns^1 ions in more covalent crystals has noted a temperature-dependent Fermi contact interaction.

Ge^{3+}, also isoelectronic to Ga^{2+}, has been created in ZnS:Ge by irradiation with 380 nm light at 77 K.[13] A comparison of the EPR parameters of the three isoelectronic species Cu^0, Ga^{2+}, and Ge^{3+} are given in Table II. The value of $|\psi(0)|^2$ for Ga^{2+}, calculated from Eq. (2), is markedly larger than those for the other two cases. This difference can at least partially be attributed to the smaller lattice size of MgO. For the Cu^0 center in alkali chlorides at 77 K, Baranov *et al.*[7] reported that the Fermi contact interaction increased about 12% in going from KCl to NaCl, with another increase of 5% from NaCl to LiCl. Evidently the more ionic nature of MgO, together with its more compact lattice combine to cause an approximately

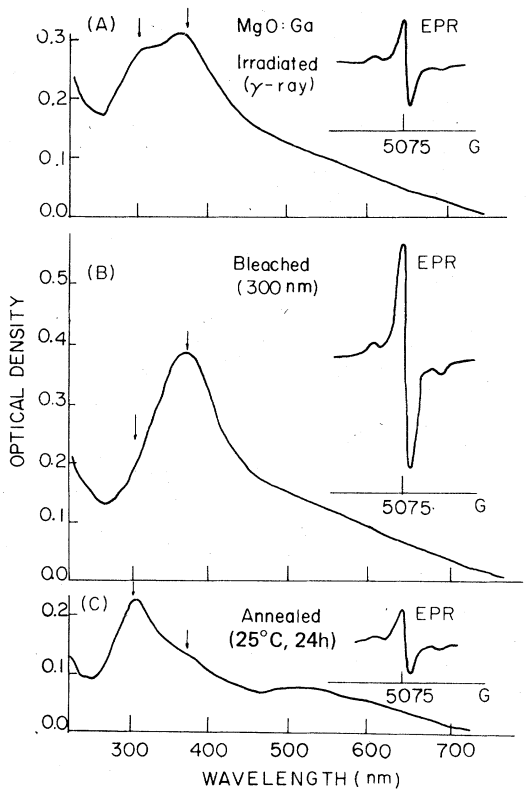

FIG. 3. Variation of room-temperature optical transmission and 77K EPR absorption with sample treatment. (a) After sample γ-irradiated to saturation and held 48 h at room temperature. (b) After subsequent 300 nm optical bleach. (c) After additional 24 h at room temperature. EPR transition is $(F=1,\ M_F=-1) \rightarrow (F=2,\ M_F=-2)$ for $^{69}Ga^{2+}$.

TABLE II. EPR parameters for $4s^1$ species in several environments.

Species	Temperature (K)	Crystal	$\lvert\psi(0)\rvert^2$ (10^{24} cm^{-3})	g	Reference
Ga^{2+}	77	MgO	53.8	1.9996	this work
Ga^{2+}	20	ZnS	38.3	1.9974	1
Ge^{3+}	77	ZnS	39.4	2.0086	13
Cu^0	atomic beam		33.5	···	14

40% greater spin density at the Ga^{2+} nucleus in MgO as opposed to ZnS.

Optical absorption measurements were also made on MgO:Ga after γ irradiation and after subsequent bleaching. The sample was irradiated to saturation and then held at room temperature for 48 h. During this time the V_{OH}- and V_{Al}-center optical and EPR absorptions decay away, but optical bands in the 300 to 400 nm region remain, along with a small Ga^{2+} EPR signal, as shown in Fig. 3(a). Subsequent optical bleaching in the 300 nm band destroys this band and increases the absorption of the 370 nm band and simultaneously increases the Ga^{2+} EPR absorption [see Fig. 3(b)]. After an additional 24 h period at room temperature the 300 nm band is partially restored while the 370 nm band, together with the Ga^{2+} EPR absorption, are partially eliminated, as shown in Fig. 3(c). From this evidence, the 370 nm band is assigned to Ga^{2+} and the 300 nm band is assigned to Ga^{1+}. Ultraviolet absorption bands have also been observed for Ga^{1+} in the alkali halides.[15] Prior to γ irradiation of MgO:Ga neither the 300 or 370 nm optical bands nor a Ga^{2+} EPR signal is present; therefore the gallium is believed to be trivalent prior to irradiation.

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