PHYSICAL REVIEW B VOLUME 22, NUMBER 3 1 AUGUST 1980

Electron paramagnetic resonance of Ir^{4+} ions in MgO and CaO

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(Received 17 December 1979)

Electron-paramagnetic-resonance spectra of Ir^{4+} were studied in single crystals of MgO and CaO. In each host an isotropic cubic spectrum and two anisotropic tetragonal spectra were observed. Models are proposed for the tetragonal centers, one with a host cation vacancy at a next-nearest-neighbor site to an Ir^{4+} ion in a [100]-type direction, and another including also a cation with a charge greater than 2 at a next-nearest-neighbor site to the vacancy on the defect axis. The tetragonal spectra exhibit quadrupole interaction. The fitting of the spin-Hamiltonian parameters to the EPR spectra was carried out by using a FORTRAN IV version of the MAGNSPEC computer program. The EPR results were used to calculate crystal-field, magnetic, and covalency parameters.

I. INTRODUCTION

The electron-paramagnetic-resonance (EPR) spectrum of Ir^{4+} ions has been extensively investigated, theoretically as well as experimentally, in several iridium salt complexes.[1,2] In oxide environments the EPR of Ir^{4+} has been studied in single crystals of yttrium gallium garnets.[3–5] The cubic spectrum of Ir^{4+} has been reported in single crystals of MgO,[6] and in powdered samples of CaO and CdO.[5] In this paper we report a detailed study of Ir^{4+} ions in single crystals of MgO and CaO.

The structure of the isomorphous crystals MgO and CaO is fcc. The impurity ions enter substitutionally for the divalent host cations. Divalent impurity ions need no charge compensation and therefore are exposed to an octahedral crystalline field due to the six O^{2-} ligands. However, charge compensation is needed when the impurity ion is trivalent or tetravalent. This can happen, for example, by the formation of vacancies of the divalent host cation. One vacancy can compensate one tetravalent or two trivalent impurity cations. Charge compensation needs only be achieved over a relatively large volume. An octahedral center means that the separation between the impurity and the compensating vacancy is greater than two unit-cell lengths. In this case the corresponding EPR spectrum in alkaline-earth oxides will be isotropic (or may exhibit a Jahn-Teller effect if the ion involved has an orbital degeneracy). Deviation from pure octahedral symmetry is obtained if the charge compensating vacancy is in the near vicinity of the impurity ion. In this case, the local symmetry will be either tetragonal or orthorhombic, depending on whether the vacancy is in the [100] next-nearest- or [110] nearest-neighbor position, respectively. EPR spectra indicate that tetragonal distortions are the most significant in the alkaline-earth oxides.[7] The observation of tetragonal centers of Ti^{3+}, Cr^{3+}, Fe^{3+}, and Mn^{4+} in MgO and CaO has been reported in the past.[8–11] Most of the Ir^{4+} centers reported here exhibit tetragonal symmetry. A small fraction of Ir^{4+} ions is located at octahedral sites, represented by a cubic isotropic spectrum. Other sites of lower symmetry were also observed and their investigation is being continued.

II. EXPERIMENTAL

Single crystals of MgO doped with 0.5 mol % $IrCl_4$ were grown by the flux evaporation method with PbF_2 as flux.[12] Single crystals of CaO doped with Ir were grown for us by W. & C. Spicer Ltd. by melting $CaCO_3$ with 0.2 mol % Ir metal powder in an electric-arc furnace. Spectrochemical analysis showed a concentration of the order of 1000 and 100 ppm Ir in the MgO and CaO crystals, respectively. The as-grown MgO crystals were yellow in color; the as-grown CaO was milky and slightly yellowish. No EPR spectra were detected which could be associated with Ir ions in the as-grown MgO crystals. After γ or x-ray irradiation the spectra of Ir^{4+} together with those of other Ir species can be observed. In CaO the EPR spectra of Ir^{4+} were observed in the as-grown crystals. A Varian *X*-band EPR spectrometer was used in the temperature range 4.2–120 K. The fitting of the spin-Hamiltonian parameters to the EPR spectra was carried out with an IBM 370/160 computer using a FORTRAN IV version of the MAGNSPEC program.[13]

III. THEORY

The electronic configuration of Ir^{4+} is $5d^5$. Experimentally, all ions studied in both $4d$ and $5d$ transition-metal groups are found to belong to the "strong-field" category. The ground state of the d^5 configuration in a strong octahedral crystal field is ${}^2T_{2g}$ (t_{2g}^5) and thus it can be treated as a hole in the t_{2g} shell. In the following treatment we neglect any admixture of the excited configurations ($t_{2g}^4e_g$, etc.). The orbital triplet T_{2g} in a cubic symmetry can be represented, in the first approximation, by a fictitious angular momentum $\tilde{L}=1$, with an effective orbital g factor $\tilde{g}_L=-1$. The eigenfunctions in this new base are given by[14]

$$|\tilde{1}\rangle = Y_1^2,\quad |\tilde{0}\rangle = (Y_2^2 - Y_{-2}^2)/\sqrt{2},\quad |-\tilde{1}\rangle = -Y_1^2 \ . \tag{1}$$

A tetragonal field splits the orbital triplet into a singlet $|\tilde{0}\rangle$ and a doublet $|\pm\tilde{1}\rangle$ with an energy separation Δ. The sign of Δ may be either positive or negative in accordance with the nature of the tetragonal field. The splitting due to the spin-orbit coupling of the orbital triplet ($\mathcal{H}_{\mathrm{so}}=\tilde{g}_L\lambda\tilde{L}\,\tilde{S}$) yields a quartet ($\tilde{J}=\frac{3}{2}$) and a doublet ($\tilde{J}=\frac{1}{2}$) with an energy separation of $\frac{3}{2}\lambda$ with respect to the quartet. $\tilde{J}=\tilde{L}+\tilde{S}$, and the spin-orbit-coupling constant is equal to $\zeta_{\pi\pi}$ and $-\zeta_{\pi\pi}$ for an electron and a hole, respectively. Here $\zeta_{\pi\pi}$ is the spin-orbit-coupling constant for an electron, between two t_{2g} molecular orbitals. The solution of the secular equation obtained from the Hamiltonian matrix of both spin-orbit coupling and tetragonal distortion yields three Kramers doublets. The ground doublet for the t_{2g}^5 configuration $A^{\pm}$ (regardless of the sign of Δ) is given by[14]:

$$A^{+}=\cos\delta|+\tilde{1}\rangle^{-}-\sin\delta|\tilde{0}\rangle^{+} \ , \tag{2a}$$

$$A^{-}=\cos\delta|-\tilde{1}\rangle^{+}-\sin\delta|\tilde{0}\rangle^{-} \ , \tag{2b}$$

where $\tan 2\delta=\sqrt{2}\lambda/(\Delta+\frac{1}{2}\lambda)$. The energy level of this state with respect to the cubic ${}^2T_{2g}$ ground state is located at

$$E_A=\tfrac{1}{2}\Delta+\tfrac{1}{4}\lambda+\tfrac{1}{2}(\Delta^2+\Delta\lambda+\tfrac{9}{4}\lambda^2)^{1/2} \ . \tag{3}$$

The spin Hamiltonian for a tetragonal spectrum can be written in the form:

$$\begin{aligned}\mathcal{H}=&\,g_{\parallel}\mu_B H_z S_z+g_{\perp}\mu_B(H_xS_x+H_yS_y)+A_{\parallel}I_zS_z\\&+A_{\perp}(I_xS_x+I_yS_y)+Q[I_z^2-\tfrac{1}{3}I(I+1)]\\&+\mu_N(H_zI_z+H_xI_x+H_yI_y) \ .\end{aligned} \tag{4}$$

The spin-Hamiltonian parameters for the $A^{\pm}$ ground doublet are

$$\begin{aligned}&g_{\parallel}=g_e\sin^2\delta-(g_e+2k_{\pi\pi})\cos^2\delta \ ,\\&g_{\perp}=-(g_e\sin^2\delta+\sqrt{2}k_{\pi\pi}\sin 2\delta) \ ,\end{aligned} \tag{5}$$

$$\begin{aligned}&A_{\parallel}=P\kappa\cos 2\delta+2N_\pi^2P\left(-\tfrac{2}{7}-\tfrac{6}{7}\cos^2\delta+\frac{3}{7\sqrt{2}}\sin 2\delta\right) \ ,\\&A_{\perp}=P\kappa\sin^2\delta-2N_\pi^2P\left(+\tfrac{1}{7}\sin^2\delta+\frac{11}{14\sqrt{2}}\sin 2\delta\right) \ ,\end{aligned} \tag{6}$$

$$Q=\tfrac{1}{14}N_\pi^2e^2Q_0(1-R)\langle r^{-3}\rangle(3\cos^2\delta-2) \ . \tag{7}$$

Here $g_e=2.0023$ is the free electron g factor. $k_{\pi\pi}$ and N_π are the orbital reduction parameter and the molecular-orbital (MO) wave-function normalization factor, respectively. κ is the core polarization factor containing covalent effects and admixtures of excited $6s$ states. e, Q_0, and $(1-R)$ are the electron charge, the nuclear electric quadrupole moment, and the Sternheimer shielding factor, respectively. $P=2\gamma_N\mu_B\mu_N\langle r^{-3}\rangle$, γ_N is the nuclear magnetogyric ratio, μ_B and μ_N are the Bohr and nuclear magnetons, respectively.

For a pure octahedral crystal field: $\Delta=0$ and $\cos^2\delta=\frac{2}{3}$. Thus one obtains $g=g_{\parallel}=g_{\perp}$, $A=A_{\parallel}=A_{\perp}$, and $Q=0$

$$g=-\tfrac{1}{3}(g_e+4k_{\pi\pi}) \ , \tag{8}$$

$$A=P(\tfrac{1}{3}\kappa-\tfrac{8}{7}N_\pi^2) \ . \tag{9}$$

IV. RESULTS

A. MgO

No spectrum which could be associated with Ir ions could be detected in the as-grown MgO crystals. After γ or x-ray irradiation the following spectra were observed:

(a) An isotropic spectrum of Ir^{4+} designated *I*. This spectrum was previously investigated by Suss *et al.*[6]

(b) Two anisotropic spectra of Ir^{4+} of tetragonal symmetry designated *T* and *T'*.

(c) An Ir^{2+} spectrum undergoing a static Jahn-Teller (JT) effect.[15]

(d) Other spectra associated with Ir^{4+} which are not yet fully interpreted.

Reduction of the crystal in hydrogen at 1000 °C produces a weak Ir^{2+} spectrum.[15]

The anisotropic tetragonal *T* spectrum was studied in the temperature range 4.2–120 K. It is a superposition of three spectra of tetragonal symmetry due to static distortions of the octahedron along the [100]-type directions. In the literature such a spectrum is sometimes called "a spectrum of three ions per unit cell." The spectrum of each site can be described by the axial spin Hamiltonian given in Eq. (2). For Ir^{4+}, $S=\frac{1}{2}$. The two stable isotopes ^{191}Ir and ^{193}Ir have, respectively, natural abundance of 38.5% and 61.5% and nuclear magnetic moments of $(0.1453\pm0.0006)\mu_N$ and $(0.1583\pm0.0006)\mu_N$.[16] Both isotopes have a nuclear spin $I=\frac{3}{2}$. The ratio of the nuclear electric quadrupole moments $^{193}Q_0/^{191}Q_0$ of the two Ir isotopes is equal to 0.91 ± 0.03.[17] $^{191}Q_0$ is about 0.9 b and $^{193}Q_0$ is about 0.82 b.[18] The parameters of the spin Hamiltonian are given in Table I. The EPR spectra of Ir^{4+} in MgO at $g_\parallel$, $g_\perp$, and $g_{[110]}$ at 52 K are shown in Figs. 1, 2, and 3, respectively. (At 77 K the spectra of the two Ir isotopes are not resolved and at 4.2 K the spectra are saturated.) Each figure consists of (a) the experimentally recorded spectrum and (b) a stick diagram of the calculated spectrum. The fitting of the spin-Hamiltonian parameters was made using the MAGNSPEC program,[13] which executes an exact diagonalization of the spin Hamiltonian 8×8 matrix (due to $S=\frac{1}{2}$ and $I=\frac{3}{2}$). The spectrum at $g_\parallel$ (Fig. 1) consists of an equally spaced, four line characteristic spectrum ($I=\frac{3}{2}$) for each isotope due to $\Delta m=0$ transitions. The separation between two adjacent lines (neglecting second-order corrections) is $A_\parallel$. The spectra of the two isotopes are only partially resolved. The quadrupole interaction does not affect the spectrum in this particular direction. In the spectrum at $g_\perp$ (Fig. 2) some of the four additional resonance lines (for each isotope) due to the quadrupole interaction are observed. These lines are the $\Delta m=\pm2$ transitions. Careful examination of the spectrum in Fig. 2 shows deviation from the features expected from perturbation theory[14] in the form of slightly unequal spacing of the hyperfine lines due to $\Delta m=0$ transitions. Further, an asymmetrical spacing of the lines due to $\Delta m=\pm2$ transitions about the two $\Delta m=0$ inner lines is not consistent with perturbation-theory predictions. Approximated expressions which well describe the positions and intensities of the spectrum at $g_\perp$ for $S=\frac{1}{2}$ and $I=\frac{3}{2}$ can be obtained by neglecting the off-diagonal matrix elements of the hyperfine interaction. The spin-Hamiltonian matrix is thus reduced to four 2×2 matrices which can be diagonalized exactly. The solution yields two groups of resonance lines[15]:

(i) A group of four lines, which we designate as group [0] (due to the four possible combinations of the + and − signs) at fields given by

$$g_\perp\mu_B(H-H_0)=\mp(\tfrac{1}{2}A_\perp)\mp(C+D)\ , \tag{10}$$

with intensities

$$I_{[0]}\propto|\sin(\alpha^+-\alpha^-)|^2\ . \tag{11}$$

(ii) Another group of four lines, which we desig-

TABLE I. Resonance parameters for Ir^{4+} in single crystals of MgO and CaO.

Host	Spectrum	g	A (10^{-4} cm^{-1})	Q (10^{-4} cm^{-1})	$Q/A_\perp$	T (K)
MgO						
	I^a	1.7385(15)	$^{193}A=26.7(5)$			77
			$^{191}A=25.0(5)$			
	T	$g_\parallel=2.261(2)$	$^{193}A_\parallel=27.0(5)$	$^{193}Q=5.5(5)$		52
			$^{191}A_\parallel=24.9(5)$	$^{191}Q=6.0(5)$		
		$g_\perp=1.460(2)$	$^{193}A_\perp=26.1(5)$		$^{193}(Q/A_\perp)=0.211$	
			$^{191}A_\perp=24.0(5)$		$^{191}(Q/A_\perp)=0.250$	
	T'	$g_\perp=1.475(2)$	$A_\perp$ and Q are the same as for the T center in MgO			
CaO						
	I	1.773(2)	$^{193}A=26.9(5)$			52
			$^{191}A=24.7(5)$			
	T	$g_\parallel=2.310(2)$	$^{193}A_\parallel=26.8(5)$	$^{193}Q=5.3(5)$		52
			$^{191}A_\parallel=24.6(5)$	$^{191}Q=5.8(5)$		
		$g_\perp=1.484(2)$	$^{193}A_\perp=26.0(5)$		$^{193}(Q/A_\perp)=0.215$	
			$^{191}A_\perp=23.8(5)$		$^{191}(Q/A_\perp)=0.244$	
	T'	$g_\parallel=2.273(2)$				
			$A_\parallel$, $A_\perp$, and Q are the same as for the T center in CaO			52
		$g_\perp=1.507(2)$				

[a] Ref. 6.

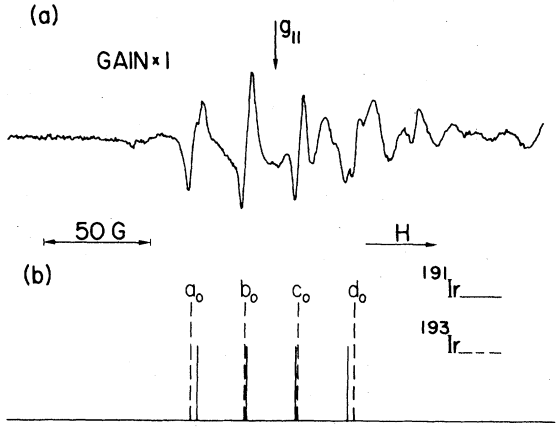

FIG. 1. (a) Tetragonal T spectrum of Ir^{4+} in MgO, at $g_\parallel$, 52 K, and 9.428 GHz. H_{dc} is along a [100] direction. (b) The calculated spectrum.

nate as group [2] at fields given by

$$g_\perp\mu_B(H-H_0)=\mp(\tfrac{1}{2}A_\perp)\mp(C-D)\ , \qquad (12)$$

with intensities

$$I_{[2]}\propto|\cos(\alpha^+-\alpha^-)|^2\ , \qquad (13)$$

where

$$C=(A_\perp^2+2A_\perp Q+4Q^2)^{1/2}\ ,$$
$$D=(A_\perp^2-2A_\perp Q+4Q^2)^{1/2}\ , \qquad (14)$$
$$\tan 2\alpha^\pm=\sqrt{3}Q/(\pm A_\perp-Q)\ ,$$

here

$$H_0=h\nu/g_\perp\mu_B\ .$$

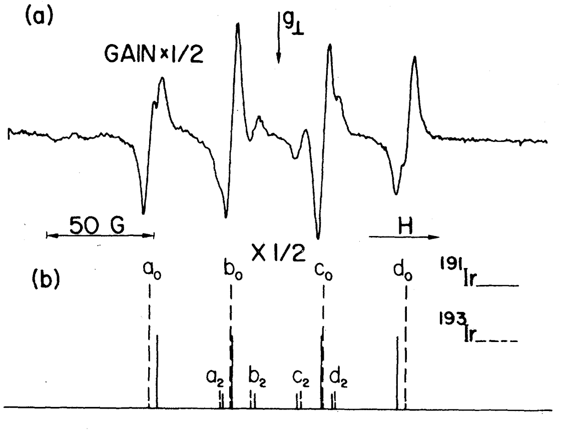

FIG. 2. (a) Tetragonal T spectrum of Ir^{4+} in MgO, at $g_\perp$, 52 K, and 9.428 GHz. H_{dc} is along a [110] direction. (b) The calculated spectrum. The intensities are multiplied by $\frac{1}{2}$.

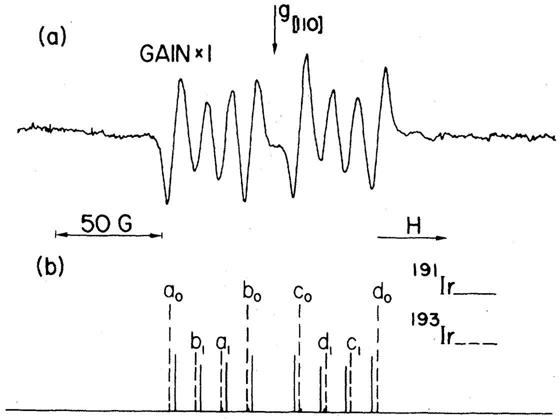

FIG. 3. (a) Tetragonal T spectrum (two sites) of Ir^{4+} in MgO at $g_{[110]}$, 52 K, and 9.428 GHz. H_{dc} is along a [110] direction. (b) The calculated spectrum. The intensities are multiplied by $\frac{1}{2}$.

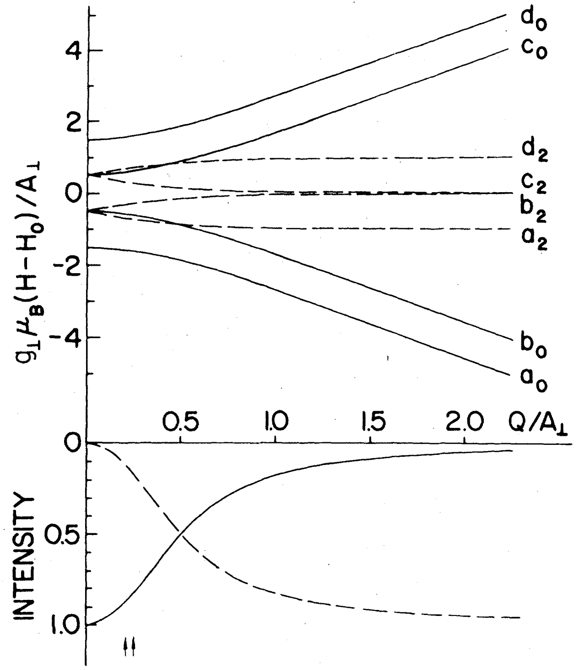

FIG. 4. Calculated positions and intensities of the resonance lines versus $Q/A_\perp$ at $g_\perp$ for a general case of $S=\frac{1}{2}$ and $I=\frac{3}{2}$. The ratios $Q/A_\perp$ for ^{193}Ir and ^{191}Ir are indicated by the small arrows at approximately 0.21 and 0.25, respectively. For accurate values of these parameters for both hosts see Table I. Solid line represents group [0], broken line represents group [2].

The calculated positions and intensities of the eight resonance lines for $g_\perp(\theta=90°)$ from the above equations are shown in Fig. 4. It can be seen that for small values of $Q/A_\perp$ one obtains a group of four strong ("allowed") lines due to the $\Delta m=0$ transitions (group [0], designated a_0, b_0, c_0, and d_0) and a group of four weak ("forbidden") lines due to $\Delta m=\pm 2$ transitions (group [2], designated a_2, b_2, c_2, and d_2). The designation of the resonance lines is consistent with that used in Ref. 14. When $Q/A_\perp$ increases, the intensity of group [0] decreases and that of group [2] increases. At $Q/A_\perp=0.5$ the intensities of both groups are equal. The assignment "allowed" and "forbidden," of course, does not have the usual meaning here because of the strong admixture of the wave functions with different m values. The separation between a_i and b_i, c_i and d_i, where $i=0,2$, is $A_\perp$.

In a general direction of H_{dc}, the treatment, which has to be handled by computer, yields 12 resonance lines. The additional lines are due to $\Delta m=\pm 1$ transitions (group [1]) and are designated as a_1, b_1, c_1, d_1. The lines a_1 and b_1 are located symmetrically between a_0 and b_0, as are c_1 and d_1 between c_0 and d_0 (Fig. 3). In the [110] direction the intensity of the lines of group [2] almost vanishes and no resolution between the spectra of the two Ir isotopes is observed. The computer calculated angular variation of one site of the spectrum is shown in Fig. 5. For this calculation the parameters given in Table I were used. The angular variation of the resonance lines relative to H_0 (where $H_0=h\nu/g\beta$) is given in the upper part and the relative intensities of the various groups are given in the lower part of Fig. 5. The agreement between the experimental and calculated results is very good.

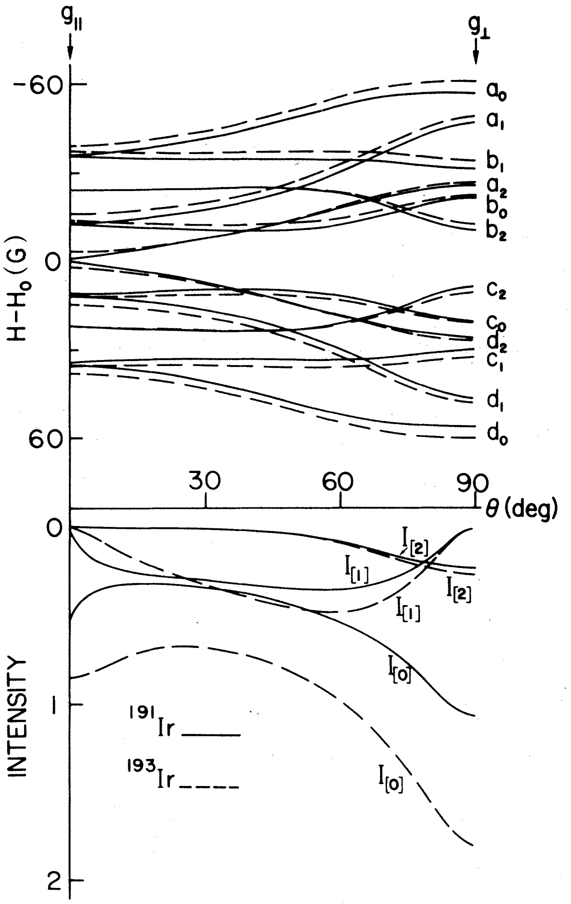

FIG. 5. Computed angular variation of one site of the tetragonal T spectrum of Ir^{4+} in MgO. The positions and intensities of the resonance lines are shown in the upper and lower parts of the figure, respectively. One line represents the average intensity of each quartet of the transitions [0], [1], and [2]. $H_0=h\nu/g\beta$ and θ is the angle between H_{dc} and the tetragonal axis of the site.

When the spectrum at $g_\perp$ is investigated at higher sensitivity one can observe an additional spectrum which we designate T'. The intensity of this spectrum is about 25 times less than that of the T spectrum given in Fig. 2. At X band the T' spectrum is only partially separated from the T spectrum. A full separation between the T and T' spectra is obtained at Q band. It was found that at $g_\perp$ these two spectra are very similar (they have the same A and Q) except for their intensities and a slight difference in the value of $g_\perp$ (see Table I). The T' spectrum in MgO was observed only in the vicinity of $g_\perp$, in other directions it broadens beyond detection. Thus no value of $g_\parallel$ and $A_\parallel$ could be measured in this host for the T' center.

B. CaO

Two types of EPR spectra of Ir^{4+} were observed in the as-grown CaO crystals: (a) an isotropic spectrum designated I; (b) two anisotropic spectra of tetragonal symmetry T and T', where T' is the spectrum of the smaller anisotropy.

γ or x-ray irradiation of the crystals produces Ir^{2+} ions which exhibit a static JT effect.[15] The spectra

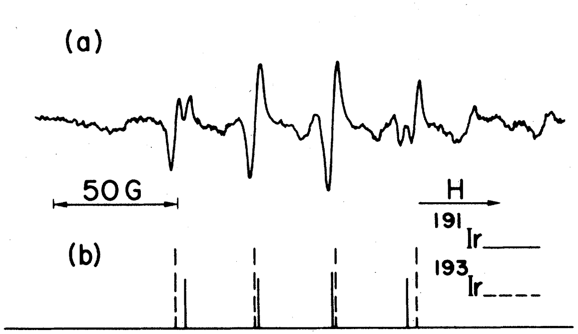

FIG. 6. (a) Isotropic spectrum of Ir^{4+} in CaO at 52 K, 9.367 GHz, and with H_{dc} along a [110] direction. (b) The calculated spectrum.

(a) and (b) are not affected significantly by irradiation. The spectrum T' vanishes after heating the crystals either in an oxygen atmosphere or in air at 1000 °C for 24 hours. This spectrum does not reappear after exposing the crystals which underwent the heat treatment to ionizing radiation. Reduction of the CaO crystals in a hydrogen atmosphere for 24 hours at 1000 °C results in the vanishing of the different types of Ir^{4+} spectra and the appearance of a weak Ir^{2+} spectrum.[15]

The intensity of the isotropic spectrum I is about 50 times less than that of the anisotropic T spectrum. The spin-Hamiltonian parameters are given in Table I. The isotropic EPR spectrum of Ir^{4+} in CaO with H_{dc} along the [110] direction is shown in Fig. 6. In the [111] direction this spectrum is hidden by the T and T' spectra.

The anisotropic spectra T and T' both have approximately the same intensity and features characteristic of a spectrum with "three ions per unit cell." The spectra can be fitted to the axial spin Hamiltonian given in Eq. (4), with the parameters given in Table I. Both spectra are very similar since both have the same $A_{\parallel}$, $A_{\perp}$, and Q and differ only in the g factors. The measured and calculated spectra for the T center in crystals heated in oxygen at $g_{\parallel}$, $g_{\perp}$, and $g_{[110]}$ are given in Figs. 7, 8, and 9, respectively. These figures are very similar to the corresponding Figs. 1–3 for the T center of Ir^{4+} in MgO. The linewidth in MgO is larger than in CaO. One of the reasons for this is that there is a larger concentration of Ir ions in MgO than in CaO (10:1), as determined by spectrochemical analysis.

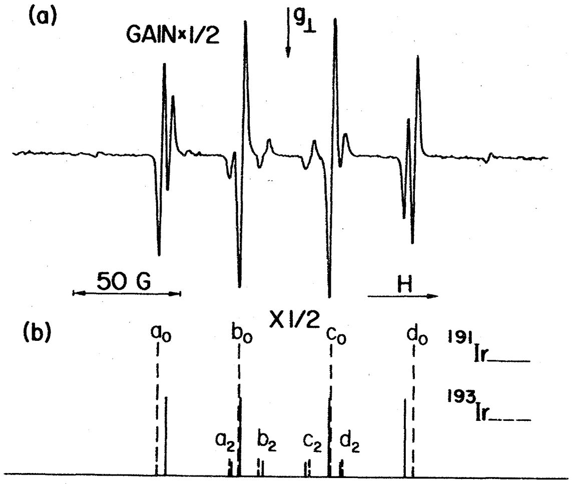

FIG. 8. (a) Tetragonal T spectrum of Ir^{4+} in a heated crystal of CaO, at $g_{\perp}$, 52 K, and 9.418 GHz. H_{dc} is along a [100] direction. (b) The calculated spectrum. The intensities are multiplied by $\frac{1}{2}$.

The computed angular variation and intensities of the T center in CaO are almost the same as for the T center in MgO and are therefore not shown here. The spectra at $g_{\parallel}$ and $g_{\perp}$ in the as-grown CaO crystals in which the T and T' centers are present are given in Fig. 10. One can find crystals taken from various parts of the melt in which the intensity of the T spectrum is greater than that of the T' spectrum, and vice versa.

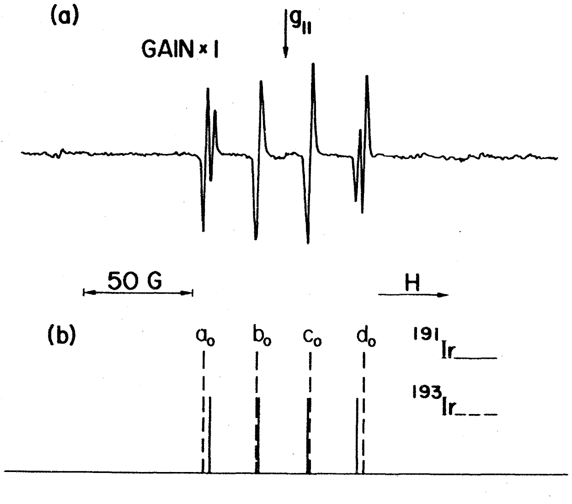

FIG. 7. (a) Tetragonal T spectrum of Ir^{4+} in a heated crystal of CaO, at $g_{\parallel}$, 52 K, and 9.418 GHz. H_{dc} is along a [100] direction. (b) The calculated spectrum.

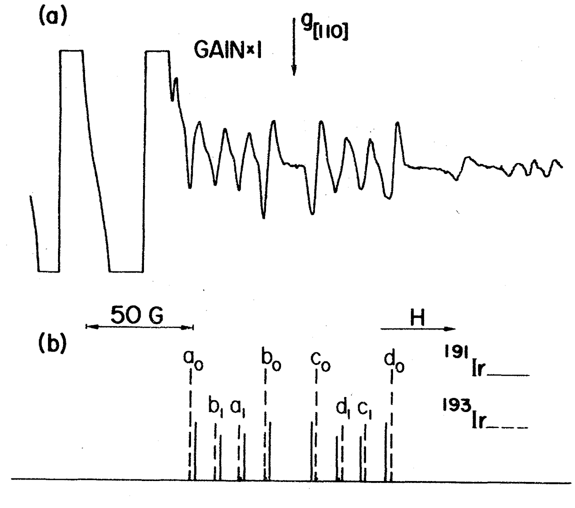

FIG. 9. (a) Tetragonal T spectrum of Ir^{4+} in a heated crystal of CaO, at $g_{[110]}$, 52 K, and 9.418 GHz. H_{dc} is along a [110] direction. (b) The calculated spectrum.

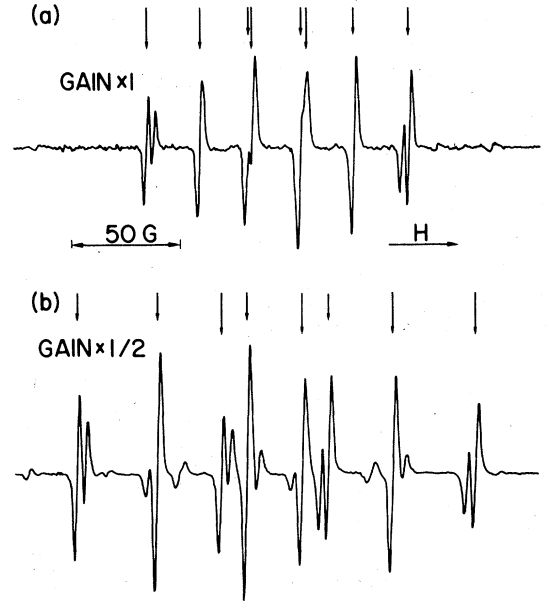

FIG. 10. Tetragonal T and T' spectra of Ir^{4+} in an untreated crystal of CaO at 52 K, 9.3 GHz, and with H_{dc} along a [100] direction. (a) The spectrum at $g_{\parallel}$. (b) The spectrum at $g_{\perp}$. The longer arrows indicate the T spectrum and the shorter arrows the T' spectrum.

V. DISCUSSION

Low-spin d^5 ions can serve as probes for the deviation of the crystal field from octahedral symmetry. Investigation of the tetragonal spectra provides interesting information on the magnitude and sign of the tetragonal field splitting as well as on the covalency and core polarization parameters. The calculations were performed in the following way. $k_{\pi\pi}$ and δ were derived from the solution of Eqs. (5) for $g_{\parallel}$ and $g_{\perp}$. For the isotropic spectrum we used Eq. (8). Substituting the value of δ into Eq. (6) and using $\langle r^{-3}\rangle = 13$ a.u.[19] for the free Ir^{4+} ion, we obtained N_π and κ. κ for isotropic spectra is obtained from Eq. (9). More detailed information on the covalency parameters can be obtained using the antibonding MO t_{2g}-type wave function[20]:

$$\psi_t = N_\pi(d_\pi - \alpha_\pi \chi_\pi) \ , \tag{15}$$

where d_π is a pure d orbital which transforms as the t_{2g} representation of the octahedral group, and χ_π is the linear combination of ligand orbitals of the same symmetry. The admixture coefficient α_π can be written $\alpha_\pi = S_\pi + \gamma_\pi$, where S_π and γ_π represent the overlap and charge-transfer contributions to the covalency. In terms of the orbital reduction $k_{\pi\pi}$ and the normalization factor N_π, α_π is given as $\alpha_\pi^2 = 2(1-k_{\pi\pi})/N_\pi^2$. The spin-orbit-coupling parameter $\zeta_{\pi\pi}$ is calculated from $\zeta_{\pi\pi} = N_\pi^2(\zeta_d^2 + \frac{1}{2}\alpha_\pi^2\zeta_p)$, where $\zeta_d = 2400$ cm^{-1} (Ref. 21) and $\zeta_p = 603$ cm^{-1} (Ref. 22) are the spin-orbit-coupling parameters for pure d and p orbitals on the Ir^{4+} and O^{2-} orbitals, respectively. λ for the t_{2g}^5 configuration is $-\zeta_{\pi\pi}$, and thus Δ is also known. All of these parameters for ^{193}Ir are given in Table II. We have used negative signs for the g factors and the hyperfine parameters. Other combinations of the signs yield unreasonable results. Negative signs for these parameters for Ir^{4+} were also obtained by Davies and Owen[23] using EPR and ENDOR techniques.

From Table I one can see that the hyperfine and quadrupole parameters of Ir^{4+} in MgO and CaO are almost the same. This is because the excited crystal-field energy levels make no appreciable contribution in the case of a d^5 low-spin configuration, while in the case of a d^7 configuration this contribution can be considerable. In the same host we obtained the same

TABLE II. Crystal-field, covalency, and magnetic parameters of Ir^{4+} in MgO and CaO.

Host	Spectrum	k	Δ/λ	κ	N_π	α_π	γ_π	S_π	$\zeta_{\pi\pi}$ (cm^{-1})	Δ (cm^{-1})
MgO										
	I[a]	0.804	0	1.600[b] (0.894)[c]						0
	T	0.807	0.355	0.882	0.891	0.697	0.534	0.163	2023	−719
CaO										
	I	0.830	0	1.583[b] (0.884)[c]						0
	T	0.833	0.364	0.897	0.892	0.649	0.522	0.127	2011	−732
	T'	0.833	0.334	0.864	0.888	0.651	0.531	0.120	1993	−666

[a] Ref. 6. [b] Calculated for $N_\pi = 1$. [c] Calculated assuming the same N_π as for the corresponding T spectrum.

value of k for both the isotropic and anisotropic spectra, which indicates that both spectra are due to the same ion (having also the same covalency) in different sites. A similar value of k (0.83) was obtained for Ir^{4+} in double halide complexes.[24] The larger value of k in CaO indicates a larger covalency in MgO. Inspection of the values of the charge-transfer parameter γ_π and the overlap contribution S_π in Table II reveals that the major contribution to the covalency is due to the charge-transfer mechanism, which in our case is about the same for both hosts. Thus the differences in covalency here are mainly due to changes in S_π, which is consistent with the larger anion-cation distance in CaO (2.45 Å) as compared with MgO (2.1 Å). The spin density $f_\pi = \frac{1}{4}\lambda_\pi^2 N_\pi^2$ in the oxygen $2p\pi$ orbitals is about 10% and 8.5% in MgO and CaO, respectively. The values of κ for the tetragonal spectra vary between 0.86 and 0.90. A similar value was obtained by Davies and Owen.[23] These values of κ correspond to $\chi = -(16.5-17.5)$ a.u., which agree very well with the theoretical values of $-(17-18)$ a.u. predicted by Freeman *et al.*[19] for d^5 ions. For the isotropic spectra two values of κ are given in Table II, one calculated assuming $N_\pi = 1$ and another assuming the same N_π as obtained for the corresponding tetragonal spectrum. The unreasonably large values obtained for $N_\pi = 1$ demonstrate clearly that this assumption is not justified.

The tetragonal field splitting was found to be negative and $|\Delta_T| > |\Delta_{T'}|$. Substituting N_π (from Table II), δ [extracted from Eq. (5)], ${}^{193}Q_0 = 0.82b$ and $(1-R) = 0.74$ (Ref. 18) into Eq. (7), yields ${}^{193}Q \simeq |10 \times 10^{-4}|\ \mathrm{cm}^{-1}$. It is suggested that the difference between this calculated Q and the experimental value $Q \simeq 5.5 \times 10^{-4}\ \mathrm{cm}^{-1}$ is due to the lattice electric field gradient. The best fit between the calculated and measured spectra was obtained for $Q/A_\perp < 0$. Since we assumed $A_\perp < 0$, we find $Q > 0$, which was also obtained by Davies and Owen.[23]

We shall discuss now the origin of the tetragonal field and the nature of the Ir^{4+} centers. From the results of the thermal treatment and ionizing irradiation, we conclude that the Ir ions enter into the MgO crystals in the trivalent diamagnetic state (ground-state configuration t_{2g}^6). Some of the ions are associated with a nearby charge compensating vacancy in the [100] direction, the others which have no local charge compensation are in sites of octahedral symmetry. It is suggested that the tetragonal centers of Ir^{3+} serve as hole-trapping sites and are therefore the source of the T and T' spectra. The Ir^{3+} ions in octahedral symmetry sites prefer to trap an electron and to become locally charge compensated, instead of trapping a hole. These ions are the source of the intense Ir^{2+} JT spectrum. Trapping of a small number of holes by Ir^{3+} in octahedral sites does, however, occur and this is the source of a weak isotropic spectrum of Ir^{4+}. In CaO the spectra of Ir^{4+} ions were observed in the as-grown crystals. This is not surprising considering the strong oxidizing atmosphere during the crystal growth. It is suggested that the Ir ions enter into CaO crystals in the trivalent and tetravalent states.

The models proposed for the T and T' centers are Ir^{4+}–O^{2-}–[++] and Ir^{4+}–O^{2-}–[++]–O^{2-}–M^+, respectively, lying along a [100]-type direction. [++] designates a host cation vacancy and M^+ is a cation having a charge greater than 2. The observation of such centers was reported in the past.[8–11] The decrease in the intensity of the T' spectrum after heating can be explained by dissociation of this center by motion of either the Ir^{4+} or M^+ ions via cation vacancies. Motion of the Ir^{4+} ions would decrease the number of both T and T' centers. It should be noted, that the T center is expected to be more stable because it is a locally neutral center.

The negative signs and the relative sizes of the axial crystal-field splittings are consistent with crystal-field theory, if we assume that the vacancy of Mg^{2+} or Ca^{2+} allows a greater attraction of the O^{2-} ion, located between the vacancy and the Ir^{4+} ion, toward the Ir^{4+} ion. This would give rise to an additional axial term in the octahedral crystal-field potential. From simple considerations one finds that the axial crystal-field splitting caused by excess attraction of the O^{2-} ion is given by

$$\Delta_T = -(9A + 60B) , \tag{16}$$

where

$$A = \mp \frac{1}{7a^3} eq(x/a)\langle r^2\rangle ,$$

$$B = \pm \frac{1}{63a^5} eq(x/a)\langle r^4\rangle .$$

Here the upper (lower) sign corresponds to an electron (hole) in the t_{2g} shell. $e(<0)$ and $q(<0)$ are the electron charge and the effective charge of the ion which creates the crystal field, respectively. x is the displacement of the O^{2-} ion and is taken to be positive for a compressed octhedron, a is the normal anion-cation distance and is equal to 2.1 and 2.45 Å for MgO and CaO, respectively. For our case we obtain $A > 0$, $B < 0$, and $|9A| > |60B|$. The values of $\langle r^2\rangle = 2.43$ a.u. and $\langle r^4\rangle = 9.38$ a.u. are taken from Ref. 25. Thus $\Delta_T < 0$, as was obtained experimentally. Substituting $|\Delta_T| \sim 700\ \mathrm{cm}^{-1}$, one gets 0.041 and 0.029 for x/a, for MgO and CaO, respectively. For the T' center the effective contribution of the excess positive charge of M^+ should be added. This contribution would be small and positive since the Ir^{4+}–M^+ distance is large, $4a$, and the charge q is now positive. Thus Δ_T and $\Delta_{T'}$ have the same sign and $|\Delta_T| > |\Delta_{T'}|$, which is in agreement with the experimental results.

VI. SUMMARY

This EPR study of Ir^{4+} ions in single crystals of MgO and CaO showed that tetravalent iridium can be stabilized in these hosts and occupies cubic sites with octahedral symmetry as well as two types of tetragonal sites. Models were proposed for the tetragonal spectra. The tetragonal spectra also exhibit a quadrupole effect. The EPR results were used to calculate crystal-field, magnetic and covalent parameters for Ir^{4+}. The signs of the tetragonal crystal-field splittings were found to be negative and their magnitudes about the same in both hosts. The hyperfine parameters were identical in both hosts within the experimental error, the same is also true for the quadrupole parameters. The major contribution to the covalency is due to the charge transfer mechanism. This contribution is about the same in both hosts. Thus the differences in covalency demonstrated by different values of k in MgO and CaO are mainly due to changes in the overlap contribution S_π, which is consistent with the larger cation-anion distance in CaO than in MgO.

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