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Jahn-Teller effect in the EPR spectrum of Pt^{3+} in MgO

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The electron-paramagnetic-resonance spectrum of Pt^{3+} was studied in single crystals of MgO. The spectrum exhibits a static Jahn-Teller effect with $\bar{\delta}/3\Gamma \gtrsim 5$ and the first excited vibronic singlet is $^2A_1$. A theoretical estimation of the spin-Hamiltonian parameters yielded values very close to those obtained experimentally.

I. INTRODUCTION

Ions possessing orbitally degenerate electronic ground states are known to be subject to the Jahn-Teller (JT) effect. In this work we report an electron-paramagnetic-resonance (EPR) study of the Pt^{3+} JT ions in single crystals of magnesium oxide. The EPR spectrum of Pt^{3+} has been investigated previously in single crystals of Al_2O_3,[1] $BaTiO_3$,[2,3] YAlG,[4] and K_2PtCl_4.[5] The electronic configuration of Pt^{3+} is $5d^7$, and as other ions studied in the $4d$ and $5d$ groups, it belongs to the "strong-ligand-field" category. In octahedral symmetry the low-spin ground state of Pt^{3+} is the orbital doublet ^2E_g ($t_{2g}^6e_g^1$), subject to the JT effect. Pt^{3+} exhibits a static JT effect in MgO, and a static effect was also reported for this ion in other oxides.[1-4]

II. EXPERIMENTAL

Single crystals of MgO doped with 0.5 mole% $PtCl_2$ were grown by the flux evaporation method.[6] In crystals grown in air, no EPR spectrum which could be associated with platinum ions was observed either in as-grown crystals, in crystals exposed to ionizing radiation, or in crystals heated in an oxygen atmosphere at 1000 °C, in spite of the fact that spectrochemical analysis indicated the presence of about 1000-ppm platinum. A weak EPR spectrum due to platinum ions was obtained only in the following two ways: (a) by gamma or x-ray irradiation of crystals grown in an oxygen atmosphere, or (b) by adding 0.5 mole% LiF to the melt and growing the crystals in an oxygen atmosphere; in this case the spectrum vanished after γ irradiation.

It appears from the intensity of the spectrum, that it is due to only a small fraction of the platinum ions present in the crystal. The behavior of the Pt spectrum in crystals grown and treated as described above supports our identification of the spectrum as Pt^{3+}, and suggests that most of the platinum ions are present in the crystal as either Pt^{2+} ($t_{2g}^6e_g^2$ configuration) or platinum-metal aggregates. An EPR spectrum of Pt^{2+} has not been observed in our crystals and we have not investigated the existence of platinum aggregates.

III. RESULTS AND DISCUSSION

The spectrum at 4.2 K is a superposition of three tetragonal spectra of almost symmetrical line shapes. In Figs. 1(a) and (b) the EPR spectrum of Pt^{3+} in MgO is shown at 4.2 K at $g_\perp$ and $g_{[110]}$, respectively.

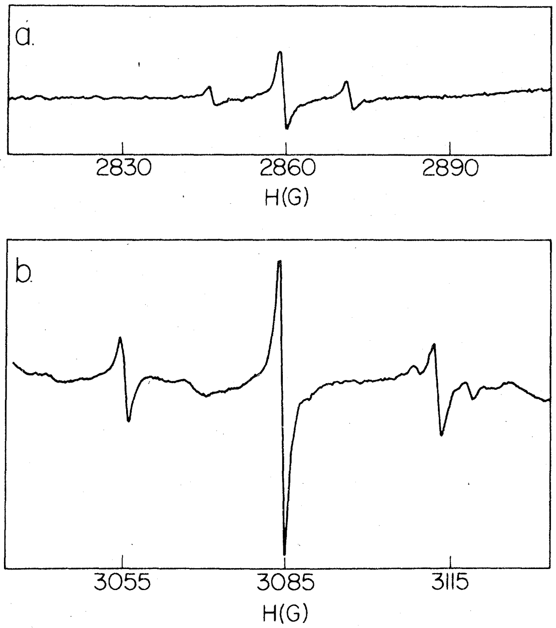

FIG. 1. EPR spectrum of Pt^{3+} in a single crystal of MgO at 4.2 K. (a) $g_\perp$ with H_{dc} along a [100] direction. (b) $g_{[110]}$ with H_{dc} along a [110] direction.

The central line is due to the isotopes with $I=0$, and the outer lines are the hyperfine structure satellites due to the ^{105}Pt isotope of natural abundance 33.7%, nuclear spin $I=\frac{1}{2}$, and nuclear magnetic moment $0.6\mu_N$.

The spectrum can be fitted to the axial spin Hamiltonian

$$\mathcal{H}=g_{\parallel}\mu_B H_z S_z+g_{\perp}\mu_B(H_x S_x+H_y S_y)+A_{\parallel}I_z S_z+A_{\perp}(I_x S_x+I_y S_y)\ . \qquad (1)$$

The parameters of the spin Hamiltonian are given in Table I.

The angular dependence of the spectrum at 4.2 K is shown in Fig. 2. The continuous lines represent the theoretically calculated angular variation using the parameters given in Table I. The measured values are designated by full circles. No isotropic spectrum was observed at 4.2 K.

Above 52 K only a single isotropic line could be observed with $H_{\rm dc}$ in the vicinity of a [111] direction. The peak-to-peak linewidth of the first derivative of the absorption line at 77 K in the [111] direction is 2.5 G. The line broadened beyond detection when $H_{\rm dc}$ was rotated away from the [111] direction. At these temperatures the hyperfine structure was obstructed by Cu^{2+} and Fe^{3+} lines, and therefore could not be detected. The measured value of $g_{\rm isotropic}$ at 77 K is equal, within experimental accuracy, to the calculated $g_{[111]}$ at 4.2 K,

$$g_{[111]}=[(2g_{\perp}^2+g_{\parallel}^2)/3]^{1/2}$$

(see Table I).

The angular variation of the spectrum and the symmetrical shapes of the absorption lines indicate that Pt^{3+} in MgO is a case of a static JT effect with $\bar{\delta}/3\Gamma \gtrsim 5$.[7] $\bar{\delta}$ is the mean-tetragonal random strain splitting and 3Γ is the "tunneling" splitting between the ground vibronic doublet and the first excited singlet $^2A_1$ or $^2A_2$. Assuming a typical value for $\bar{\delta}$ of about 4 cm^{-1},[7,8] we obtain $3\Gamma=0.8\ \mathrm{cm}^{-1}$. Thus, practically, the ground state is a vibronic triplet. Its three components Φ_X, Φ_Y, and Φ_Z are Born-Oppenheimer products representing distortions of the oxygen octahedron around the central ion along the x, y, and z directions, respectively.[9] Inspection of the g values given in Table I shows that $g_{\perp}>g_{\parallel}$ and $g_{\parallel}<g_e$. g_e is the free-electron g factor and is equal to 2.0023. This shows that the electronic part of Φ_Z, for example, is the $E_g(\theta)$ state, and the octahedron is elongated in the z direction. In this case the first excited state is $^2A_1$, and V, and β, the linear and the nonlinear JT coupling coefficients, are both positive.

In our case the following formulas are valid[8] to the first order of the spin-orbit interaction, $\zeta\vec{l}\cdot\vec{s}$,

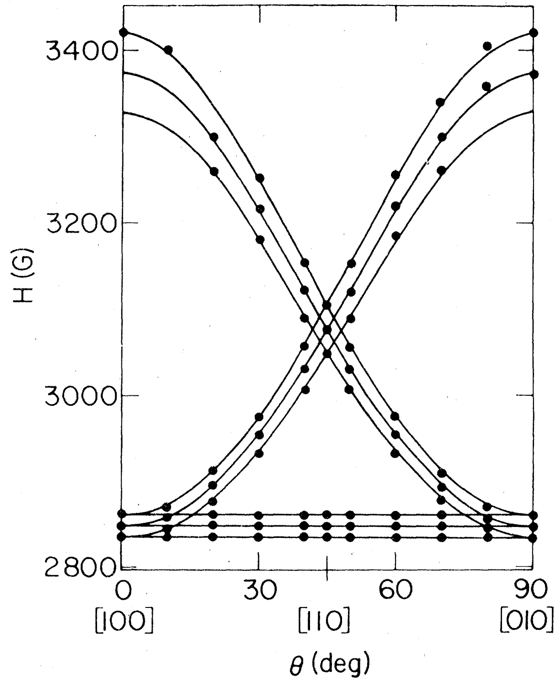

FIG. 2. Angular dependence of the EPR spectrum of Pt^{3+} in a single crystal of MgO at 4.2 K in a (100)-type plane. The full circles designate measured values. The continuous lines represent the theoretically calculated angular variation using the parameters given in Table I.

TABLE I. Resonance parameters for Pt^{3+} in single crystals of MgO.

g		A (10^{-4} cm^{-1})	T (K)
$g_{\parallel}$	$=1.9690\pm0.0005$	$A_{\parallel}=84.1\pm0.5$	4.2
$g_{\perp}$	$=2.3442\pm0.0005$	$A_{\perp}=26.0\pm0.5$	
$g_1=(g_{\parallel}+2g_{\perp})/3$	$=2.2186$		
$g_{[111]}=[(g_{\parallel}^2+2g_{\perp}^2)/3]^{1/2}$	$=2.2262$		
$g_{\rm isotropic}$	$=2.2259\pm0.0005$		77

$$g_{\parallel} = g_e - 4k_{\pi\sigma}\zeta_{\pi\sigma}\left[\frac{1}{\Delta_2} - \frac{1}{\Delta_4}\right] , \tag{2}$$

$$g_{\perp} = g_e + k_{\pi\sigma}\zeta_{\pi\sigma}\left[-\frac{1}{\Delta_2} + \frac{1}{\Delta_4} + \frac{3}{\Delta_3} + \frac{3}{\Delta_5}\right] , \tag{3}$$

where $k_{\pi\sigma}$ is the orbital reduction factor defined as

$$k_{\pi\sigma} = \langle \tilde{t}_{2g} | L | \tilde{e}_g \rangle / \langle t_{2g} | L | e_g \rangle .$$

t_{2g} and e_g are pure d orbitals, and $\tilde{t}_{2g}$ and $\tilde{e}_g$ are the corresponding molecular orbitals. $\zeta_{\pi\sigma}$ is the spin-orbit coupling between $\tilde{t}_{2g}$ and $\tilde{e}_g$ orbitals for an electron. $\Delta_i (i = 1,2,3,4,5)$ are the separations, in increasing order, between the ground state and the

$$^4T_1(^3A_2),\ ^2T_1(^3A_2),\ ^2T_2(^1E) ,$$
$$^2T_1(^1E),\ ^2T_2(^1A_1)$$

excited states of the $t_{2g}^5 e_g^2$ crystal-field configuration.[10]

From Eq. (2) one obtains $g_{L\parallel} \equiv g_{\parallel} - g_e < 0$, as in our case. A negative $g_{L\parallel}$ was also obtained for Pt^{3+} in $BaTiO_3$,[2,3] YAlG,[4] and for the isoelectronic Ir^{2+} in MgO and CaO.[8] For Pt^{3+} in Al_2O_3,[1] as well as for Rh^{2+} in MgO,[11] and CaO,[12] a positive $g_{L\parallel}$ was obtained indicating, as we shall see in what follows, cases where the crystal field is not very strong. This positive g shift can be explained by adding the second-order terms in the form $(\zeta/\Delta_i)^2$ to the right-hand side of Eq. (2). The main contribution will be from the term[13] $+2(\zeta/\Delta_1)^2$ which becomes appreciable near the crossover of the ^2E-$^4T_1$ levels (at $Dq/B = 2.15$) of the Tanabe-Sugano diagram[10] for a d^7 configuration. For sufficiently large values of Dq/B (i.e., very strong crystal-field cases) the term $2(\zeta/\Delta_1)^2$ can be neglected, which results in a negative g shift, as in our case.

Our experimental parameters $g_{\parallel}$ and $g_{\perp}$ were found to be in a good agreement with those estimated from Eqs. (2) and (3) for $Dq = 2500$ cm^{-1} and $B = 330$ cm^{-1} given by Höchli and Müller[14] for Pt^{3+} in Al_2O_3. Thus using the Tanabe-Sugano diagrams[10] and $Dq/B = 7.5$, we obtain the excited-state separation values Δ_i $(i = 1,2,3,4,5)$,

$$18000 \text{ cm}^{-1} ,\ 25000 \text{ cm}^{-1},\ 25400 \text{ cm}^{-1},$$

$$26700 \text{ cm}^{-1} ,\ 35000 \text{ cm}^{-1} ,$$

respectively. Taking $k_{\pi\sigma}\zeta_{\pi\sigma}/\zeta_d = 0.42$ and $\zeta_d = 4200$ cm^{-1} according to Lacroix, Höchli, and Müller,[13] one gets $g_{\parallel} \sim 1.992$ and $g_{\perp} \sim 2.356$, values which are very close to those obtained from our EPR experiment (Table I).

Finally we discuss the hyperfine structure parameters and determine the signs of $A_{\parallel}$ and $A_{\perp}$. In our case $A_{\parallel}$ and $A_{\perp}$ are given by[8]

$$A_{\parallel} = P\left[\frac{N_\pi N_\sigma}{k_{\pi\sigma}} g_{L\parallel} - \kappa + \tfrac{4}{7}N_\sigma^2 + \tfrac{2}{7}N_\pi N_\sigma \zeta_{\pi\sigma} \times \left[-\frac{2}{\Delta_1} + \frac{1}{2\Delta_2} - \frac{3}{2\Delta_3} - \frac{3}{2\Delta_4} + \frac{3}{2\Delta_5}\right]\right] , \tag{4}$$

$$A_{\perp} = P\left[\frac{N_\pi N_\sigma}{k_{\pi\sigma}} g_{L\perp} - \kappa - \tfrac{2}{7}N_\sigma^2 - \tfrac{1}{7}N_\pi N_\sigma \zeta_{\pi\sigma} \times \left[-\frac{2}{\Delta_1} + \frac{1}{2\Delta_2} - \frac{3}{2\Delta_3} - \frac{3}{2\Delta_4} + \frac{3}{2\Delta_5}\right]\right] . \tag{5}$$

$P = 2\gamma_N \mu_B \mu_N \langle r^{-3} \rangle$, N_σ, and N_π are the coefficients of the e_g and t_{2g} functions in the molecular orbitals $\tilde{e}_g$ and $\tilde{t}_{2g}$, respectively. κ is the core polarization factor, containing the effect of covalent bonding. γ_N is the nuclear magnetogyric ratio. $g_{L\parallel}$ and $g_{L\perp}$ are $g_{\parallel} - g_e$ and $g_{\perp} - g_e$, respectively.

For a strong Jahn-Teller coupling, the isotropic and anisotropic parts of the hyperfine parameters[9] are

$$A_1 = \tfrac{1}{3}(A_{\parallel} + 2A_{\perp}) , \tag{6}$$

$$A_2 = \tfrac{2}{3}(A_{\perp} - A_{\parallel}) . \tag{7}$$

These hyperfine parameters A_1 and A_2 are not to be confused with the excited singlets $^2A_1$ and $^2A_2$. For all of the possible combinations of the signs of our experimental values of $A_{\parallel}$ and $A_{\perp}$ (see Table I), $A_1 A_2 < 0$. Using Eqs. (4) – (7), one obtains for A_1 and A_2 the expressions

$$A_1 = P\left[\frac{1}{3}\frac{N_\pi N_\sigma}{k_{\pi\sigma}}(g_{L\parallel} + 2g_{L\perp}) - \kappa\right] , \tag{8}$$

$$A_2 = P\left[\frac{2}{3}\frac{N_\pi N_\sigma}{k_{\pi\sigma}}(g_{L\perp} - g_{L\parallel}) - \tfrac{4}{7}N_\sigma^2 - \tfrac{2}{7}N_\pi N_\sigma \zeta_{\pi\sigma} \times \left[-\frac{2}{\Delta_1} + \frac{1}{2\Delta_2} - \frac{3}{2\Delta_3} - \frac{3}{2\Delta_4} + \frac{3}{2\Delta_5}\right]\right] . \tag{9}$$

Assuming $k_{\pi\sigma} = k_{\pi\pi} = 0.8$ as for Ir^{4+} in MgO,[15] one gets $\zeta_{\pi\sigma} = 2200$ cm^{-1}. Using the approximation $\zeta_{\pi\sigma} = N_\pi N_\sigma \zeta_d$ one finds $N_\pi N_\sigma \cong 0.52$. Substitution of these numerical values into Eq. (9) and using a value of 12.65 a.u. for $\langle r^{-3} \rangle$, which is an average of two values cited in the literature for Pt^{3+},[2,3] gives $A_2 \cong -40 \times 10^{-4}$ cm^{-1}. This value of A_2 is very close to the value -38.7×10^{-4} cm^{-1}, obtained for A_2 from Eq. (7) taking a positive sign for the experimentally obtained parameters $A_{\parallel}$ and $A_{\perp}$. From this it can be concluded that the sign of both $A_{\parallel}$ and $A_{\perp}$ is positive. Thus inserting $A_{\parallel} = +84.1 \times 10^{-4}$ cm^{-1} and

$A_\perp = +26.0 \times 10^{-4}\ \mathrm{cm}^{-1}$ into Eq. (6), one gets
$A_1 = +45.3 \times 10^{-4}\ \mathrm{cm}^{-1}$.

A rough estimate of the core polarization factor κ can be made from Eq. (8). Using the above determined covalency parameters, we obtain $\kappa \cong 0.07$. The quantity χ, characteristic of the density of the unpaired spins at the nucleus, is related to κ by[16] $\chi = -\frac{3}{2}\kappa\langle r^{-3}\rangle$, which yields $\chi = -1.35$ a.u. Freeman *et al.*[17] calculated χ for divalent $5d$ ions and obtained values between -17 and -18 a.u. Our deviation from the calculated values of χ may be due to covalent effects and partial admixing of a $6s$ wave function which gives rise to a positive contribution to the isotropic hyperfine interaction.

IV. SUMMARY

The EPR spectrum of Pt^{3+} in MgO exhibits a static JT effect. From the angular variation of the spectrum and from the symmetrical line shapes, we conclude that $\bar{\delta}/3\Gamma \gtrsim 5$. Since we have $g_\parallel < g_\perp$, it follows for a d^7 low-spin configuration that the first excited vibronic level is a singlet $^2A_1$, and that V and β, the linear and nonlinear coupling coefficients, respectively, are positive. The calculated values of $g_\parallel$, $g_\perp$, and A_2, from expressions developed in a previous study,[8] were found to be in very good agreement with the experimental ones. This indicates that the crystal-field parameters Dq and B,[14] as well as the effective spin-orbit coupling constant[13] for Pt^{3+} in $\mathrm{Al_2O_3}$, are also valid for MgO. These calculations enabled us also to conclude that the signs of the hyperfine parameters A_1 and A_2 are positive. The negative g shift ($g_{L\parallel} < 0$) justifies the approximation in the calculation of the g factors, in which the second-order terms of the spin-orbit interaction were neglected. This further supports the use of the large value of $Dq/B\,(=7.5)$, characteristic of a very strong crystal field.

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