

Spin Relaxation of  $\text{Fe}^{1+}$  in  $\text{MgO}$  via Excited Electronic States\*†

J. S. BENNETT

*Solid State Physics Branch, Physical Sciences Laboratory, Redstone Arsenal, Alabama 35809*

(Received 22 December 1969)

The spin-lattice relaxation time  $T_1$  in the ground-state Kramers doublet of  $\text{Fe}^{1+}$  in  $\text{MgO}$  has been measured in a fast travelling-wave-tube X-band spectrometer by pulsed saturation from 10 to 23 K and by line broadening from 23 to 37 K. By simultaneously measuring recovery from pulsed saturation and the relaxation-induced component  $[\Delta H(T) - \Delta H(0)]$  of the Lorentzian EPR linewidth at 23 K, the absolute scale for  $1/T_1$  from linewidth was determined to be  $(4.7 \pm 0.6) \times 10^7 \text{ sec}^{-1}/\text{Oe}$ . The data from 10 to 37 K are accurately described over seven decades of time by  $1/T_1 = BT^9 + C'/(e^{\Delta'/T} - 1) + C''/(e^{\Delta''/T} - 1)$ , where  $B = (1.2 \pm 0.1) \times 10^{-7}/\text{sec K}^9$ ,  $C' = (2.2 \pm 0.4) \times 10^{10}/\text{sec}$ ,  $C'' = (2.7 \pm 2.3) \times 10^{13}/\text{sec}$ ,  $\Delta' = 213 \pm 4 \text{ K}$ , and  $\Delta'' = 450 \pm 30 \text{ K}$ . The temperature dependence is consistent with the interpretation that spin-lattice relaxation in the ground-state Kramers doublet of  $\text{MgO}:\text{Fe}^{1+}$  occurs predominantly by resonant phonon scattering involving excited electronic states at  $\sim 150$  and  $\sim 310 \text{ cm}^{-1}$ . Comparison of the excited-state energies with predictions from the crystal-field model for  $3d^7$  ions in cubic  $\text{MgO}$  indicates a large crystal-field strength parameter or covalent bonding with  $\lambda/\lambda_0 = 0.57$ , the orbital reduction factor as low as 0.65, and some evidence for inadequacies in the model.

## I. INTRODUCTION

IRON is known to be a major contaminant of the purest crystalline magnesium oxide available to date.<sup>1,2</sup> In untreated crystals, iron occurs predominantly in the stable divalent and trivalent forms having  $3d^6$  and  $3d^5$  electronic configurations, respectively.<sup>3</sup> However, rather large concentrations of the metastable monovalent ( $3d^7$ ) ion  $\text{Fe}^{1+}$  can be produced by ionizing radiation at the expense of the stable valence states. Concomitant valence changes of other impurities and the formation of trapped hole centers maintain charge neutrality within the crystal.<sup>4</sup>

Some properties of  $\text{MgO}:\text{Fe}^{1+}$  are known from earlier electron paramagnetic resonance (EPR) experiments. Orton *et al.*<sup>5</sup> first observed the EPR spectrum of  $\text{Fe}^{1+}$  in x-ray-irradiated  $\text{MgO}$ , as given in Sec. II. More recently, measurements of the spin-lattice coupling constants and relaxation at 35 GHz have been briefly discussed.<sup>6</sup> To our knowledge, neither the infrared nor optical absorption spectrum for  $\text{MgO}:\text{Fe}^{1+}$  has been reported but a thermoluminescence peak occurring at about 390 K in x-ray-irradiated  $\text{MgO}$  has been associated<sup>1</sup> with  $\text{Fe}^{1+}$ .

The purpose of this paper is to report new results obtained from measurement and analysis of the temperature dependence of electron spin relaxation in the Kramers doublet ground state of  $\text{MgO}:\text{Fe}^{1+}$  at 9.2 GHz.

The data, extending over eight decades in the relaxation time, are explained by the usual theory<sup>7,8</sup> for spin relaxation by emission, absorption, and inelastic scattering of lattice phonons by  $3d^7$  ions in a point-charge model of the  $\text{MgO}$  lattice. The measurements described in Sec. IV include apparently the first simultaneous observation of EPR recovery from pulsed saturation and relaxation-induced line broadening for an  $S' = \frac{1}{2}$  spin system.<sup>9</sup> The combined measurements at constant temperature and magnetic field permit an empirical determination of the absolute scale of the effective relaxation time due to the lifetime of the spin within the ground-state Kramers doublet. An unusual feature of the line-broadening data is the appearance of excess broadening due to a second Orbach relaxation process.<sup>8</sup> In Sec. V, the new experimental results are compared with predictions from crystal-field theory and with similar results reported for other iron-group ions in  $\text{MgO}$ .

## II. BACKGROUND

Calculations for the  $3d^7$  electron configuration in a point-charge lattice<sup>10</sup> have been moderately successful in explaining the EPR and optical spectra,<sup>11</sup> spin relaxation,<sup>12</sup> and uniaxial stress effects<sup>13</sup> for  $\text{MgO}:\text{Co}^{2+}$  a system isoelectronic to  $\text{MgO}:\text{Fe}^{1+}$ . The point-charge model is recognized to be a crude approximation to the  $\text{MgO}:\text{Fe}^{1+}$  system, but a brief summary of results from crystal-field theory serves as a convenient background for interpreting the spin-relaxation data.

A partial energy-level diagram for a  $3d^7$  ion in an

\* Paper based on a portion of a dissertation submitted to the University of Alabama in partial fulfillment of the requirements for the Ph.D. degree.

† Work supported in part by the U. S. Army Research Office, Durham, N. C.

<sup>1</sup> B. Henderson and J. E. Wertz, *Advan. Phys.* **17**, 749 (1968).

<sup>2</sup> Y. Chen and W. A. Sibley, *Phys. Rev.* **154**, 842 (1967).

<sup>3</sup> R. L. Hansler and W. G. Segelken, *J. Phys. Chem. Solids* **13**, 124 (1960).

<sup>4</sup> J. E. Wertz, P. Auzins, J. H. E. Griffiths, and J. W. Orton, *Discussions Faraday Soc.* **28**, 136 (1959).

<sup>5</sup> J. W. Orton, P. Auzins, J. H. E. Griffiths, and J. E. Wertz, *Proc. Phys. Soc. (London)* **78**, 554 (1961).

<sup>6</sup> K. A. Müller and W. Berlinger, *Bull. Am. Phys. Soc.* **12**, 40 (1967).

<sup>7</sup> J. H. Van Vleck, *Phys. Rev.* **57**, 426 (1940).

<sup>8</sup> R. Orbach, *Proc. Roy. Soc. (London)* **A264**, 458 (1961).

<sup>9</sup> Simultaneous measurements of EPR recovery from pulsed saturation and line broadening were recently made for the  $S' = \frac{3}{2}$  spin system,  $\text{Cr}^{3+}$  in  $\text{MgO}$ , over a temperature range of 40 K. See Ref. 21.

<sup>10</sup> A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A206**, 173 (1951).

<sup>11</sup> W. Low, *Phys. Rev.* **109**, 256 (1958).

<sup>12</sup> M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A283**, 433 (1964).

<sup>13</sup> E. B. Tucker, *Phys. Rev.* **143**, 264 (1966).

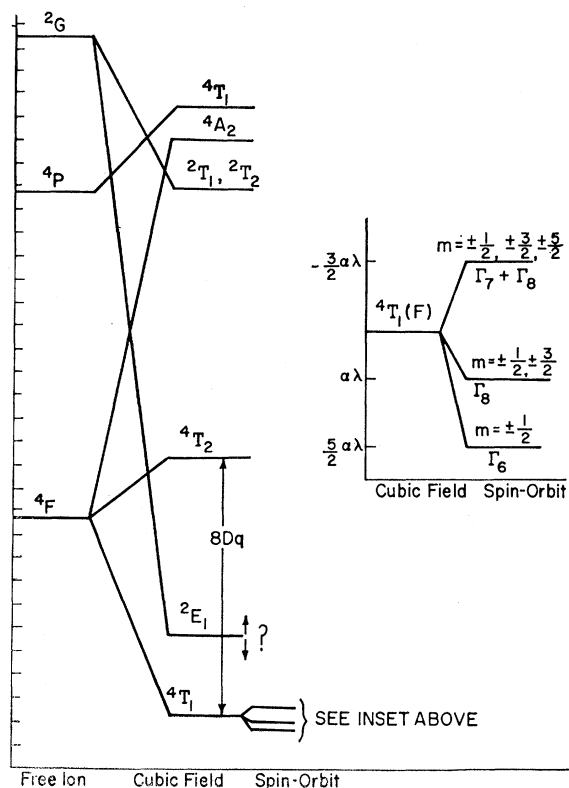


FIG. 1. A partial energy-level diagram for  $3d^7$  ions in MgO due to the combined action of the octahedral crystal field of a point-charge lattice and spin-orbit coupling. For  $\text{Fe}^{1+}$ , the location of the  ${}^2E_1$  level is uncertain but it is likely to be shifted below the  ${}^4T_2$  state, as discussed in the text. The  ${}^4T_1$  ground-state spin-orbit levels, shown on the right, are labeled with their symmetry properties and eigenvalues. The value of  $\alpha$  is approximately  $\frac{2}{3}$ , and the spin-orbit coupling constant  $\lambda$  is negative.

octahedral crystal field is shown in Fig. 1. The  ${}^4F$  free-ion ground state is split into two orbital triplets ( ${}^4T_1$  and  ${}^4T_2$ ) and a singlet ( ${}^4A_2$ ), arranged in order of increasing energy. The  ${}^2E_1$  component of the  ${}^2G$  excited state is strongly lowered by the crystal field and, for field strengths  $\geq 2000 \text{ cm}^{-1}$ , it crosses all the quartet levels and becomes the ground state.<sup>14</sup> To our knowledge, the crystal-field strength parameter  $Dq$  has not been measured for  $\text{MgO}:\text{Fe}^{1+}$  and, therefore, the relative position of the levels is undetermined. However, one might reasonably expect approximately the same order as measured<sup>11</sup> for isoelectronic  $\text{MgO}:\text{Co}^{2+}$ . Figure 1 indicates the  ${}^2E_1$  component may be shifted below the  ${}^4T_2$  level for  $\text{MgO}:\text{Fe}^{1+}$  corresponding to larger  $Dq$  than for  $\text{Co}^{2+}$ . A larger  $Dq$  would be consistent with  $\langle r_0^4 \rangle$ , the mean fourth-power ionic radius, being  $\sim 40\%$  greater.<sup>13</sup>

The spin-orbit interaction splits the  ${}^4T_1({}^4F)$  state into levels of symmetry  $\Gamma_6$ ,  $\Gamma_8$ , and  $\Gamma_7 + \Gamma_8$  with effective spins of  $\frac{1}{2}$ ,  $\frac{3}{2}$ , and  $\frac{5}{2}$ . The usual theoretical treatment<sup>10,11</sup> introduces a fictitious orbital angular momentum  $l'$

<sup>14</sup> Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan* **9**, 766 (1954).

which operates in the orbital triplet manifold and has an effective orbital Landé factor  $\alpha$  such that  $\lambda \mathbf{l}' \cdot \mathbf{S} = -\alpha \lambda \mathbf{l}' \cdot \mathbf{S}$ , where  $\lambda$  is the effective spin-orbit coupling constant. A representation is used in which both  $l'_z$  ( $\pm 1$  or 0 in the triplet) and  $S_z$  are diagonal. Secular equations are then set up for each value of  $m = l'_z + S_z$  and solved for the eigenvalues indicated on the left side of the inset in Fig. 1.

The value of  $\alpha$  will be less than  $\frac{3}{2}$  by an amount proportional to the mixing of the  ${}^4P$  excited state into the  ${}^4F$  ground state. Because the energy interval to the  ${}^4P$  state is large, the mixing will be correspondingly small (of the order of 10%)<sup>11</sup> and our purpose will be adequately served if we use the approximation  $\alpha = \frac{3}{2}$ .

The effective spin-orbit coupling constant for an ion in a crystal is often found to be 60–90% of the free-ion value  $\lambda_0$ . Since  $\lambda_0 = -115 \text{ cm}^{-1}$  for the  $\text{Fe}^{1+}$  ion,<sup>15</sup> the energy separation of the spin-orbit levels is predicted to be  $E(\Gamma_8 - \Gamma_6) = -\frac{3}{2}\alpha\lambda \leq 250 \text{ cm}^{-1}$  and  $E(\Gamma_{7,8} - \Gamma_6) = -4\alpha\lambda \leq 700 \text{ cm}^{-1}$  on the basis of the first-order calculation.

The spectroscopic splitting factor for the  $\Gamma_6$  Kramers doublet ground state, including a second-order contribution due to admixture of the  ${}^4T_2({}^4F)$  state by the spin-orbit interaction, is given by<sup>11</sup>

$$g = 10/3 + \frac{2}{3}\alpha k' - 15\lambda/16Dq, \quad (1)$$

where  $8Dq$  is the energy interval  $E({}^4T_2 - {}^4T_1)$ , and  $k'$  is the orbital reduction factor introduced by Stevens<sup>16</sup> to take account of the reduction in spin-orbit coupling due to covalent bonding and overlap of the ligands. If the system is perfectly ionic and there is no distortion of the  $d$  atomic wave functions,  $k'$  is 1. Any covalency reduces  $k'$  below unity.

The microwave absorption spectrum<sup>5</sup> of  $\text{MgO}:\text{Fe}^{1+}$  consists of a single line having isotropic  $g = 4.15 \pm 0.01$  and linewidth varying as the ratio 1:3:6 when the applied magnetic field is parallel to the [111], [110], and [100] crystal axes, respectively. The source of the linewidth anisotropy is uncertain. Current evidence<sup>5</sup> indicates crystal imperfections may produce a distribution of both positive and negative tetragonal distortions at the  $\text{Fe}^{1+}$  sites in the crystal. With exception of the linewidth variation, the EPR results are in good agreement with theoretical predictions for  $3d^7$  ions in octahedral crystal fields. The measured  $g$  value is consistent with Eq. (1) when values of  $k'$ ,  $\lambda$ , and  $Dq$  comparable to those measured for other  $3d$  ions in MgO are used.

The theory of spin-lattice relaxation for isolated Kramers ions is well established and many detailed accounts of the subject can be found in the literature.<sup>17</sup>

<sup>15</sup> T. M. Dunn, *Trans. Faraday Soc.* **57**, 1441 (1961).

<sup>16</sup> K. W. H. Stevens, *Proc. Roy. Soc. (London)* **A219**, 542 (1953).

<sup>17</sup> An excellent collection of papers on the subject may be found in *Spin Lattice Relaxation in Ionic Solids*, edited by A. A. Manenkov and R. Orbach (Harper and Row, New York, 1966).

A dilute system of paramagnetic ions in thermal equilibrium with a crystal lattice may be maintained in a Boltzmann distribution over available spin states by direct emission and absorption of single phonons, resonant two-phonon (Orbach) processes, and inelastic (Raman) scattering of phonons.<sup>7,8</sup> If spin-lattice relaxation is observed within a ground-state doublet separated from excited states by an energy interval  $\Delta \gg kT$ , a single time constant  $T_1$  is sufficient to describe the exponential decay toward the thermal equilibrium distribution after an initial disturbance of the spin population. The temperature dependence of  $T_1$  reflects the relative importance of the direct, Raman, and Orbach relaxation processes. Assuming that the phonon spectrum can be described by a Debye distribution and  $T \ll \Theta_D$ , the relaxation rate for a Kramers system is given by<sup>8</sup>

$$1/T_1 = AH_0^4 T + BT^9 + \sum C' (e^{\Delta/kT} - 1)^{-1}, \quad (2)$$

where the  $A$ ,  $B$ , and  $C'$  terms are due to direct, Raman, and Orbach relaxation, respectively;  $H_0$  is the applied magnetic field; and  $k$  is Boltzmann's constant. The sum is over all electronic excited states for which there is a possibility of resonance between the phonons and the electronic excitation; for MgO:Fe<sup>1+</sup>, the  $\Gamma_8$  and  $\Gamma_7 + \Gamma_8$  levels should be considered.<sup>18</sup>

### III. EXPERIMENTAL PROCEDURE

#### Samples

Relaxation measurements were made on four MgO single crystals obtained from three different sources. The EPR spectra for stable valence states of chromium, manganese, iron, and vanadium were detected in each crystal before treatment. Charge-transfer processes initiated by 50-kV x rays altered the valence states of some of the impurity ions. For example, before treatment, sample No. 1 was determined to contain  $\sim 3$  parts per million (ppm) Cr<sup>3+</sup> and Fe<sup>3+</sup>,  $\sim 5$  ppm V<sup>2+</sup>,  $< 50$  ppm Fe<sup>2+</sup>, and  $\sim 9$  ppm Mn<sup>2+</sup>. After 2-h x-ray irradiation at room temperature, the analysis showed Cr<sup>3+</sup> and Mn<sup>2+</sup> approximately unchanged in concentration and  $\sim 11$  ppm Fe<sup>3+</sup>,  $\sim 5$  ppm Fe<sup>1+</sup>,  $< 50$  ppm Fe<sup>2+</sup>,  $\sim 30$  ppm V<sup>2+</sup>, and  $\sim 27$  ppm V<sub>1</sub> trapped hole centers.

Samples No. 1, No. 2, and No. 3 used for the measurements reported in Sec. IV were irradiated for 2, 4, and 6 h, respectively. It was necessary to irradiate the thick samples ( $\sim 3$  mm) on opposite sides for equal periods of time to produce a uniform distribution of irradiation products. The samples were shielded from light during irradiation and afterward while stored in liquid nitrogen. In samples kept continuously for 6 months in this manner, the intensity of the EPR signals from Fe<sup>1+</sup> and the V<sub>1</sub> trapped hole center decayed with a half-life of approximately 6 weeks.

<sup>18</sup> G. Peckham, Proc. Phys. Soc. (London) **90**, 657 (1967).

When irradiated samples were left at room temperature and exposed to light, significant bleaching occurred within a few hours. The Fe<sup>1+</sup> concentration varied from  $\sim 5$  to  $\sim 40$  ppm in these crystals.

A low concentration of Fe<sup>2+</sup> was important to our success in measuring intrinsic values of relaxation time for Fe<sup>1+</sup>. It was known that Fe<sup>2+</sup> relaxes very fast<sup>19</sup> ( $\sim 100$   $\mu$ sec at 4 K) and, because the spectra overlap, cross-relaxation of Fe<sup>1+</sup> to Fe<sup>2+</sup> was anticipated. Sample No. 4, containing several hundred ppm Fe<sup>2+</sup>, was treated to produce an observable concentration of Fe<sup>1+</sup>. The value of the Fe<sup>1+</sup> relaxation time measured at 4.2 K in this sample was found to be several orders of magnitude faster than in the other three samples. This is interpreted in Sec. IV to mean that cross-relaxation to Fe<sup>2+</sup> becomes the dominant relaxation mechanism at Fe<sup>2+</sup> concentrations of several hundred ppm. The EPR spectrum of Fe<sup>2+</sup> was detected very weakly in sample No. 3 and not at all in samples No. 1 and No. 2, these being the purest MgO crystals available. The Fe<sup>1+</sup> relaxation time at 4.2 K was observed to be the same for these three samples.

#### Measurement of Direct Recoveries

Measurements of Fe<sup>1+</sup> EPR recovery from pulsed saturation were carefully made from 1.2 to 23 K using a fast X-band traveling-wave-tube spectrometer<sup>20,21</sup> designed to measure short relaxation times of the order of 1.0  $\mu$ sec at static applied magnetic field. The resonance was saturated with 20 mW of pulsed power and monitored with the lowest power which would yield an acceptable signal-to-noise ratio, typically  $< 5$   $\mu$ W. Care was taken to determine whether measured values of relaxation time were independent of saturating power and pulse width and monitor power. The reflection-type cavity resonated in the TE<sub>102</sub> rectangular mode, typically at 9.2 GHz. The decay of the stored energy in the cavity with loaded  $Q$  of 3000 limited the shortest observable relaxation to a  $T_1$  of 0.4  $\mu$ sec.

Relaxation times shorter than 5  $\mu$ sec were determined from the slope of a line fit to voltage-time points on a semilog plot of the oscilloscope trace of the EPR recovery. Longer relaxation times were extracted by integrating the recovery signals by repetitive time sampling and electronic logarithmic conversion.<sup>19,20</sup> The improved signal-to-noise ratio from signal averaging allowed many of the EPR recoveries to be followed over more than 99% of the initial perturbation from the equilibrium signal. Either method was judged to give the relaxation time to an accuracy better than  $\pm 10\%$ .

Possible saturation effects by the monitor power at the lowest temperatures [ $T \leq 8$  K] were checked by

<sup>19</sup> E. L. Wilkinson, R. L. Hartman, and J. G. Castle, Jr., Phys. Rev. **171**, 299 (1968).

<sup>20</sup> R. L. Hartman, J. S. Bennett, and R. A. Jensen, Bull. Am. Phys. Soc. **13**, 244 (1968).

<sup>21</sup> R. L. Hartman, J. S. Bennett, and J. G. Castle, Jr., Phys. Rev. **B 1**, 1946 (1970).

monitoring recovery from pulsed saturation while modulating the magnetic field sinusoidally at low frequency. The ratio of the modulation amplitude to the  $\text{Fe}^{2+}$  EPR linewidth was  $\sim 20/1$ . The technique<sup>22</sup> was to sweep through the EPR line several times during the saturating pulse and subsequent recovery. As a result, the average monitor power during recovery was less than  $1/20$  of that in the case of a static applied field. Since no difference was found in the relaxation times measured by the two methods, the monitor power used with static applied fields at low  $T$  was judged to produce negligible spin heating effects within 10% accuracy. The same technique with modulation amplitude slightly greater than the EPR linewidth permitted simultaneous observation of the recovery of all, or any part, of the line envelope.<sup>23</sup>

#### Measurement of Line Broadening

Relaxation times in the temperature range 23–37 K were determined from the lifetime broadening of the  $\text{Fe}^{2+}$  EPR line (line broadening). The first derivative of the absorption line at fixed temperature and frequency was displayed on the  $y$  axis of an  $xy$  recorder. Position on the  $x$  axis was a linear function of the applied magnetic field stabilized to 1 part in  $10^6$ . Care was taken to insure the line shape was not affected by the 100-Hz field modulation by using an amplitude of less than  $\frac{1}{10}$  of the observed separation of the peaks in the first derivative EPR signal.

The line shape was nearly Lorentzian at all temperatures, as described in detail in Sec. IV. Therefore, the field separation between the peaks of the first derivative of the line,  $\Delta H(T)$ , was a useful parameter for characterizing changes in the line shape at all  $T$ . A “hole” burned into the  $\text{Fe}^{2+}$  line at 4.2 K healed almost independently of the rest of the line, indicating a high degree of inhomogeneous broadening.

The lifetime-induced contribution  $\Delta H_l(T)$  to the linewidth of an inhomogeneous Lorentzian line shape is given by  $[\Delta H(T) - \Delta H(0)]$ , where  $\Delta H(0)$  is the low-temperature linewidth.<sup>24,25</sup> Assuming the lifetime to be inversely proportional to  $\Delta H_l(T)$  and the relationship between  $T_1$  and the lifetime to be independent of  $T$ , the value of  $T_1$  from lifetime broadening was calculated by

$$1/T_1 = \epsilon[\Delta H(T) - \Delta H(0)]. \quad (3)$$

Absolute values of  $1/T_1$  were obtained from the line profiles by determining the proportionality constant  $\epsilon$  from direct recoveries and  $\Delta H_l(T)$  measured at the same temperature as described in Sec. IV.

<sup>22</sup> D. R. Locker and D. C. Look, *J. Appl. Phys.* **39**, 6119 (1968).

<sup>23</sup> J. G. Castle, Jr., P. F. Chester, and P. E. Wagner, *Phys. Rev.* **119**, 953 (1960).

<sup>24</sup> H. J. Stapleton and K. L. Brower, *Phys. Rev.* **178**, 481 (1969).

<sup>25</sup> J. S. Bennett, Ph.D. dissertation, University of Alabama, 1969 (unpublished).

#### Measurement of Temperature

Temperatures below 4.2 K were measured by helium vapor pressure. Temperatures between 4.2 and 30 K were measured with carbon resistors which had been calibrated using a germanium resistor in zero magnetic field. The resistance was read to a precision corresponding to  $\sim 0.1$  K. Temperatures above 20 K were also measured with a copper-constantan thermocouple using an ice water reference junction.

Temperature gradients were minimized by bonding the sample to the metal cavity wall with G.E. 7031 adhesive and embedding the thermometers in the cavity wall with the aid of epoxy. The heating resistors were mounted in thick aluminum bars and bonded to the sides of the cavity to increase thermal conductivity from the resistors and help maintain an isothermal environment for the crystal. Measurements were made only after the system reached a stable temperature, usually within 15 min after changing the temperature controller.

#### IV. EXPERIMENTAL RESULTS

The spin-relaxation times  $\tau$  plotted in the range 4.2–23 K in Fig. 2 were measured by recovery from pulsed saturation with  $H_0 \approx 1600$  Oe. All of the relaxation signals were single exponential recoveries over more than 30 dB of the initial perturbation from the equilibrium EPR signal.

Measurements were made on three samples varying in  $\text{Fe}^{2+}$  concentration from 5 to 40 ppm prepared as described in Sec. III. In sample No. 3, measurements were made at 10.0 and 12.5 K with two different concentrations. The relaxation time was initially measured with  $\sim 40$  ppm  $\text{Fe}^{2+}$ . The sample was subsequently bleached to  $\sim 5$  ppm  $\text{Fe}^{2+}$  and  $\tau$  measured again. The relaxation time at each concentration was found to be the same within  $\pm 10\%$ .

Pulsed saturation data were taken for each sample with the applied magnetic field  $H_0$  oriented parallel to the [111], [110], and [100] crystal axes. Below  $\sim 10$  K,  $\tau$  exhibited angular dependence and the extremum values were measured to be the same for all the samples. Values of  $\tau$  measured between 1.2 and 4.0 K (off scale in Fig. 2) were temperature independent. All recoveries from pulsed saturation above 10 K were independent of spin concentration, direction of  $H_0$ , and sample.

We are unable to determine clearly the effective relaxation mechanism below 10 K. Consequently, the correct values to be subtracted from the data around 10 K to obtain the relaxation times due to the Raman process are uncertain. The angular dependence agrees with the prediction of Kumar *et al.*<sup>26</sup> for the spin-lattice relaxation even though the absolute value of  $T_1$ , calculated using uniaxial stress data,<sup>6</sup> is orders of magnitude slower than the measured value of  $\tau$ . The data below

<sup>26</sup> S. Kumar, T. Ray, and D. K. Ray, *Phys. Rev.* **176**, 489 (1968).

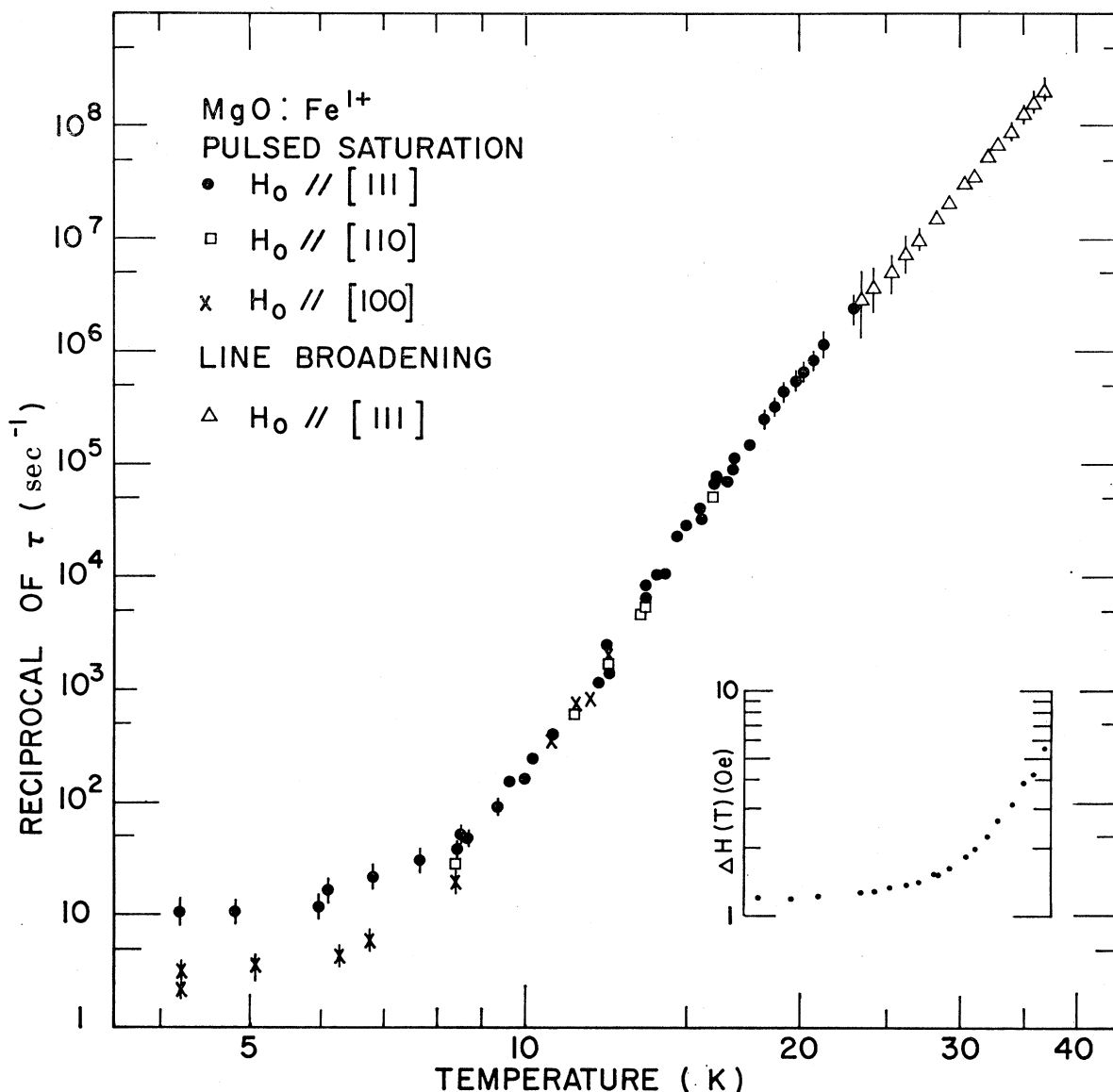


FIG. 2. The temperature dependence of the observed relaxation rate  $1/\tau$  between the Zeeman levels of the ground-state Kramers doublet for  $\text{Fe}^{1+}$  in  $\text{MgO}$ . Three crystals varying in  $\text{Fe}^{1+}$  concentration from 5 to 40 ppm were used for the measurements. The data were taken with the applied magnetic field  $H_0$  along three different crystal directions. Typical error for data points shown without error bars is  $\sim \pm 10\%$ .

10 K can be explained in terms of spin diffusion within the  $\text{Fe}^{1+}$  ions and cross-relaxation to other ions such as  $\text{Fe}^{2+}$ . A similar explanation was given for  $\text{Co}^{2+}$  in  $\text{MgO}$  at much higher spin concentrations.<sup>12</sup> Some difficulty remains with the angular dependence of  $\tau$  for  $\text{Fe}^{1+}$  being independent of spin concentration.

In any case, the low-temperature relaxation process amounts to only a 10% correction for  $\tau$  measured at 10 K and becomes immeasurably small for  $T > 12$  K. Therefore, we arbitrarily chose to fit the data in the region above 4.2 K with a function linear in temperature of the form  $A'T$ .

A weighted least-squares method was used to fit the

temperature dependence of the pulsed saturation data (only the data for  $H_0 \parallel [111]$  for  $T < 10$  K were included) to sums of terms of the form of Eq. (2) representing multiple Raman and Orbach processes. A 50% reduction in the standard deviation  $\sigma$  was assumed to be sufficient reason to discard terms from the general equation and consider the corresponding relaxation mechanism to be absent. A minimum value of  $\sigma = 0.109$  was obtained by using an expression similar to Eq. (2), namely,  $1/\tau = A'T + BT^9 + C'/(e^{\Delta'/T} - 1)$ , with the parameters (listed with standard errors)  $A' = 2.1 \pm 0.1 \text{ K}^{-1} \text{ sec}^{-1}$ ,  $B = (1.2 \pm 0.1) \times 10^7 \text{ K}^{-9} \text{ sec}^{-1}$ ,  $C' = [(2.2 \pm 0.4) \times 10^{10}] \text{ sec}^{-1}$ , and  $\Delta' = 213 \pm 4 \text{ K}$ . Without any con-

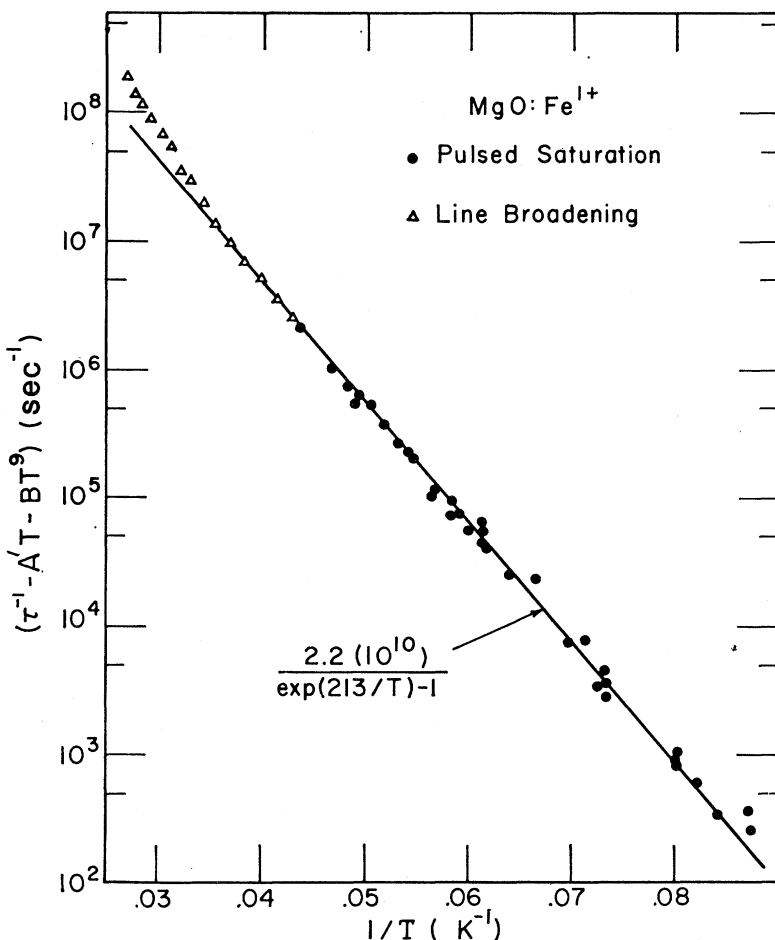


FIG. 3. The relaxation time for MgO: Fe<sup>2+</sup> plotted to show the exponential temperature dependence for  $T > 12$  K. Values plotted on the ordinate are the observed relaxation rates  $1/\tau$ , adjusted by subtracting the contributions from (a) an arbitrary relaxation process which fits the data below 10 K with  $A' = 2.1 \text{ K}^{-1} \text{ sec}^{-1}$  and (b) a Raman relaxation process which accounts for as much as 50% of the relaxation only between 10 and 12 K with  $B = 1.2 \times 10^{-7} \text{ K}^{-9} \text{ sec}^{-1}$ , as discussed in the text.

tribution from a  $T^9$  process, the best fit that could be obtained with a single exponential term yielded a large  $\sigma$  of 0.293 and a 10% reduction in the value of  $\Delta$ . The exponential temperature dependence of the pulsed saturation data for  $T > 12$  K can be seen in Fig. 3 where the terms  $A'T + BT^9$  have been subtracted from the observed relaxation times and the difference plotted as a function of  $1/T$ .

Relaxation times plotted above 23 K in Fig. 2 were determined from EPR line broadening as described in Sec. III. The observed values of  $\Delta H(T)$  for the sample having the smallest  $\Delta H(0)$  when  $H_0 \parallel [111]$  ( $\sim 1.2$  Oe) are plotted in the lower-right-hand corner of Fig. 2. The line shapes were nearly Lorentzian at each temperature from 4.2 to 37 K and at all angles. For example, a normalized first derivative Lorentzian line shape was greater than the first derivative EPR signal by 20% at 26.6 K, 10% at 31.0 K, and 0% at 35.0 K compared at  $3\Delta H(T)/2$  from the center of the line. The line was shown to be inhomogeneously broadened by "hole burning" experiments performed at 4.2 K. The line envelope was observed to recover uniformly with the same  $\tau$  within  $\pm 10\%$ .

The values of  $1/\tau$  from line broadening calculated by Eq. (3) are shown by open triangles in Figs. 2 and 3. The proportionality constant  $\epsilon$  is found to be  $(4.7 \pm 0.6) \times 10^7 \text{ sec}^{-1}/\text{Oe}$  by comparing line broadening with the EPR recovery from pulsed saturation at  $\sim 23$  K. The continuity of the spin-relaxation data obtained in this manner can be seen in Fig. 3 where, clearly, the temperature dependence of all the data below  $\sim 28$  K, both line broadening and pulsed saturation, is accurately given by  $1/(e^{213/T} - 1)$ .

Above  $\sim 28$  K, the single exponential function is noticeably below the measured relaxation rate. The excess line broadening is shown in greater resolution in Fig. 4, where measured values of  $\Delta H(T) - \Delta H(0)$  for the Fe<sup>2+</sup> line are plotted as a function of  $1/T$ . The difference between the data for  $T > 28$  K and the function  $1/(e^{213/T} - 1)$  is accurately described by a second exponential term of the same form. Without considering phonon bottleneck effects of the Orbach process,<sup>27</sup> no

<sup>27</sup> W. J. Brya and P. E. Wagner, Phys. Rev. **147**, 239 (1966); R. Adde, S. Geschwind, and L. R. Walker, in *Proceedings of the Fifteenth Colloque Ampere*, edited by P. Ayerbuch (North-Holland, Amsterdam, 1969), p. 460.

other relaxation function based on a consistent physical model varies fast enough with  $T$  to account for the excess line broadening. A least-squares fit of all the line-broadening data to the equation

$$\Delta H_i(T) = D'(e^{213/T} - 1)^{-1} + D''(e^{\Delta''/T} - 1)^{-1} \quad (4)$$

gave the low standard deviation  $\sigma = 0.058$  with the parameters (listed with standard errors)  $D' = 510 \pm 30$  Oe,  $D'' = (5.1 \pm 4.2) \times 10^5$  Oe, and  $\Delta'' = 450 \pm 30$  K.

## V. DISCUSSION

All of the measured relaxation times  $\tau$  above 10 K were independent of sample and Fe<sup>1+</sup> spin concentration down to 5 ppm. Therefore, we consider values of  $\tau$  plotted in Fig. 2 above 10 K to be intrinsic to the MgO:Fe<sup>1+</sup> spin-lattice interaction and, henceforth, consider the values given by

$$1/T_1 = 1/\tau - A'T \quad (5)$$

to be the spin-lattice relaxation rate due to two-phonon scattering processes.

The temperature dependence of  $1/T_1$  for MgO:Fe<sup>1+</sup> in the range 10–37 K is accurately described by a sum of functions expected for relaxation of Kramers ions by Raman and Orbach processes. The contribution from the Raman relaxation function needed for a best least-squares fit of the data is as much as 50% only below 12 K. The data above 12 K can be interpreted in terms of two Orbach relaxation functions with effective excited states at  $\Delta' = 150$  cm<sup>-1</sup> and  $\Delta'' = 310$  cm<sup>-1</sup> above the ground-state doublet. The value of  $\Delta'$  is well determined since the same exponential function describes the data over more than five decades in the time constant. A second low-lying electronic excited state, indicated by the data at  $T > 28$  K, would be expected for  $3d^7$  ions in MgO. Similar low-lying energy levels ( $\sim 305$  cm<sup>-1</sup>) have been inferred from high-temperature susceptibility measurements<sup>28</sup> of iso-electronic MgO:Co<sup>3+</sup>. The energies  $\Delta'$  and  $\Delta''$  correspond to frequencies in the acoustic branch of the measured phonon spectrum of MgO.<sup>18</sup> Phonon states in this energy range will be adequately populated at  $T > 12$  K so the resonant two-phonon (Orbach) process can become an effective relaxation mechanism.

Without considering the possibility of a low-lying <sup>2</sup>E<sub>1</sub> level as discussed in Sec. II, if one takes the excited states at  $\Delta'$  and  $\Delta''$  to be the  $\Gamma_8$  and  $\Gamma_7 + \Gamma_8$  spin-orbit levels derived from the <sup>4</sup>T<sub>1</sub> ground state of Fe<sup>1+</sup> in an octahedral cubic field, the measured value of  $\Delta' \approx 9\lambda/4$  implies that  $\lambda/\lambda_0 \approx 0.57$  ( $\lambda_0 = -115$  cm<sup>-1</sup>). Furthermore, by means of Eq. (1) using  $g = 4.15$ ,  $\lambda \approx -66$  cm<sup>-1</sup> from our measurements, and  $Dq \approx 1000$  cm<sup>-1</sup> (a value comparable to the 960 cm<sup>-1</sup> measured optically<sup>11</sup> for iso-electronic MgO:Co<sup>2+</sup>), one finds the orbital reduction factor  $k' \approx 0.75$ . The value of  $k'$  is relatively insensitive to the choice of  $Dq$  since a factor of 2 in the assumed

<sup>28</sup> P. Cossee, *Mol. Phys.* **3**, 125 (1960).

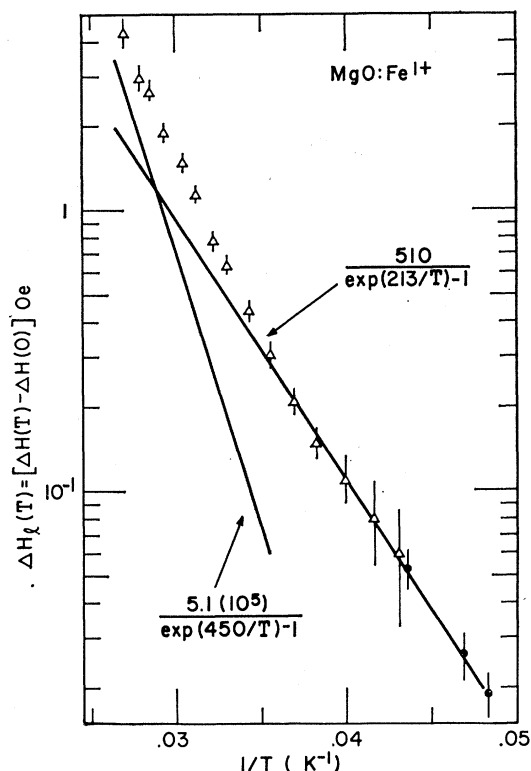


FIG. 4. The relaxation-induced contribution to the peak-to-peak separation of the derivative EPR line  $\Delta H_i(T)$  of MgO:Fe<sup>1+</sup> plotted as a function of the reciprocal of lattice temperature. These data were taken with the applied magnetic field parallel to the [111] crystal axis to produce the smallest residual linewidth. The three points shown by filled circles in the lower-right-hand side are the three highest pulsed saturation data points in Fig. 3 converted to equivalent values of  $\Delta H_i(T)$  according to the empirical scale  $4.7 \times 10^7$  sec<sup>-1</sup>/Oe.

value would only change  $k'$  by 0.03. It should be recalled from Sec. II, however, we have neglected the admixing of the <sup>4</sup>P level into the ground state which could have the effect of reducing the value<sup>11</sup> of  $k'$  as low as 0.65.

These values of  $\lambda$  and  $k'$ , though considerably reduced from free-ion values, seem to be consistent with values reported in the literature for other iron-group ions in MgO (Table I) which have comparatively

TABLE I. Comparison of the reduction in spin-orbit coupling constants and orbital reduction factors  $k'$  for some iron-group ions in MgO. The ratios of the mean fourth- to second-power radii,  $\langle r_0^4 \rangle / \langle r_0^2 \rangle$ , were calculated from the values listed in Ref. 13 in atomic units. (1 a.u. = 0.53 Å).

Ion	$\langle r_0^4 \rangle / \langle r_0^2 \rangle$	$\lambda/\lambda_0$	$k'$	Reference
Fe <sup>1+</sup>	4.73	0.57	0.65–0.75	This paper
V <sup>2+</sup>	4.64	0.61	...	a
Cr <sup>3+</sup>	2.97	0.69	0.72	a, b
Co <sup>2+</sup>	2.92	0.75	0.85–0.89	c
Ni <sup>2+</sup>	2.69	0.76	...	d

<sup>a</sup> Hiroshi Watanabe, *Operator Methods in Ligand Field Theory* (Prentice-Hall, Englewood Cliffs, N. J., 1966), p. 124.

<sup>b</sup> W. Low, *Phys. Rev.* **105**, 801 (1957).

<sup>c</sup> See Refs. 11 and 13.

<sup>d</sup> W. Low, *Phys. Rev.* **109**, 247 (1958).

large ionic radii.<sup>13</sup> Reduction in  $\lambda$  from the free-ion value is frequently attributed to covalency effects. Because of the larger ionic radius of  $\text{Fe}^{2+}$ , the effects of covalency and overlap are likely to be enhanced as compared to  $\text{Co}^{2+}$  in the same crystal structure. It is significant that in the case of  $\text{MgO}:\text{Fe}^{2+}$  where measurements indicated a similarly large 50% reduction in spin-orbit coupling, Ham *et al.*<sup>29</sup> considered this too great a reduction to be reasonably attributed to covalency and showed that dynamic Jahn-Teller quenching of the spin-orbit interaction was probably a more likely source.

An additional point of interest is that the ratio of energies of the two excited states effective in the spin relaxation was measured to be  $\Delta''/\Delta' \approx 2.1 \pm 0.2$ , whereas the first-order crystal-field approximation discussed in Sec. II predicts this ratio to be  $\sim 30\%$  greater, i.e.,  $E(\Gamma_7 - \Gamma_6)/E(\Gamma_8 - \Gamma_6) \approx 2.7$ , independent of the reduction in  $\lambda$  to first order. The second-order splitting of the  $\Gamma_7 + \Gamma_8$  level is of the order of  $\lambda^2/8Dq$  and is far too small to account for the observed difference. If one considers that the level at  $\Delta''$  was indicated solely on the basis of line-broadening data and the difficulty in drawing clear conclusions from such information, the 30% difference could conceivably be attributed to experimental uncertainty in linewidth measurements. However, the difference may indicate inaccuracies in the physical model to the same extent that the anisotropic EPR linewidth does.

There seem to be at least three possible means by which the lower ratio could be obtained by changes in the model. First, a weak tetragonal component to the predominantly cubic crystal field would cause the  ${}^4T_1(O_h)$  ground state to split into a singlet and doublet.<sup>10</sup> Spin-orbit coupling would then split these levels into six Kramers doublets which would be separated in a manner depending on the sign and strength of the tetragonal field. Thus, the spacing indicated by our measurements could be explained assuming the levels at  $\Delta'$  and  $\Delta''$  are doublets. Second, if the cubic crystal-field strength was of the order of  $2000 \text{ cm}^{-1}$ , the  ${}^2E_1$  component of the excited  ${}^2G$  state could be close to the  ${}^4T_1$  ground state,<sup>14</sup> and significant changes in spin-orbit interaction would result in a different energy-level scheme.<sup>11</sup> As a third possibility, a strong dynamic Jahn-Teller interaction would appear to be able to account for the observed ratio.<sup>29</sup> However, there is reason to believe the spin-orbit interaction stabilizes the ground state of  $3d^7$  ions in MgO against a Jahn-Teller instability.<sup>30</sup> A clear choice of the correct ex-

planation for the observed ratio  $\Delta''/\Delta'$  does not seem possible without additional information.

## VI. CONCLUSIONS

The spin-relaxation time intrinsic to the doublet ground state of  $\text{Fe}^{2+}$  in single-crystal MgO has been measured as a function of temperature at 9.2 GHz for spin concentrations up to 40 ppm. The measurements included observing, apparently for the first time, simultaneous relaxation-induced line broadening and recovery from pulsed saturation for an  $S' = \frac{1}{2}$  spin system. The combined measurements give improved accuracy in the absolute values of lifetimes deduced from severe line broadening by reducing the uncertainty to be only the experimental uncertainty in the linewidth itself. Observation of intrinsic  $\text{Fe}^{2+}$  spin-lattice relaxation in these crystals was limited apparently by cross relaxation to  $\text{Fe}^{2+}$  for  $T < 10 \text{ K}$ . The temperature dependence of the relaxation time constant  $T_1$  defined by Eq. (5) for  $\text{MgO}:\text{Fe}^{2+}$  in the range 10–37 K is accurately expressed by

$$1/T_1 = BT^9 + C'/(e^{\Delta'/T} - 1) + C''/(e^{\Delta''/T} - 1), \quad (6)$$

where  $B = (1.2 \pm 0.1) \times 10^{-7} \text{ sec}^{-1} \text{ K}^{-9}$ ,  $C' = (2.2 \pm 0.4) \times 10^{10} \text{ sec}^{-1}$ ,  $C'' = (2.7 \pm 2.3) \times 10^{13} \text{ sec}^{-1}$ ,  $\Delta' = 213 \pm 4 \text{ K}$ , and  $\Delta'' = 450 \pm 30 \text{ K}$ . This temperature dependence is consistent with the interpretation of spin-lattice relaxation of Kramers ions by Raman and Orbach processes. To our knowledge, Orbach relaxation from two sets of excited states with well-separated energy values has not been observed previously.

Calculations based on the usual theory for  $3d^7$  ions in the octahedral crystal field of MgO using the measured energies of the excited states  $\Delta'$  and  $\Delta''$  indicate that the orbital reduction factor  $k'$  may be in the range 0.65–0.75 and the effective spin-orbit coupling constant  $\lambda = -66 \text{ cm}^{-1}$ . The low values of these parameters for  $\text{Fe}^{2+}$  compared to other iron-group ions in MgO is consistent with the expected enhancement of covalency and overlap effects because of the larger ionic radius. However, there is some evidence for inaccuracies in the model, as discussed in Sec. V.

## ACKNOWLEDGMENTS

I would like to express my sincere appreciation to Dr. J. G. Castle, Jr., for providing the crystals for these measurements and serving as a constant source of encouragement throughout this research. I am equally indebted to Dr. R. L. Hartman for advice regarding the experimental measurements. The assistance of Army Daniel and J. T. Givens during the experiments is gratefully acknowledged. I also thank Dr. I. Miyagawa, Dr. J. D. Stettler, E. L. Wilkinson, and Dr. W. G. Gamble for many helpful discussions.

<sup>29</sup> F. S. Ham, W. M. Schwarz, and M. C. M. O'Brien, *Phys. Rev.* **185**, 548 (1969).

<sup>30</sup> F. S. Ham, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, to be published). Ham's chapter is also available as Report No. 68C246 from General Electric R & D Center, Schenectady, N. Y.