

Spin-lattice relaxation of Fe^{3+} in iron doped magnesium oxide

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Spin-lattice relaxation measurements for $\text{Fe}^{3+}/\text{MgO}$ were carried out in the temperature range from 4.2 to 27 K at 37.5 Hz utilizing the pulse saturation method. This revealed a close agreement with the theoretical predictions, demonstrating a T^{-1} behaviour at low temperatures as a direct process and a $T^{-4.6}$ variation as a raman process at higher temperatures, with a transition temperature near 20 K between these two regimes. Measurements of t_1 were carried out for samples with iron concentrations of 140, 310 and 110 ppm and gave the values of 1.0, 0.8 and 0.1 msec, respectively, at 4.2 K. This confirms that the inverse proportionality of t_1 with concentration holds over this range of samples. Variation of relaxation time t_1 with crystal orientation for the central transition of $\text{Fe}^{3+}/\text{MgO}$ revealed two minima that were explained as due to cross-relaxation mechanisms. Comparison of our results with both those computed by Shiren at 10 GHz and the experimental results of Castle and Feldman at the same frequency showed that a $t_1 \propto (\text{frequency})^{-4}$ law was obeyed. The present data has provided another example of an *S*-state ion behaving in the manner predicted by the present theories of relaxation.

1. Introduction

The main interest in studying the spin-lattice relaxation of Fe^{3+} in magnesium oxide crystals is that it provides another example of an *S*-state ion in a well-known lattice structure. In a previous publication [1] the authors have shown that the spin-lattice relaxation rate of Gd^{3+} in CaWO_4 varied with temperature at T^{-3} in the Raman region of relaxation, instead of the T^{-5} law which is expected for an *S*-state ion. This behaviour was explained as an effect of the defects in the crystal, as was previously observed by Castle *et al.* [2] in irradiated quartz. Moreover, this study is complementary to the line width studies on $\text{Fe}^{3+}/\text{MgO}$ reported by Thorp *et al.* [3] and was made using the same series of doped single crystals.

The magnesium oxide structure is that of the well-known sodium chloride; of the type *MX*, where *M* denotes the metal ion or atom and *X* an electronegative element, e.g. oxygen in the oxides,

or fluorine or chlorine in the halides, etc. The lattice is fcc of space group O_h^5 as indicated by Cornwell [4], (the point group is O_h and the assignment of superscript by Schonflies is rather arbitrary). Each magnesium atom has a co-ordination number of 6, the neighbours being at the vertices of a regular octahedron. In this octahedral co-ordination the ionic radii, according to Kelly and Groves [5], for Mg^{2+} and O^{2-} are 0.65 and 1.40 Å respectively. Wyckoff [6] gave the lattice parameter as $a_0 = 4.2112$ Å. By doping the single crystals of MgO with iron, the latter is expected to go into the lattice by substitution at the magnesium sites; the predominant valency state is Fe^{3+} as concluded by Thorp *et al.* [3] in their recent work on ESR* linewidths of Fe^{3+} in MgO , whose optical measurements also revealed features indicative of Fe^{3+} . This, besides the observed ESR spectra at X- and Q-bands (9.1 and 35.5 GHz) gave confirmation of their conclusion.

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*ESR = electron spin resonance.

Further support is given by the comparison of the ionic radii of Fe^{3+} which, at 0.64 \AA [5], is almost the same as the corresponding Mg^{2+} ion. The extra positive charge on the Fe^{3+} ion however requires that there should be some mechanism for charge compensation in the crystal. Since there was no deliberate doping of a univalent element to maintain charge neutrality, this will be the vacancy compensation mechanism, i.e. 1 Mg^{2+} vacancy for every 2 Fe^{3+} ion in magnesium sites.

2. Experimental

The single crystals of iron-doped magnesium oxide, upon which measurements were made, were obtained from W. & C. Spicer Ltd. (Cheltenham), having been grown by electrofusion using pure powdered ferric oxide and pure powdered magnesia as the starting materials. The iron concentrations in the samples used in this work were 140, 310 and 710 ppm; these had been determined by optical spectrographic analysis (Johnson-Matthey Ltd.) to an accuracy of about 2%. Neither optical examination nor X-ray back reflection photographs, used to orient the samples, revealed any evidence of macroscopic cracking, flaws, strain or mosaic formation. This led us to assume that the samples were of good crystalline quality. The pulse saturation technique [7, 8] was used for the spin-lattice relaxation measurements at 37.5 GHz. Measurements were carried out for the central $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition and the temperature was varied in the range from 4.2 to 27 K.

3. Results

3.1. Observation of two decay rates

The crystals were oriented so that the magnetic field H was along the $\langle 100 \rangle$ direction. In most of the plots produced from the photographs of the exponential decay curves, the existence of two relaxation rates could be observed as in Fig. 1. The longer relaxation time was taken as the spin-lattice relaxation time t_1 , whilst the shorter relaxation time could be attributed to some contribution from the energy levels of the system in a cross-relaxation mechanism, as discussed by Manenkov and Prokhorov [9]. Previous experimental results on $\text{Fe}^{3+}/\text{MgO}$ at 10 GHz by Castle and Feldman gave two values for the exponents in the rate equation and were published by Shiren [10]. Our results are given in Table I where they are compared with Shiren's computed values and the measurements of Castle and Feldman of t_1 for

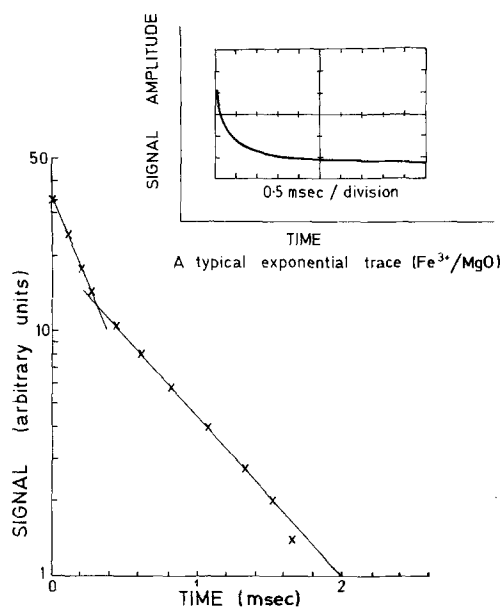


Figure 1 A semilogarithmic plot of the exponential recovery trace at 4.2 K and 37.5 GHz.

TABLE I Observations of more than one decay constant in the relaxation of $\text{Fe}^{3+}/\text{MgO}$ at 4.2 K.

Present results t_1 at 37.5 GHz (msec)	Computed t_1 [10] at 10 GHz (msec)	Measured t_1 [10] at 10 GHz (msec)
0.8	50	7714.3
0.3	26	23.8
	7.6	

$\text{Fe}^{3+}/\text{MgO}$. This Table shows the presence of more than one component in the relaxation decay of $\text{Fe}^{3+}/\text{MgO}$, in both the experimental and predicted data, although direct comparison of the results is not convenient at this stage because of the difference in the operating frequencies.

3.2. Temperature dependence of t_1

Measurements of spin-lattice relaxation time t_1 were made in the temperature range from 4.2 to 27 K for the $\text{Fe}^{3+}/\text{MgO}$ sample of 310 ppm Fe doping. The magnetic field was directed along the $\langle 100 \rangle$ direction of the crystal and we monitored the relaxation of the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition. An araldite block was used to let the sample warm up slowly enough to record the exponential recovery traces at varying temperatures, as was explained in a previous publication [1]. The variation of t_1 in the range of temperatures studies is depicted in

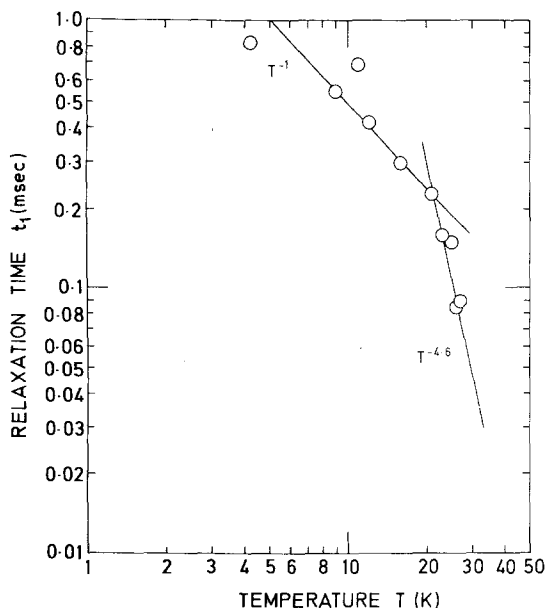


Figure 2 Temperature dependence of t_1 ; $\text{Fe}^{3+}/\text{MgO}$, 310 ppm Fe, at 37.5 GHz.

Fig. 2. This shows two regimes of dependence on temperature T , as T^{-1} at lower temperatures and $T^{-4.6}$ above about 20 K. The values of t_1 were derived from the photographs of the exponential decay traces at the corresponding temperature by choosing the longest relaxation time as the spin-lattice relaxation time at that temperature.

3.3. Concentration dependence of t_1

Measurements of t_1 were carried out for $\text{Fe}^{3+}/\text{MgO}$ samples with iron concentrations of 140, 310 and 710 ppm. The results are given in Table II. The agreement between the experimental and the predicted values of t_1 according to a (concentration) $^{-1}$ law is good, confirming that the inverse proportionality holds over this concentration range.

3.4. Angular variation of t_1

The variation of relaxation time t_1 with crystal orientation for the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition for $\text{Fe}^{3+}/\text{MgO}$ has been experimentally investigated. Three samples of iron concentrations 140, 310, 710 ppm were examined at liquid helium temperature

TABLE II Concentration dependence of t_1

Concentration (ppm)	Measured t_1 (msec)	Predicted t_1 (msec)
140	1.0	1.0
310	0.8	0.5
710	0.1	0.2

(4.2 K). The spin-lattice relaxation times were measured in the angular range $\theta = 0^\circ$ to 90° , where θ is the angle between the magnetic field H and the $\langle 100 \rangle$ direction of the crystal. The angular dependence behaviour of these three samples is depicted in Fig. 3. The sample of 310 ppm Fe showed two apparent minima at angles θ of about 30° and 75° , having values of t_1 as 0.44 and 0.49 msec, respectively. This behaviour was not evident for the other two samples (140 and 710 ppm Fe). However, we noticed that the 310 ppm Fe sample did not show 'extra' lines in the ESR spectrum as did the 140 and 710 ppm Fe samples, which might indicate that they are not exactly similar and differences in behaviour might arise.

4. Discussion

4.1. The two decay rates in the recovery trace

Shiren's computations of t_1 , given in Table I, were based on deriving the rate equations, as already given by Andrew and Tunstall [11], for the different energy levels available in the system studied. For ions with $S = 5/2$ and the $\Delta m = 1$ transitions there are, in general, three relaxation rates in the return to equilibrium from saturation or inversion. Experimentally the relaxation behaviour of a particular level will frequently be dominated by one of the relaxation rates if it has a large amplitude constant. The final part of the recovery trace, which has the longest component, gives the spin-lattice relaxation time t_1 .

4.2. Temperature dependence

From the theories of relaxation, Kronig [12], Van Vleck [13], Orbach [14], Orbach and Blume [15],

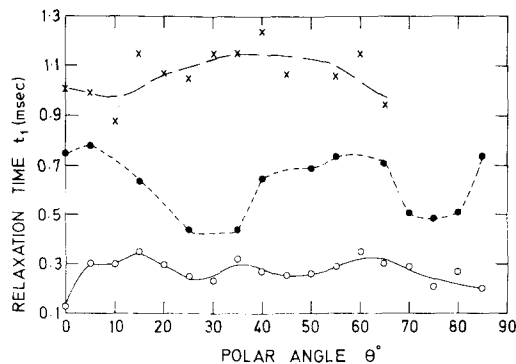


Figure 3 Angular variation of t_1 ; $\text{Fe}^{3+}/\text{MgO}$, $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition at 4.2 K and 37.5 GHz. Fe content - - - - 140 ppm, 310 ppm, ——— 710 ppm.

and Walker [16] we may formulate a general equation that gives the dependence of spin-lattice relaxation time on temperature as

$$t_1 = AT^m + BT^n + C \exp(-\Delta_C/kT) \quad (1)$$

where A , B and C are constants. In the first term (in the absence of a bottleneck or cross-relaxation effects) $m = 1$, indicating the occurrence of a direct process. In the second term, corresponding to the Raman process, $n = 7$ for a non-Kramers ion or $n = 9$ for a Kramers ion. The last term represents the Orbach mechanism, where Δ_C is the energy splitting of the excited state above the ground level. As we are dealing with an s -state ion we may expect that the Orbach–Blume mechanism will be effective, giving rise to a dominating T^5 term in Equation 1 instead of the normal Raman process. There is experimental evidence for the T^5 Raman behaviour in several s -state ions, as discussed by Gill [17].

The observed dependence of t_1 on temperature agrees with the theoretical predictions demonstrating a T^{-1} behaviour as a direct process at low temperatures and a $T^{-4.6}$ variation as a Raman process at high temperatures with a transition temperature near 20 K between these two regions. Knowledge of the transition temperature T_C at which the Raman process begins to dominate over the direct process can provide information about the Debye temperature of the crystal. This was attempted by carrying out analysis similar to that previously made for $Gd^{3+}/CaWO_4$ by Ammar [18]. Here, however, the difference is that we shall start with a known value of T_C to derive the Debye temperature θ_D , whereas in the previous treatment the reverse situation applied. The relation between T_C and θ_i (the Debye temperature for a defected crystal) could be approximated to

$$T_C \simeq \frac{1}{2} \theta_i^{2/3}. \quad (2)$$

From Fig. 5.2, $T_C = 20$ K, hence $\theta_i = 253$ K. Also as we are dealing with Fe^{3+} ions which substitute for Mg^{2+} ions in the MgO single crystal we may use the relation

$$\theta_i = m^{-1/2} \theta_D \quad (3)$$

where m is the ratio of the atomic masses of iron to magnesium ions. Therefore,

$$\theta_i = \left(\frac{55.847}{24.305} \right)^{-1/2} \theta_D$$

giving

$$\theta_D = 383 \text{ K.}$$

For comparison, we find from the physical tables [19] that the Debye temperature for MgO has been given as 946 K. This was reported by Barron *et al.* in 1959 [20], when studying the heat capacity of crystalline magnesium oxide. It was found that their published value was the Debye temperature at 0 K (θ_D) and from their plotting of θ_D versus temperature in the range $20 < T < 300$ K we found that θ_D at 77 K is nearly 750 K.

The value of T_C is in exact agreement with that reported by Pace, Sampson and Thorp, 1961, [21] in their studies on synthetic sapphire (Fe^{3+}/Al_2O_3) at 34.6 GHz. Using a pulse saturation method, they found that the main features of the variation of the relaxation times showed a T^{-1} dependence on temperature up to 10 K and a transition to a region of T^{-5} occurred at about 20 K.

Also, Kask *et al.*, 1963 [22], studied the paramagnetic relaxation of the Fe^{3+} ion in corundum (Al_2O_3) in the 3 cm range by utilizing the pulse saturation method. The temperature dependence of t_1 was determined in the interval 2 to 80 K. It was shown that t_1 varied approximately as T^{-1} in the region from 2 to 5 K. In the interval 5 to 15 K, t_1 varied anomalously slowly and in the 20 to 80 K range, t_1 varied as T^{-6} .

4.3. Concentration dependence

It has long been observed that at sufficiently low temperatures and sufficiently high concentrations of paramagnetic impurities the transfer of energy from a spin system to the lattice may be dominated by concentration-dependent relaxation processes. One explanation was suggested by Van Vleck, 1960 [23], that the spins in the crystal cross-relax to some paramagnetic sites which relax rapidly to the lattice. The rapid relaxing sites may, for example, consist of spins of paramagnetic species having exceedingly short spin-lattice relaxation times, spins located in distorted crystal fields, or exchange-coupled clusters of two or more ions which relax rapidly to the lattice as a result of phonon modulation of the exchange coupling. In studying the spin-lattice relaxation of Cr^{3+} ions in ruby crystals, Standley and Vaughan, 1965 [24], suggested that the observed concentration-dependence is possibly due to impurity ions that constitute the fast relaxing centres. Solomon in 1966 [25] studied the concentration-

dependence of spin-lattice relaxation times for Mn^{2+} and Fe^{3+} in MgO at 9.6 GHz utilizing the technique of saturation recovery. He found that t_1 is roughly proportional to the inverse of concentration. From the results shown in Table II, we may conclude that for Fe^{3+}/MgO studied, t_1 obeys a (concentration) $^{-1}$ law.

4.4. Angular variation

The decrease in t_1 values at certain angles could be explained by cross-relaxation between two or more transitions. From previous studies on linewidths of Fe^{3+}/MgO by Thorp *et al.* [3], it was indicated that at these angles of minimum t_1 values the $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$ and $\frac{1}{2} \leftrightarrow \frac{3}{2}$ transitions are expected to overlap with the main transition, $\frac{1}{2} \leftrightarrow -\frac{1}{2}$. Donoho, 1964 [26], worked out theoretically the form of the angular dependence for Cr^{3+} in ruby. Although no such theoretical treatment was attempted for Fe^{3+}/MgO , we may conclude that the angular dependence of the relaxation time is a consequence of the variation in admixture between states as the angle θ changes.

4.5. Frequency dependence

Since the measurements of t_1 reported here were made at 37.5 GHz only, they provide no information on the frequency dependence of the relaxation time. However, Shiren [10] has reported computed values of t_1 at 10 GHz, also, in the same publication, Castle and Feldman have published measured values of t_1 at 10 GHz. On reviewing the laws of dependence of t_1 on frequency f , two particular cases arise, as discussed by Thorp *et al.*, 1972 [27]; (a) the behaviour of the ion represented by an isolated Kramers doublet showing $t_1 \propto f^{-4}$, and (b) the non-Kramers ion which gives $t_1 \propto f^{-2}$. Applying these two laws to our results we find that the $t_1 \propto f^{-4}$ law is better obeyed, Table III. For comparison of results we refer to Davis and Wagner, 1964 [28], who showed that potassium cobaltcyanide containing Fe^{3+} obeyed equation $t_1 = aH^{-4}T^{-1}$ very closely, displaying a $t_1 \propto H^{-4}$ dependence (or $t_1 \propto (\text{frequency})^{-4}$) for the direct process at helium temperatures from 4 to 12 GHz. This, in fact, agrees with the predictions of Van Vleck, 1940 [13], for the spin-lattice relaxation time dependence on magnetic field at low temperatures in the direct region of relaxation, for an isolated Kramers doublet. Van Vleck concluded that regarding the dependence on field strength his calculations also

TABLE III Application of f^{-2} and f^{-4} laws of dependence of t_1 on frequency

Source	t_1 (msec)		
C-F*, (at 10 GHz)	714.3	23.8	
S†, (at 10 GHz)	50	26	7.6
f^{-2} law for C-F values	50.8	1.7	
f^{-2} law for S values	3.6	1.8	0.5
f^{-4} law for C-F values	3.6	0.1	
f^{-4} law for S values	0.3	0.1	0.04
Present measurements (at 37.5 GHz)	0.8	0.3	

*C-F = Castle, Feldman *et al.* [2].

†S = Shiren [10].

apply to Fe^{3+} (in iron alum) as well as Cr^{3+} (in chrome alum).

Finally, we may conclude that this data has provided another example of an S-state ion behaving in the manner predicted by the present theories of relaxation.

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