JOURNAL OF MATERIALS SCIENCE 15 (1980) 2647–2650

ESR line broadening of Fe^{3+} in Fe/MgO at low temperatures

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Electron spin resonance linewidths of Fe^{3+} in single crystal MgO were examined at 9 GHz for crystals having iron concentrations of 2300 ppm and 4300 ppm over the temperature range 293 to 4.2 K. For the $+1/2 \rightarrow -1/2$ transition the linewidth remains constant from 293 to about 15 K, below which line broadening occurs. From 15 to 4.2 K the linewidth increases steadily without any change in the g value of the line. At 4.2 K the width of the line is about 3.7 times larger than at 77 K for each concentration. The lineshapes are Lorentzian over the whole temperature range examined and the data suggested that the effects observed below 15 K were due to non-secular line broadening mechanisms (the "10/3" effect) originally proposed by Anderson and Weiss.

1. Introduction

In a recent publication, Thorp *et al.* [1] reported that the ESR linewidths of Fe^{3+} in single crystal MgO at 9 GHz were determined by exchange narrowing throughout the temperature range from 293 to 77 K. These linewidth measurements have now been extended to the liquid helium temperature range, using the same specimens on which high temperature data was available in an attempt to establish which linewidth mechanisms held at lower temperatures. There have been several previous studies of the low temperature ESR behaviour of Fe^{3+}/MgO. Feher [2] observed the angular dependence of linewidth for the $+1/2 \rightarrow -1/2$ transition of Fe^{3+} in MgO and reported that there was an increase in linewidth in going from 77 K to liquid helium temperatures. In a sample containing 200 ppm Fe^{3+} Feher found that, at 10GHz, the linewidth at 1.2 K was about 2.5 times larger than that at 77 K, but gave no explanation. Stoneham *et al.* [3] also reported that the ESR linewidth of Fe^{3+} in single crystal MgO at 19.4 GHz was broadened as a function of decreasing temperature in the liquid helium range and suggested that this resulted from motional narrowing of the linewidth due to dipolar interaction with Fe^{2+} ions. In the present measurements any contribution to linewidth resulting from motional narrowing due to Fe^{2+} ions can be neglected for the following reasons. In the MgO crystals used by Stoneham *et al.* the ratio of Fe^{2+} to Fe^{3+} ions was 4:1. Here, however, the crystals (which contained a detectable amount of Fe^{2+} in the as grown state [1]) were heat treated in air at 1200° C for about 30 h. Evidence from X-ray and ESR measurement made by Cordischi *et al.* [4] shows that heating to 700° C in air for about five h is sufficient to oxidize Fe^{2+} completely to Fe^{3+}; consequently, effects attributable to Fe^{2+} could be neglected.

Line broadening due to non-secular mechanisms, often called the 10/3 effect, was first proposed by Anderson and Weiss in 1953 [5] in connection with the line broadening in some paramagnetic salts such as $Fe_2(SO_4)_3$, $Fe(NH_4)(SO_4)_2$, $MnSO_4$ and $MnCl_2$. A more detailed theoretical treatment was given by Kubo and Tomita in 1954 [6]. Further experimental evidence was obtained by several workers including Abe *et al.* [7, 8] in the single crystals of potassium cupric chloride, ammonium cupric chloride and coppertrichloroacetate monohydrate; Rogers *et al.* [9] in DPPH and Henderson *et al.* [10] in potassium cupric chloride. The 10/3 effect refers to the increase in magnetic resonance linewidth which occurs in an exchange narrowed situation when the Zeeman frequency becomes comparable to the effective exchange frequency; in the theoretical treatments

0022–2461/80/102647–04 $02.40/0

it is explained by the inclusion of non-secular spin–spin terms.

2. Experimental technique

The doped crystals on which measurements were made were obtained from W and C Spicer Ltd., (Cheltenham) having been grown by electrofusion using pure powdered ferric oxide and pure powdered magnesia as starting materials. The iron concentrations of the crystals (examined 2300 ppm and 4300 ppm respectively) had been determined by optical spectrographic analysis (Johnson–Matthey Ltd.) to an accuracy of about 2%.

The ESR measurements were made using a conventional 9 GHz spectrometer as described elsewhere [1], which was now equipped with a helium cryostat. The incident microwave power in the sample cavity was less than 0.20 mW and the magnetic field modulation frequency was 125 Hz.

3. Experimental results

For both crystals, the linewidth observed for the $+1/2 \leftrightarrow -1/2$ transition at any particular value of θ_H remained constant throughout the temperature range 293 to about 15 K. However there is, as reported previously [1], a variation of linewidth with polar angle. Below 15 K the linewidth increases rapidly without any change in the g value of the line. The spectra of one of the samples is shown in Fig. 1, which refers to a specimen containing 2300 ppm Fe^{3+} taken at $\theta_H = 0°$. In Fig. 2 the observed peak-to-peak widths are plotted as a function of temperature. The linewidths, defined as the width between points of maximum slope (ΔH_{ms}), were obtained directly from the derivative plots. For each sample the width at 4.2 K was about 3.7 times larger than that observed at 77 K.

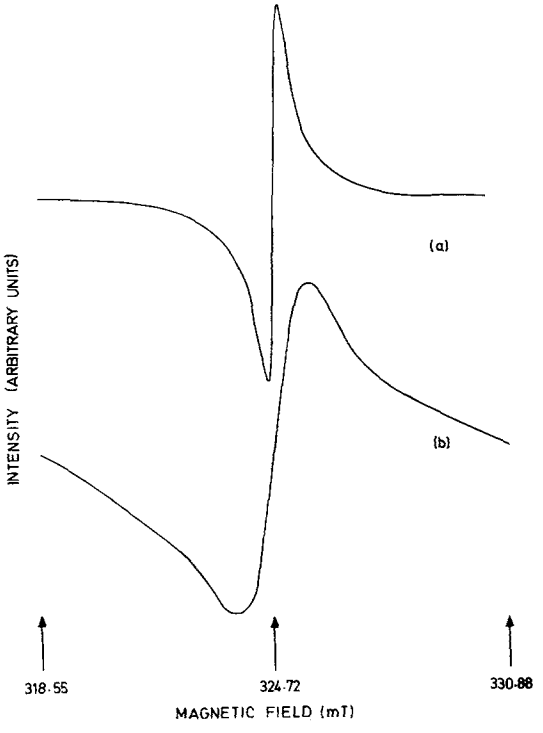

Figure 1 Derivative lineshape for $-1/2 \rightarrow +1/2$ transition; Fe^{3+}/MgO (2300 ppm), (a) 77 K, (b) 4.2 K; $\theta_H = 0°$, 9.1 GHz.

4. Discussion

To examine the nature of the interactions involved in the line broadening at low temperatures lineshape analysis and moment calculations were made, following the methods described elsewhere [11]; the results are tabulated in Table I.

The data of Table I showed that the observed linewidths at 4.2 K were about 3.7 times larger than that at 77 K. Even so, these broadened linewidths were still very much less than the values predicted on the basis of the known concentrations by dipolar theory which strongly suggested that they were not determined by dipolar interactions. Analysis of the lineshapes showed, firstly, that the values of the ratio $M_4^{1/4}/M_2^{1/2}$ (where M_2 and M_4 are respectively the second and fourth moments) at low temperatures were similar to the figures quoted elsewhere [1] for exchange narrowed ESR lines and, secondly, that the values of the ratio $\Delta H_{ms}/\Delta H_{1/2}$ (where ΔH_{ms} is the

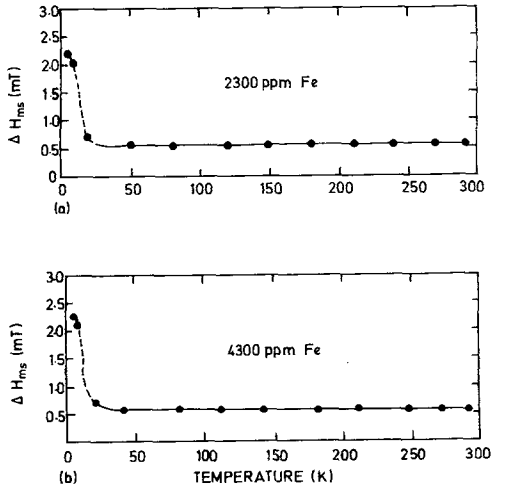

Figure 2 Temperature dependence of the linewidth; $\theta_H = 0°$, 9.1 GHz, $-1/2 \rightarrow +1/2$ transition.

TABLE I Lineshape data of Fe^{3+}/MgO at 77 and 4.2 K

Iron concentration (ppm)	Temperature (K)	Experimental linewidths (mT)	Calculated dipolar linewidth (mT) [1]	Moment ratio $M_4^{1/4}/M_2^{1/2}$	$\frac{\Delta H_{rms}}{\Delta H_{1/2}}$ (obs)
2300	77	0.58	42.58	1.40	0.452
	4.2	2.20	42.58	1.35	0.414
4300	77	0.63	58.44	1.41	0.570
	4.2	2.38	58.44	1.34	0.545

derivative linewidth and $\Delta H_{1/2}$ is the width of the integrated line at half-height) were consistent with those expected for Lorentzian lineshapes. An example is shown in Fig. 3, which refers to a crystal containing 2300 ppm Fe^{3+}. This evidence indicated that exchange narrowing mechanisms were present and were indeed the dominant factor affecting the linewidth of all temperatures down to 4.2 K.

To establish whether the exchange energy was comparable to the Zeeman energy, values of J were derived from the spectra recorded at 4.2 K. The half linewidth ($\Delta\omega$) expressed in frequency units is related to $\Delta H_{1/2}$ by $\Delta\omega = 2\pi g\beta/h(\frac{1}{2}\Delta H_{1/2})$ and the exchange energy (J) is related to $\Delta\omega$ by

$$\Delta\omega = \langle\Delta\omega^2\rangle \text{ dipolar}/J/\hbar$$

in which $\langle\Delta\omega^2\rangle$ is the second moment of the line and is dependent on concentration [1]. The comparison is given in Table II, which shows that, in particular for the lower concentration, the values are comparable.

It has been reported by Abe *et al.* [8] in the crystal coppertrichloracetate that the 10/3 effect was reduced and its onset shifted towards lower temperatures as the resonance frequency increased from 9 to 23 GHz; the observed lineshape remained Lorentzian throughout the temperature range from 293 to 4.2 K. Kubo and Tomita [6] showed theoretically that the 10/3 effect should become smaller at shorter wavelengths (i.e. $\omega_0 \gg \omega_{exch.}$) because of the disappearance of the non-secular broadening. Some Japanese experiments show that the 10/3 factor tends to disappear if one goes to high microwave frequencies; for example, Ono *et al.* [12] found in the crystal $CuK_2Cl_4 \cdot 2H_2O$ that the 10/3 effect which was pronounced at 9.96 GHz had completely disappeared at 38.9 GHz. This conclusion appears to be confirmed by the results of Ammer *et al.* [13] and Vesquez [14] who did not report any line broadening at liquid helium temperatures and 35.5 GHz in the same Fe^{3+}/MgO specimens as used here.

There are several other possible sources of line broadening. These include broadening due to strain, described by Feher [2], and broadening due to point defects and dislocations, discussed by Stoneham [15]. However, Feher reported that the effect of strain broadening on the $+1/2 \leftrightarrow -1/2$ transition of Fe^{3+}/MgO is negligible; further-

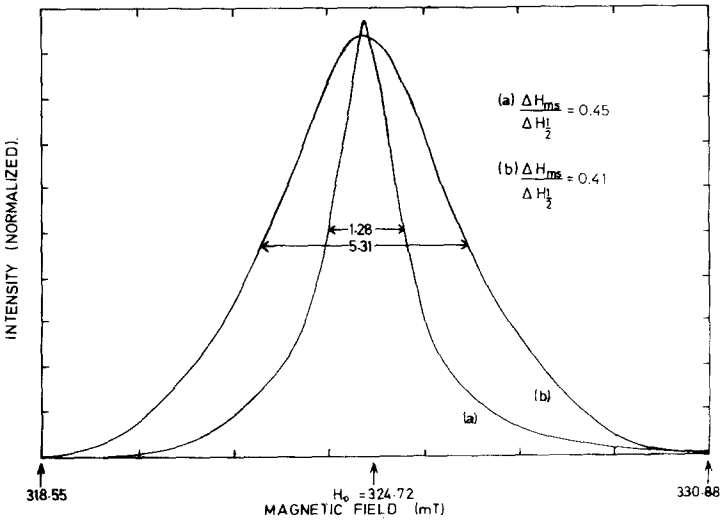

Figure 3 Integrated lineshapes for $-1/2 \rightarrow +1/2$ transition, (2300 ppm Fe) (a) 77 K; (b) 4.2 K; $\theta_H = 0°$, 9.1 GHz.

TABLE II Comparison between exchange energy and Zeeman energy

Iron concentration (ppm)	Temperature (K)	Exchange energy (GHz)	Zeeman energy (GHz)
2300	4.2	6.375	9.1
4300	4.2	14.56	9.1

more, the point defect broadening is not likely to be important because it arises from size difference effects and here the value of ionic radius of Fe^{3+} (0.645 Å) is less than that of Mg^{2+} (0.72 Å) [16]. A further possible source of broadening is an inhomogeneous distribution of dislocations which would produce a nearly Gaussian lineshape [15]. It has also been shown theoretically by Sabirov [17] that the width of the resonance line of an exchanged narrowed line may be increased and its shape may become Gaussian at low temperatures, when $\omega \gg kT$, where ω is the Larmor spin frequency; however, in our experimental situation $kT \gg \omega$. We cannot rule out the possibility of some contributions to line broadening due to unresolved hyperfine lines of ^{57}Fe, $I = 1/2$; which have been found experimentally [18, 19] at 20 K and have a hyperfine constant $A = 10$ Gauss. The broadening from unresolved hyperfine structure results in a Gaussian lineshape [15]. In our crystals the observed lineshape is Lorentzian, so none of the mechanisms leading to a Gaussian lineshape can be important.

5. Conclusions

In summary, the present experiments confirm that exchange narrowing mechanisms dominate the linewidth over the whole temperature range from 77 to 4.2 K. The observed linewidths at 4.2 K, under conditions where the exchange energy was comparable with the Zeeman energy, were 3.7 times larger than at 77 K; this compares well with the value of 3.3 predicted by theory and the results show that the 10/3 effect is operative in the liquid helium temperature range.

Acknowledgements

It is a pleasure to express our thanks to C. Savage and T. C. Harcourt for their assistance in specimen preparation. M. D. H. wished to thank the University of Rajshahi, Bangladesh, for the award of a research scholarship.

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Received 6 March and accepted 31 March 1980.