Qatar Univ. Sci. J. (2004), 24 :69 - 78

Strain Broadening of E.P.R. Linewidths in Fe/MgO Single Crystals and Powders

A.S. Al-Hawery*, J.S. Thorp and A.R. Skinner****

* Solid State Physics Group, King Khalid Military Academy,
P.O. Box 26554, Riyadh 11496, Saudi Arabia.

** Physics Department, University of Durham, Durham, U.K.

تأثير عرض الرنين المغناطيسي في مادة الحديد مع أوكسيد المغنيزيوم في حالة البلورة وحالة المسحوق

عبد العزيز الهويري* و جون ثورب** و ألين سكينر**

* مجموعة فيزياء الجوامد، كلية الملك خالد العسكرية
ص . ب : ٢٦٥٥٤، الرياض ١١٤٩٦، المملكة العربية السعودية

** قسم الفيزياء، جامعة درم، إنجلترا

تم قياس الرنين المغناطيسي لمنتصف المقطع الانتقالي لطيف الحديد +٣ في مادة الحديد مع أوكسيد المغنيزيوم على هيئة بلورة وهيئة مسحوق عند تردد ٩ جيجا هيرتز قبل وبعد التسخين، أظهر التسخين عند درجة حرارة ٥٠٠ مئوية خلال يوم كامل للتراكيز المختلفة التي تتراوح بين ٣١٠-١١٩٠٠ (وجزء من المليون) أن عرض خط طيف الرنين المغناطيسي يتغير تبعاً لتغيير التركيز تغيراً واضحاً في حالة البلورة بينما يتغير تغيراً خفيفاً في حالة المسحوق.

Keywords: *E.P.R., Fe/MgO, Crystals.*

ABSTRACT

The E.P.R. linewidth of the $M = +1/2 \leftrightarrow -1/2$ transition of Fe^{3+} spectrum of Fe/MgO single crystals and powders have been measured at 9 GHz before and after annealing. The nominal iron concentrations ranged from 310 to 11900 p.p.m. Specimens were annealed at 500°C up to 24 hours. For single crystal, annealing produced reductions in peak-to-peak linewidth (ΔHpp) which occurred in two stages for all the specimens examined. The values of the first and second decay rates were found to be concentration dependent. For powdered single crystal, annealing produced an increase in the peak-to-peak linewidth (ΔHpp).

1. Introduction

Magnesium oxide is used commercially purely for its refractory properties or as an electrically insulating refractory material. The ion Fe^{3+} usually occupies octahedral symmetry sites in magnesium oxide [1]. Some electron spin resonance (E.P.R.) data on Fe^{3+}/MgO has been reported in the literature [2-7].

In real crystal lattice, distortions are always present. They may arise from a variety of causes including strain, such as that created when the dopant ion and the cation of the host lattice differ in size, point defects, such as vacancies and interstitial ions, planar defects such as stacking faults and dislocations. The combined effect of all types of crystal imperfection is to create a strain field. The strain field may either change the point symmetry at the paramagnetic ion or preserve the point symmetry but change the crystal field parameters slightly. In the former situation any change in the symmetry of the site occupied by a paramagnetic ion will dramatically alter its E.P.R. spectrum. The effect of uniaxial stresses on the paramagnetic spectra of Fe^{3+} in MgO has been discussed by Feher [8].

In this paper we discuss the reduction in linewidth observed in both single crystal and powdered single crystal Fe/MgO specimens which had been subjected to annealing heat treatments in order to remove residual strain arising during the growth by electrofusion [9] of the doped crystals.

2. Results and Discussion

2.1 Experimental results for Fe/MgO single crystals

2.1.1 As-grown specimens, spectra parallel to <100>

Spectra were recorded from all five iron doped MgO single crystals on the Varian V4205-15 spectrometer at room temperature with the magnetic field parallel to a < 100 > -type direction in the crystal. The dopant concentrations in the samples examined were 310, 2300, 4300, 8500 and 11900 p.p.m. by weight.

A typical trace is shown in Figure 1 which refers to a crystal containing 310 p.p.m. of iron. The illustrated spectrum is well known, being first reported by Low [2], and since then by several other groups of workers [2-7]. It is due to the $\Delta M = \pm 1$ transitions of isolated Fe^{3+} ions in sites of octahedral symmetry.

The cubic Fe^{3+} spectrum consists of a central $M = +1/2 \leftrightarrow -1/2$ transition symmetrically surrounded by two pairs of fine structure lines. When H// < 100 >, the inner pair of fine structure lines (corresponding to the $M = \pm 5/2 \leftrightarrow \pm 3/2$ transitions) are located at 2a from the central transition and the outer pair of fine structure lines (corresponding to the $M = \pm 3/2 \leftrightarrow \pm 1/2$ transitions) are located at $\pm \frac{5}{2}$ a from the central transition (where a is the cubic crystalline field splitting parameter).

For all samples, $M = +1/2 \leftrightarrow -1/2$ the line was recorded separately using an expanded magnetic field scale in order to measure its peak-to-peak linewidth and the g-value. The values of g and peak-to-peak linewidth,

$$\Delta H_{M = +1/2 \leftrightarrow -1/2},$$

obtained at each dopant concentration are given in Table 1.

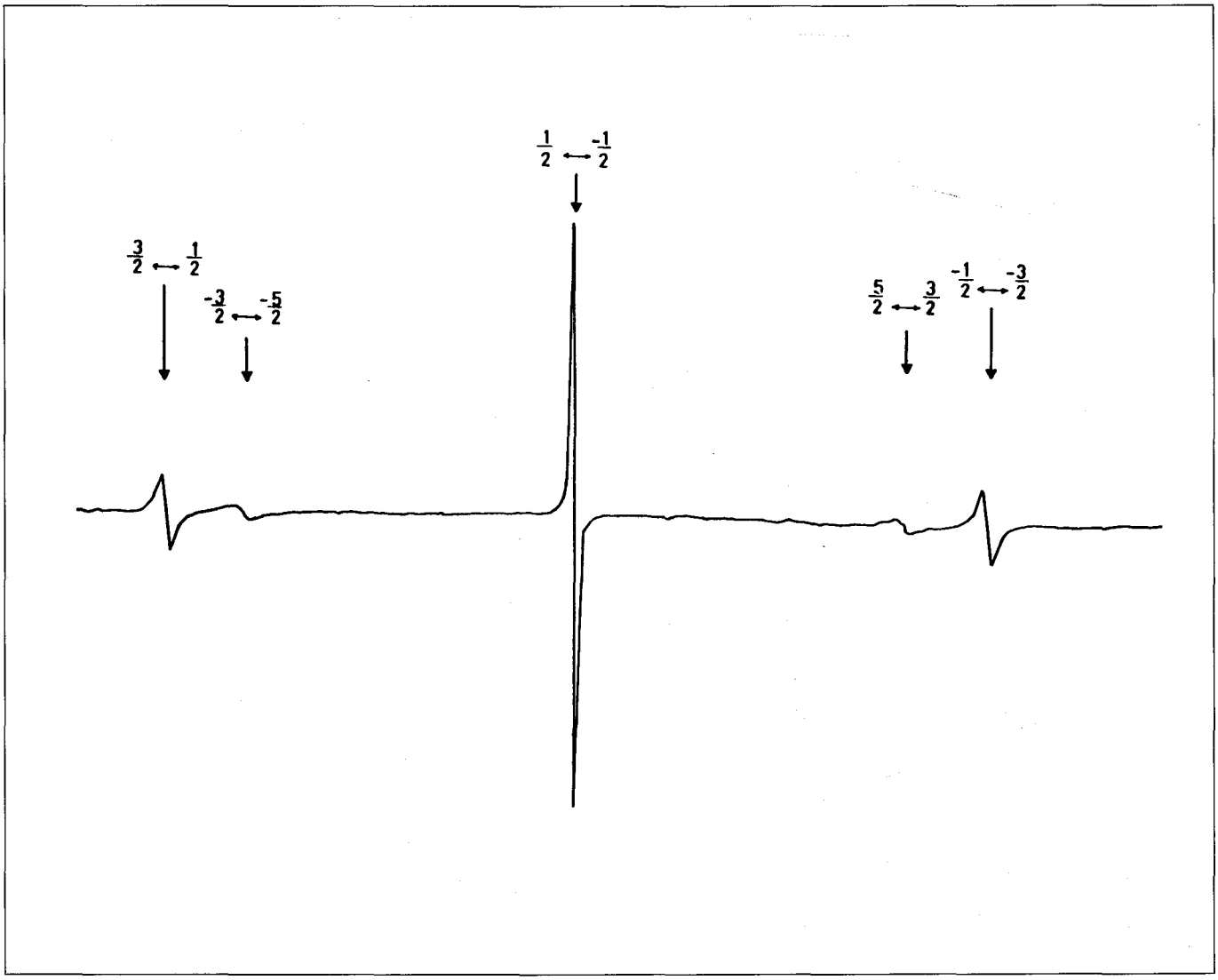

Figure 1: Detail of E.P.R. spectrum of single crystal Fe / MgO: 310 ppm Fe, 300K, H // <100>, 9.3810GHZ

Iron Concentration (p.p.m.)	Linewidth ΔHpp(mT) M = +1/2 ↔ -1/2	g-value	Frequency (GHz)
310	0.508	2.0034	9.3810
2300	0.518	2.0038	9.3810
4300	0.536	2.0032	9.3805
8500	0.557	2.0039	9.3810
11900	0.587	2.0027	9.3805

Table 1: EPR parameters for single crystal Fe/MgO samples; H // <100>, 300K.

An increase in the width of the $M = +1/2 \leftrightarrow -1/2$ transition implies an increase in the concentration of isolated Fe^{3+} ions in cubic sites. This in turn will lead to an increase in the concentration of cation vacancies required to provide electrical compensation for the single excess positive charge, which each Fe^{3+} ion has with respect to the Mg^{2+} ion of the host lattice, which it replaces. Increasing the cation vacancy concentration will also increase the degree of lattice distortion in the crystal thereby enhancing the contribution of strain broadening towards the width of the fine structure lines. So the compensating cation vacancies must be located quite near to the isolated Fe^{3+} ions in cubic sites in order to produce distortion in the regions of the lattice occupied by these ions but not so close that they alter the symmetry of the sites occupied by the Fe^{3+} ions.

2.1.2 Annealing of single crystal Fe/MgO

For heat treatment, each sample was loaded in a boat and placed in the centre of a furnace. A thermocouple was located as close as possible to the sample boat and a temperature controller connected to monitor the required temperature.

The heat treatments were completed at 500°C for different lengths of time for samples containing several different levels of iron, i.e. 310, 2300 and 4300 p.p.m. After each annealing period the samples were allowed to cool down gradually (from 500°C to room temperature through five hours). The g-value and

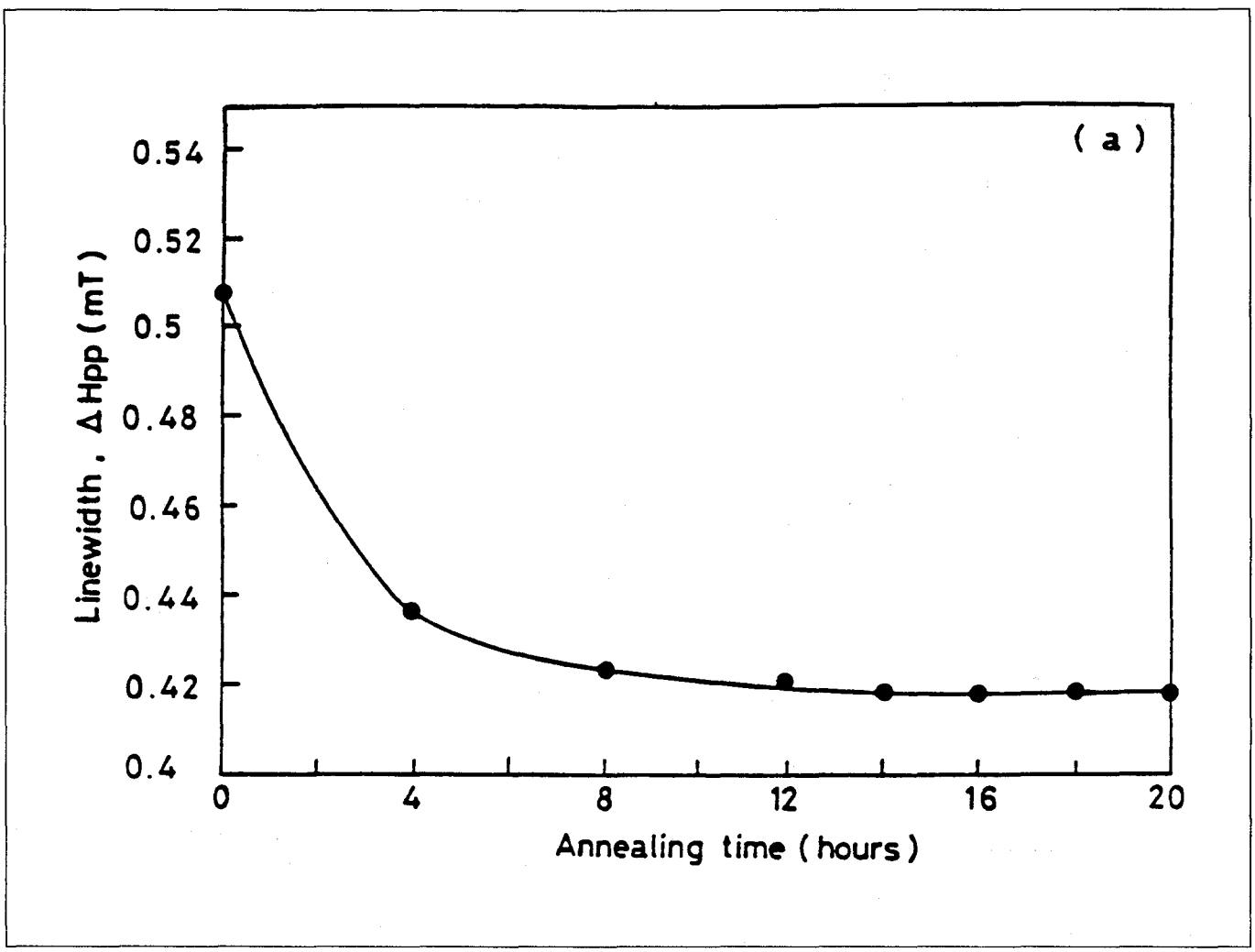

Figure 2a: Variation of linewidth (ΔHpp) with annealing time, single crystal Fe/MgO, 310 ppm Fe, H // <100>, 300K.

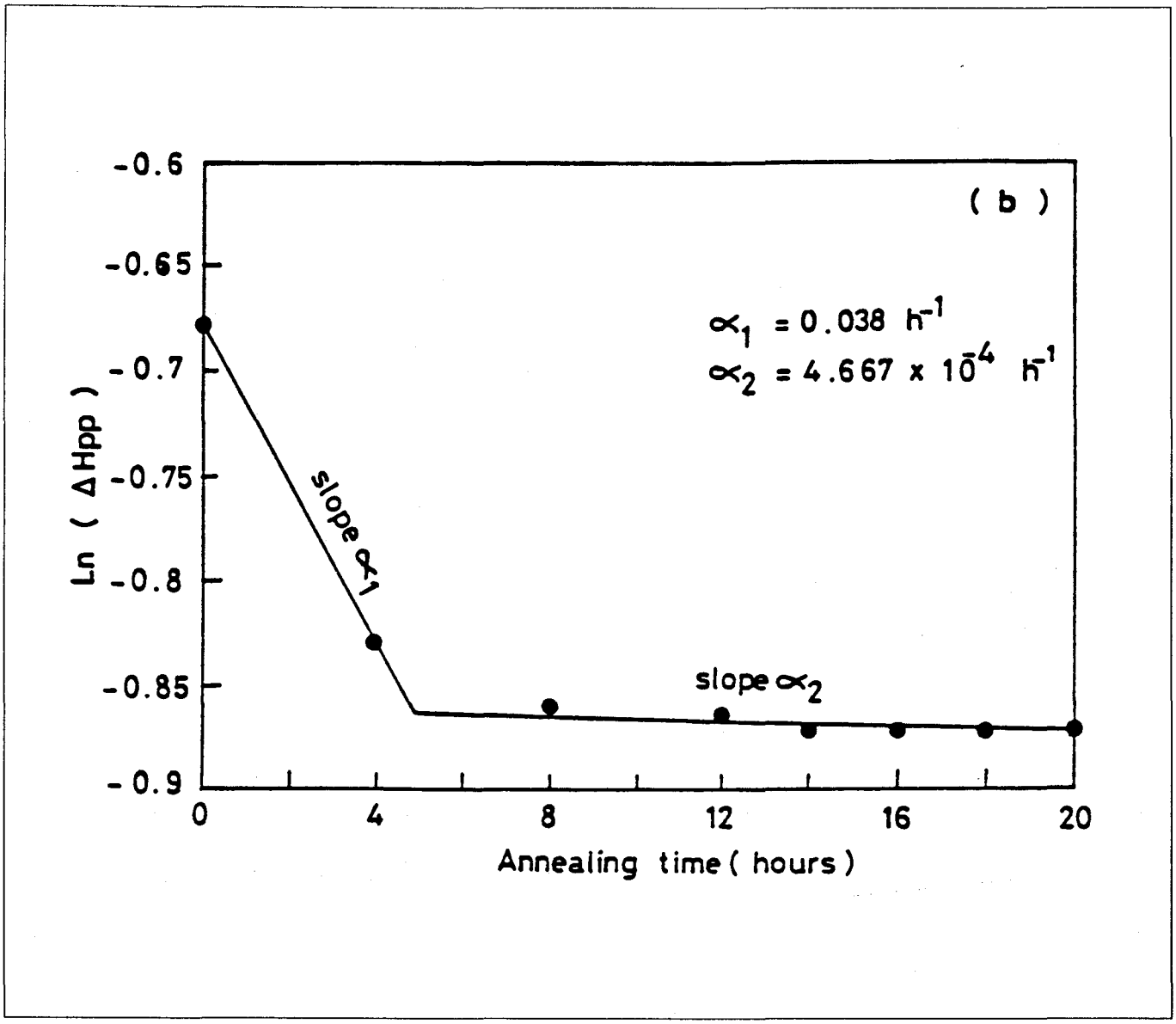

Figure 2b: Variation of Ln (ΔHpp) with annealing time, single crystal Fe/MgO, 310 ppm Fe, H // <100>, 300K.

peak-to-peak linewidth of the central transition, ΔHpp, were measured for each spectrum after each annealing time. There was no change in the g-value but it was found that there was a decrease in the peak-to-peak linewidth, ΔHpp, with annealing time increasing until a constant value was eventually reached. This is shown graphically in Figure 2 which refers to the 310 p.p.m. Fe crystal. It appears from Figure 2a that there was an exponential decay of the form:

$$[\Delta Hpp]_t = [\Delta Hpp]_o \quad \exp(-\alpha t) \qquad (1)$$

where $[\Delta Hpp]_t$ is the peak-to-peak linewidth after heat treatment of t hours, $[\Delta Hpp]_o$ is the peak-to-peak linewidth before heat treatment and α is a constant and may be determined from the slope of the plot of ln $[\Delta Hpp]$ against annealing time t.

This was confirmed by the semi-log plot shown in Figure 2b. It reveals, however, two linear regions of different slopes, representing two separate decay times. Similar annealing experiments were made with two other single crystals, containing 2300 and 4300 p.p.m. Fe, respectively, and the data are shown in Figure 3. Each of these crystals also exhibited a two-stage reduction in linewidth resulting from annealing. The collected decay rate data are given in Table 2.

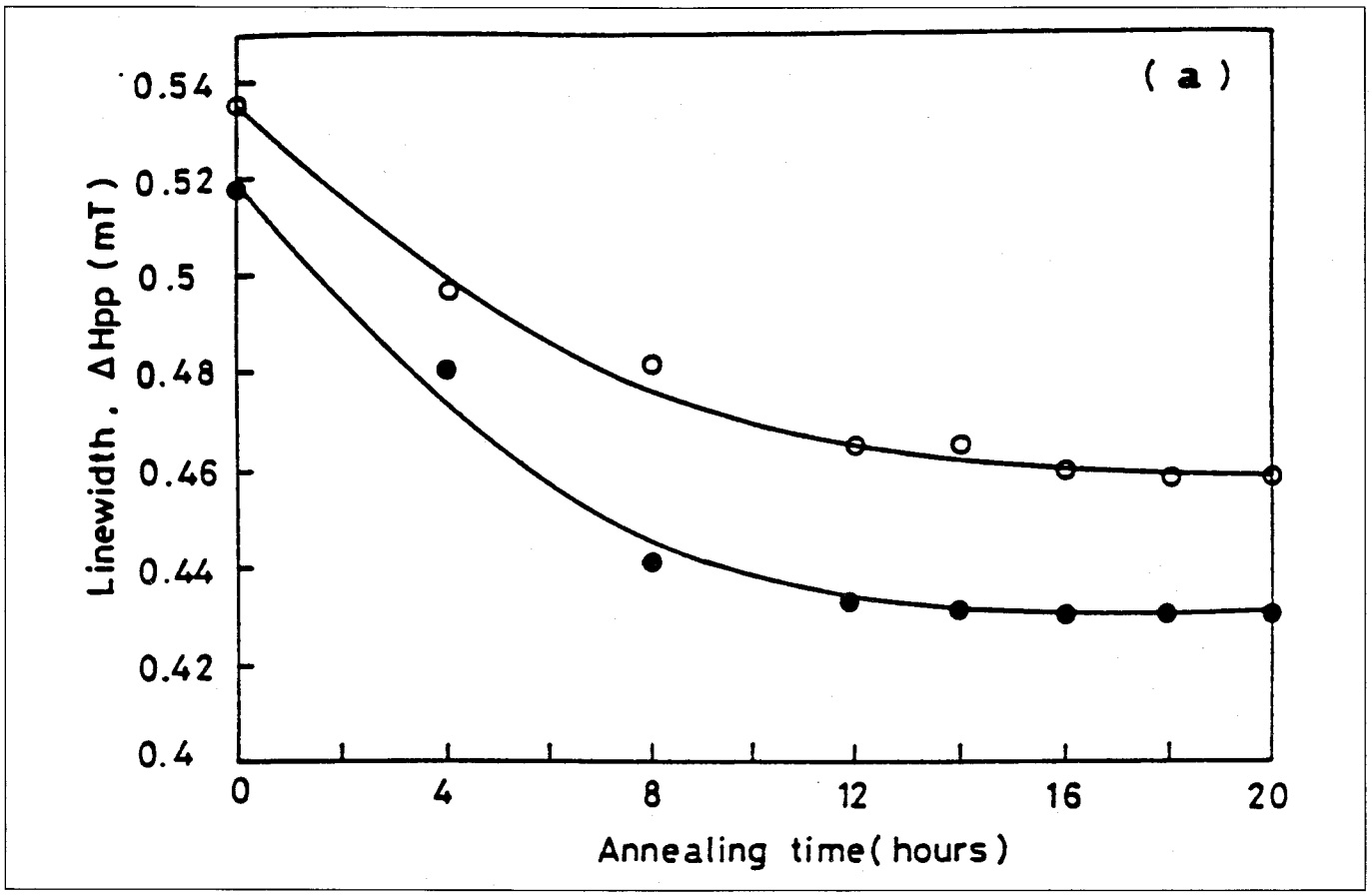

Figure 3a: Variation of linewidth (ΔHpp) with annealing time, single crystal Fe/MgO, 4300 ppm Fe(o), 2300 ppm FE(•). H // <100>, 300K.

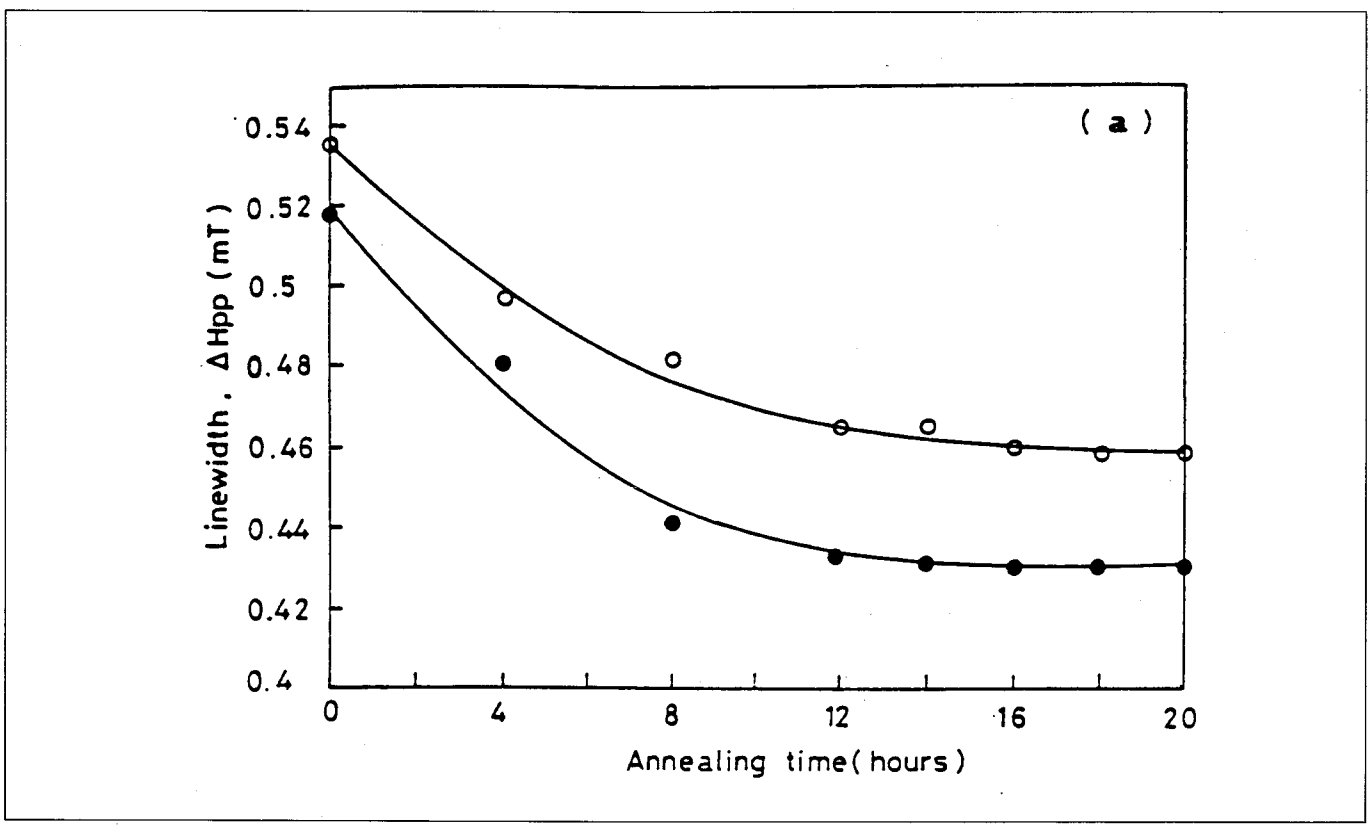

Figure 3b: Variation of ln (ΔHpp) with annealing time, single crystal Fe/MgO, 4300 ppm Fe(o), 2300 ppm FE(•). H // <100>, 300K.

Concentration (p.p.m.)	$\alpha_1(h^{-1})$	$\alpha_2(h^{-1})$
310	0.038	4.666×10^{-4}
2300	0.017	1.2×10^{-3}
4300	0.014	2.1×10^{-3}

Table 2: Values of first and second decay rates for single crystal Fe/MgO.

The contribution of strain broadening towards the width of any given line is proportional to $(2M - 1)^2$ [2]. Therefore, the width of the $M = +1/2 \leftrightarrow -1/2$ line is unaffected by the presence of random internal stresses in the crystal ($(2M - 1)^2 = 0$ for this transition) and the magnitude of the width of this line is attributed to the effects of dipolar interactions between the isolated Fe^{3+} ions in cubic sites. It is proposed that in addition to the line broadening attributable to the effects of dipolar interactions (this source of broadening contributes a component towards the total linewidth equal to the width of the $M = +1/2 \leftrightarrow -1/2$ line) the $M = \pm 3/2 \leftrightarrow \pm 1/2$ and $M = \pm 5/2 \leftrightarrow \pm 3/2$ lines are further broadened because of the presence of random internal strains in the crystals examined (for these lines $(2M - 1)^2 \neq 0$).

The annealing procedure has no effect on the g-value in good agreement with those measured for the corresponding as received single crystals and also with those reported in the literature [1-6]. However, in all cases the width of the $M = +1/2 \leftrightarrow -1/2$ transition is greater whilst the average widths of the fine structure transitions are less in the spectrum of the annealed single crystal than in the spectrum of the corresponding as received single crystal. The annealing process produces an overall reduction in the amount of lattice distortion in the regions immediately surrounding isolated Fe^{3+} ions in cubic sites, thereby leading to an overall reduction in the widths of the fine structure transitions.

2.2 Experimental results for Fe/MgO powders

2.2.1 Characterization of the E.P.R. spectra

Powders were prepared from single crystal chippings of five iron doped MgO samples. The chippings were crushed and powders were sieved through a 185μm mesh. Spectra were recorded from all five powders and comparison with the single crystal spectra shows that the two are almost identical and confirms that the powder spectrum can be identified with isolated Fe^{3+} ions sites of octahedral symmetry.

A typical trace is shown in Figure 4 which refers to a powdered single crystal containing 2300 p.p.m. of iron. A line at a magnetic field value corresponding to g = 1.9800 was clearly visible in all the recorded spectra. This line is due to the isotropic $M = +1/2 \leftrightarrow -1/2$ and $M = \pm 3/2 \leftrightarrow \pm 1/2$ transitions of Cr^{3+} ions in cubic sites which are coincident (it is labelled "Cr^{3+}" in Figure 4).

Five almost equally spaced lines which are also visible in all the recorded spectra have been attributed to the $M = +1/2 \leftrightarrow -1/2$, m transitions of isolated Mn^{2+} ions in sites of octahedral symmetry and are labelled accordingly in Figure 4. Although there are six such lines in the cubic Mn^{2+} spectrum the $M = +1/2 \leftrightarrow -1/2$, $M = +1/2$ transition overlaps with and is obscured by the cubic Cr^{3+} central transition.

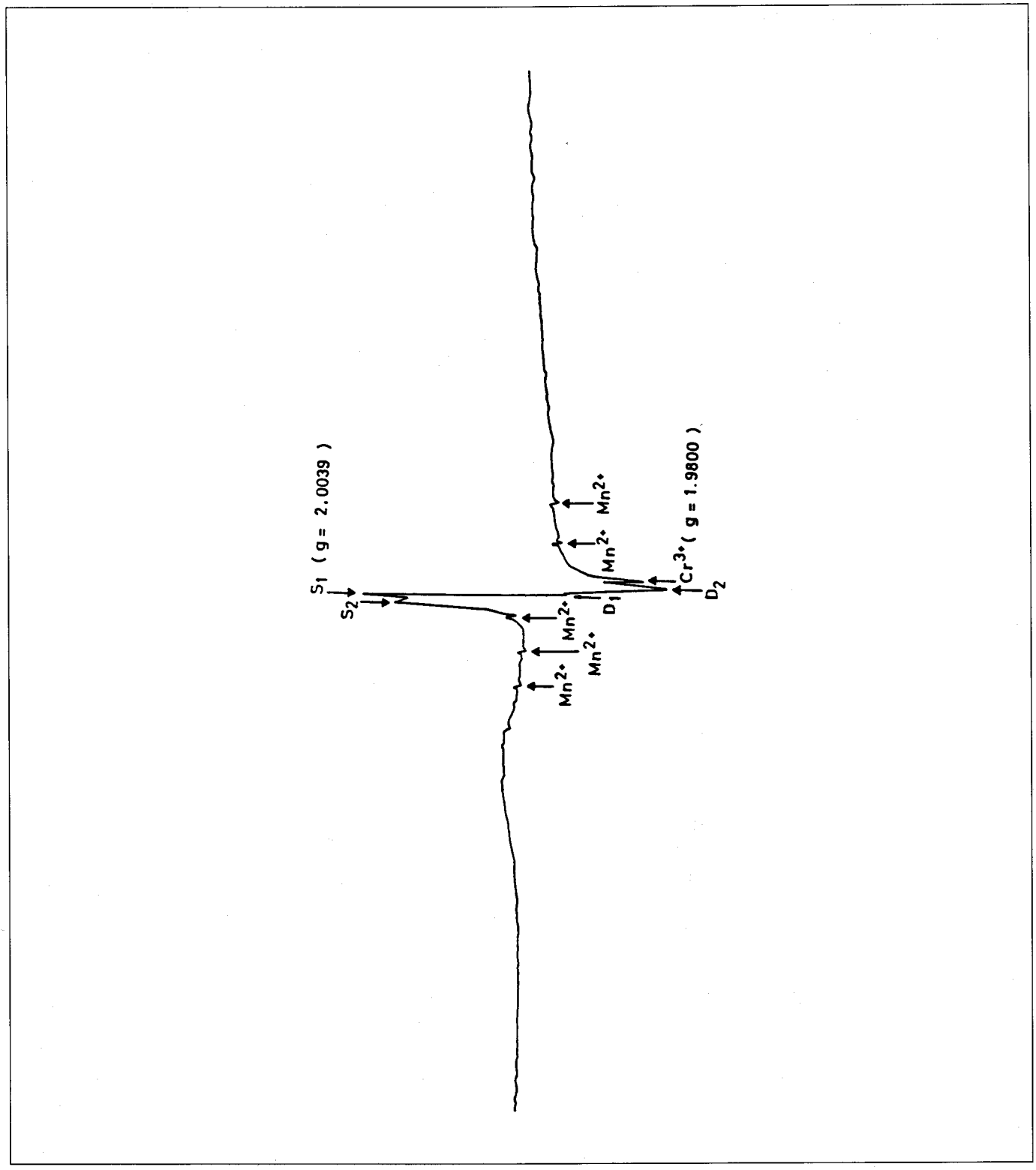

Figure 4: Detail of E.P.R. spectrum of powdered Fe/MgO, 2300 ppm Fe, 300 K, 9.3795 GHz.

The features labelled S_1, S_2, D_1 and D_2 in Figure 4 are all attributable to the $M = +1/2 \leftrightarrow -1/2$ transition of isolated Fe^{3+} ions located in cubic symmetry sites. S_1 and S_2 are shoulders and D_1 and D_2 are divergences in the powder absorption curve of this transition. The shoulders and divergences attributable to the fine structure transitions of Fe^{3+} ions in cubic sites are not observed. This is probably because these transitions are highly anisotropic and so their total intensity is spread out over a wide range of magnetic field. Thus, the features (shoulder and divergences) in the powder absorption curves of these transitions will be

of very low amplitude and it is likely that they are lost in the background noise of the recorded spectra.

The experimentally observed behaviour agrees in principle with the predictions of the simulation procedure discussed by Skinner [10] and Beltran - Lopez and Castro -Tello [11] (namely that the single crystal $M = +1/2 \leftrightarrow -1/2$ transitions of $6_{S5/2}$ ions in a cubic field is split into four components when the sample is powdered).

The g-values given in Table 3 for the three single crystal powdered examined were determined from the magnetic field position of the shoulder S_1 (=H_o) on the experimental spectra since $g = h\nu/\beta H_o$ [2]. The observed separation of D_2 and S_1 (= $49a^2/30H_o + \tau / \sqrt{3}$) in the powder spectrum of each doped sample was used to determine the linewidth, ΔHpp, (= $2\tau / \sqrt{3}$) between points of maximum slope. The values of linewidth, ΔHpp, and g-value agree within experimental error with those obtained from the single crystal samples (Table 1) and also with those published in the literature [1-7,11].

Iron Concentration (p.p.m.)	g-value	D Hpp (mT) M=+1/2 ↔ 1/2	Frequency
310	2.0043	1.642	9.3785
2300	2.0039	0.900	9.3790
4300	2.0027	0.969	9.3785

Table 3: EPR parameters for powdered Fe/MgO Samples, 293K.

Computer simulations of the powder spectrum of Fe^{3+} in octahedral sites in MgO were also undertaken [10]. The values of ΔHpp and g-value determined experimentally from the single crystal spectrum at a particular dopant concentration were used to simulate the powder spectrum at the same dopant concentration. Because of this, the computed powder spectrum at any given dopant concentration should, if the simulation procedure is valid, be identical to the experimental single crystal spectrum at the same dopant concentration. This was found to be the case.

2.2.2. Annealing of powder specimens

The powders doped with 310, 2300 and 4300 p.p.m. of iron were heat treated at 500°C for 24 hours and then gradually cooled down to room temperature over a period of 10 hours.

Analysis of the traces using the method described in the previous section revealed that the heat treatment had no effect on the spectrum of the sample doped with 310 p.p.m. Fe but the heat treatment had modified the spectra of the samples doped with 2300 and 4300 p.p.m. of iron recorded prior to the heat treatment as follows: the relative peak heights of the shoulders S_1 and S_2 were reversed and the linewidth of the isolated Fe^{3+} ion spectrum (deduced from the separations of the features S_1 and D_2) increased (from 0.900 mT prior to heat treatment to 2.043 mT after heat treatment in the case of the sample doped with 2300 p.p.m. of iron and from 0.969 mT prior to heat treatment to 2.942 mT after heat treatment in the case of the sample doped with 4300 p.p.m. of iron). The reversal of the peak heights of the shoulders S_1 and S_2 caused by the heat treatment indicates that, to some extent, it removes lattice strain present in the powders

prior to heat treatment. This is because lattice strain may result in the crystal field parameters (there is only one parameter, a, in the case of the Fe^{3+} spectrum) having a range of distributed values [11] without changing the overall symmetry of the sites occupied by the isolated Fe^{3+} ions (which would drastically alter their E.P.R. spectrum). Hence, as the field position of S_1 is independent of a, whereas that of S_2 is not, in a strained sample S_2 will be broadened and consequently its peak height reduced relative to that of S_1. Removal of the strain by the "annealing" heat treatment sharpens up the shoulder S_2 to the extent that its peak height actually exceeds that of the shoulder S_1. As in the single crystal case, the likely source of the lattice strain is cationic vacancies (required to compensate the single excess positive charge of the Fe^{3+} ions relative to the Mg^{2+} ions of the host lattice) which must be far enough removed from the substitutional dopant ions so as to only distort and not to change the symmetry of the sites they occupy.

3. Conclusion

Analysis of the E.P.R. spectra indicates that, in both the single crystals and powders examined, a small fraction of the dopant exists as isolated Fe^{3+} ions in cubic sites (the Fe^{3+} ions probably substitute for Mg^{2+} ions) and that the remainder of the dopant exists as Fe^{3+} ions clustered together. The regions of the host lattice immediately surrounding isolated Fe^{3+} ions in both the single crystal and powder samples are strained is indicated by the fact that, prior to heat treatment, the fine structure transitions in the single crystal isolated ion spectrum are broader than the $M = +1/2 \leftrightarrow -1/2$ transition and also by the fact that after heat treatment the peak heights of the shoulders S_1 and S_2 are reversed in the powder spectrum of isolated Fe^{3+} ions. The effect of heat treatment upon the isolated ion powder spectrum indicated that, at least to some extent, it relieves the lattice strain in the regions surrounding the isolated Fe^{3+} ions. Further evidence for the "annealing" effect of the heat treatment is provided by the fact that it reduces the widths of the fine structure transitions in the single crystal isolated ion specturm and increase the width of the same fine structure transitions in the powdered specimen.

REFERENCES

[1] **W. Low,** *Proc. Phys. Soc. (London)* **B69** (1956) 1169.

[2] **W. Low,** *Phys. Rev.* **105** (1957) 792.

[3] **J.E. Wertz, J.W. Orton and P. Auzins,** *J. Appl. Phys.* **33** (1962) 322.

[4] **J.S. Thorp, R.A. Vasquez, C. Adcock and W. Hutton,** *J. Mat. Sci.* **11** (1976) 89.

[5] **F.A. Modine, E. Sonder and R.A. Weeks,** *J. Appl. Phys.* **48** (1977) 3514.

[6] **A.D. Inglis and J.S. Thorp,** *J. Mat. Sci.* **16** (1981) 1887.

[7] **A.D. Inlis, G.J. Russell and J.S. Thorp,** *J. Mat. Sci.* **17** (1982) 2939.

[8] **E.R. Feher,** *Phys. Rev.* **136** (1964) A145.

[9] **H.E. Buckley,** *Crystal Growth* (John Wiley, New York, 1951).

[10] **A.R. Skinner,** *Ph. D. Thesis*, Durham University, (1981).

[11] **V. Beltran-Lopez and J. Castro-Tello,** *J. Mag. Res.* **39** (1980) 437.