Electron spin resonance linewidths of Fe$^{3+}$ in magnesium oxide

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Electron spin resonance linewidths of Fe$^{3+}$ in single crystal MgO at 9 GHz were examined experimentally and theoretically for a range of Fe$^{3+}$ concentration. In contrast to the behaviour expected from dipolar broadening the experimental derivative peak-to-peak linewidth for the $\frac{3}{2} \leftrightarrow -\frac{1}{2}$ transition, about 0.6 mT at 77 K and a polar angle of 0°, was independent of concentration from 140 to 8500 ppm. The calculated dipolar linewidths greatly exceeded those observed and values of the ratio of moments $M_1/M_2$ derived from the experimental data lay between 1.33 and 1.48. Optical examination, coupled with heat-treatment experiments, confirmed that the predominant valency state present was Fe$^{3+}$. The data suggested that Fe$^{3+}$ entered the lattice substitutionally, occupying magnesium sites, and that the linewidths were determined by exchange narrowing over the whole concentration range examined.

1. Introduction
Magnesium oxide is widely used commercially, often in its fused or powdered forms, either purely for its refractory properties or, more specifically, as an electrically insulating refractory material. In the latter context, which has been the subject of much work over the past two decades [1, 2], questions still remain as to the possible role of impurities in influencing the electrical properties and breakdown at high temperatures. As part of a further study of some of these effects an investigation has been made of the electron spin resonance behaviour of a number of doped magnesias in an attempt to establish the location of the dopant atoms and so provide specimens of known structural characteristics on which electrical conductivity and dielectric loss measurements might subsequently be made. Some electron spin resonance data on magnesium oxide doped with transition element ions, for example Fe, Co, Cr and Ni has previously been reported in the literature [3] and the characteristic parameters of the spin-Hamiltonian calculated for crystalline fields having cubic symmetry. There is, however, little detailed information available either on the question of the sites actually occupied by the dopant atoms or on the nature of the interactions between the latter.

Information of this nature has recently been obtained in several materials, including doped calcium tungstate [4, 5] and alumina [6, 7], by making a comparison between the observed esr linewidths and those predicted from dipolar broadening. It was decided to adopt a similar approach with iron-doped magnesia. This paper presents the results of the linewidth comparison made for the $\frac{3}{2} \leftrightarrow -\frac{1}{2}$ transition of Fe$^{3+}$.

2. Experimental techniques
The doped single crystals on 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 specimens examined ranged from 140 to 11 900 ppm; these had been determined by optical spectrographic analysis (Johnson–Matthey Ltd) to an accuracy of about 2%. The crystalline quality was good and neither optical examination nor X-ray back-reflection photographs, used to orient the specimens, revealed any evidence of macroscopic cracking, flaws, strain or mosaic formation. The crystals were coloured, varying from pale green at 140 ppm Fe to dark green at 11 900 ppm Fe; optical absorp-
timation spectroscopy revealed features, described in detail later, which were taken as indicative of Fe $^{3+}$. Visual examination showed the coloration, and hence the doping level, to be quite uniform over each of the individual specimens, which typically had dimensions of 9.8 mm x 7 mm x 2.61 mm, chosen, to suit the spectrometer cavity requirement.

The electron spin resonance measurements were made using a conventional 9 GHz spectrometer equipped with phase sensitive detection and giving output spectra in derivative form. Some difficulty was experienced in matching the spectrometer cavity. The match between the input waveguide and the cavity depended quite critically on the size of the specimen and, to a lesser extent, on the doping level and it was found necessary to incorporate a continuously variable matching unit. This consisted of a brass plunger passing through the broad face of a section of rectangular guide mounted immediately above the rectangular TE$_{102}$ cavity, the position of the plunger could be adjusted from the cryostat head. Spectra were recorded, at both 293 and 77 K, by sweeping the magnetic field slowly through a known range. The magnetic field calibrations were obtained using a proton resonance magnetometer system in which the probe could be located exactly in the position normally occupied by the specimen.

3. Experimental results

Initial measurements were made to establish the form of the spectrum in each specimen. An example of this is shown in Fig. 1 which refers to a specimen containing 310 ppm Fe examined at 293 K. The spectrum at $\theta_H = 0^\circ$ shows a total of five lines of which the one centred at about $g = 2$ is the most prominent. The field values at which the transitions occurred were compared with the values expected from the energy level diagram [8, 9]. There was close agreement and on this basis, and in view of the similarity between Fig. 1 and the features of the 1.15 cm region spectrum reported by Low [3], it was felt justifiable to attribute the spectrum to Fe $^{3+}$ in octahedral sites.

Some specimens showed weak additional lines which were thought to be due to impurities. Measurements of the magnetic field values at resonance for the transitions and linewidth determinations were made as functions of polar angle.

The iso-frequency plots showed that, while the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition was nearly isotropic, the other transitions were markedly anisotropic. The variations for the $\frac{3}{2} \leftrightarrow \frac{1}{2}$ and $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$ transitions are depicted in Fig. 2. At angles near $\theta_H = 30^\circ$ and $\theta_H = 60^\circ$ there is overlap with the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition which, by contrast, was found to be much less anisotropic. Low [3] has previously reported

![Figure 1](image1.png)

**Figure 1** Esr spectrum of Fe$^{3+}$/MgO; room temperature, $\theta_H = 0^\circ$, 9.10 GHz, 310 ppm Fe.

![Figure 2](image2.png)

**Figure 2** Isofrequency plot, $\frac{3}{2} \leftrightarrow \frac{1}{2}$ and $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$ transitions, 9.09 GHz.

![Figure 3](image3.png)

**Figure 3** Isofrequency plot, $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition, 9.09 GHz.