THE TEMPERATURE DEPENDENCE OF THE LINEWIDTH OF IRON GROUP IONS IN MgO

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The linewidths of the paramagnetic resonance lines of Fe^{1+}, Fe^{3+} and Mn^{2+} in MgO decrease as a function of increasing temperature in the helium range. This decrease appears to result from a motional narrowing of the contribution to the linewidth from dipolar interaction with Fe^{2+} ions as the Fe^{2+} relaxation rate becomes comparable with the frequency width of the line studied.

THE WIDTHS of electron spin resonance lines in solids provide a measure of the interactions between the magnetic ions and, at elevated temperatures, of spin lattice relaxation rates. Generally linewidths increase monotonically with temperature. We have found that the linewidths of Fe^{1+}, Fe^{3+} and Mn^{2+} in MgO all decrease first as a function of temperature. Here we interpret this decrease in terms of a motional narrowing of the dipolar broadening due to Fe^{2+} also present in these crystals with one order of magnitude larger concentration, and we verify the explanation quantitatively.

A single side-band superheterodyne K-band spectrometer working near 19.4 GHz with a cylindrical TE 011 mode cavity was used in the temperature range from 4.2 to 300°K. Stable temperature settings were assured with a 2.1 at.% AuCo—copper differential thermocouple in conjunction with a propertional heat controller. It consists of a Dial-A-Volt constant voltage source, Keithley 149 milli-microvoltmeter and a Hewlett Packard 6963A power supply for the heater on the covity. A cold-finger cooling system was employed.

The derivatives of the absorption lines were recorded on an x-y plotter then the peak-to-peak separation evaluated. Furthermore, care was taken not to saturate the signals in the low temperature range (over 80 dB attenuation at 100 mW input power. The samples used were machined from nominally 'pure' optical MgO single crystals. They were $1.3 \times 1.4 \times 6$ mm in size with the long axis oriented parallel to a [110] crystal direction. The latter was aligned parallel to the rotation axis of the 9″ Varian magnet. The data shown in Fig. 1 are for $H \parallel [111]$. For this direction there is no strain broadening for the Fe^{1+} ion due to an accidental vanishing spin lattice interaction coefficient $g_5 = 2g_{44}^1$ in MgO. Thus the total width at 4.2°K is due to dipolar broadening.

Approximate impurity ion concentrations were obtained by measuring at 300°K the $\pm 1/2$ lines of Mn^{2+} in the sample MgO and those of a $Mn^{2+}:ZnS$ standard of the laboratory, from which $n(Mn^{2+}) = 1.2 \times 10^{18}$ cm^{-3} was obtained. Then the relative intensity of the $Mn^{2+}:MgO$ line was compared to those of Fe^{3+} at 77°K and the latter to those of Fe^{1+} and Fe^{2+} at 4.2°K. Taking into account the different g-values and transition

probabilities this yielded $n(Mn^{2+}):n(Fe^{3+})$:
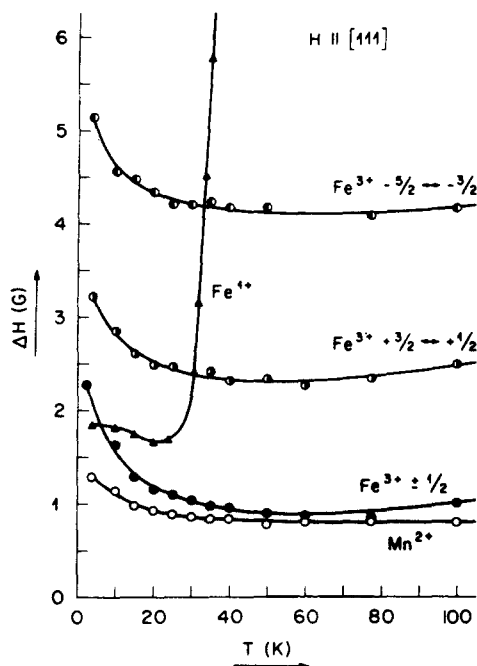$n(Fe^{1+}):n(Fe^{2+}) = 1 : 2 : (0.7 \pm 0.2) : (8 \pm 4)$.

FIG. 1. Linewidth narrowing as a function of temperature of the $\pm 1/2$ lines of Fe^{1+}, Fe^{3+} and Mn^{2+} as well as $+1/2 \rightarrow +3/2$ and $-3/2 \rightarrow -5/2$ of Fe^{3+} for $H \parallel [111]$ in MgO containing $(1 \pm 0.5) \times 10^{19}$ cm^{-3}Fe^{2+} ions.

At low temperatures (below about 15°K) the line widths are primarily determined by the dipolar interactions between magnetic ions in the crystal. In this limit the line widths should be temperature independent. At higher temperatures, above 30°K for Fe^{1+}, the line widths are determined by spin-lattice relaxation, and increase rapidly with temperature. In both these limits the broadening mechanisms are well understood, and agree quantitatively with theoretical estimates. Thus the Kittel—Abrahams method[1] and the estimates of defect concentrations give reasonable estimates of the line-width at low temperatures. Similarly, standard spin-lattice relaxation theory[3] and the observed spin-lattice coupling coefficient for MgO : Fe^{1+} [1] give a relaxation rate consistent with the observed Orbach process.[4]

At intermediate temperatures, however, the linewidths show for Fe^{3+} and Fe^{1+} minima; it is this novel feature we discuss here. We propose

that the minimum appears because the contribution of Fe^{2+} to the dipolar broadening is greatly reduced when the Fe^{2+} relaxation rate becomes sufficiently fast. A similar effect may have been seen before in electron spin resonance,[5] but in this case the effect was inferred, rather than observed directly.
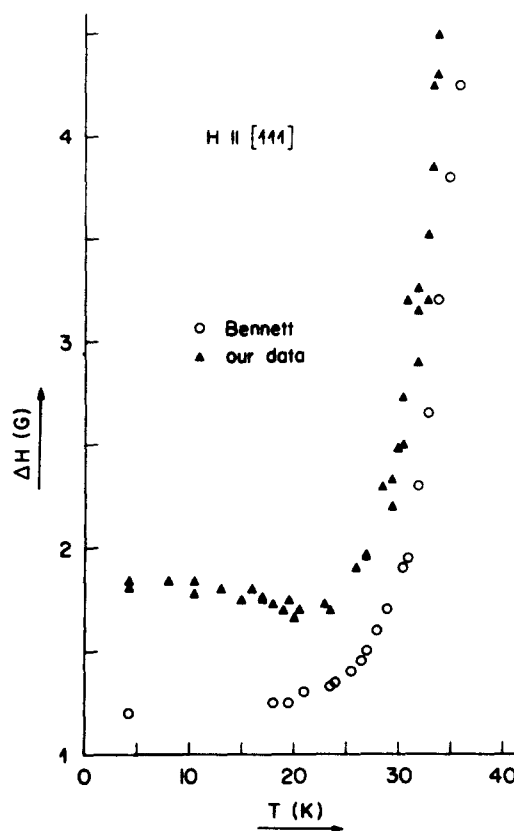

FIG. 2. Comparison of linewidth behavior of Fe^{1+} resonances at $g = 4.15$ for $H \parallel [111]$ in MgO for our sample containing 10^{19} cm^{-3}Fe^{2+} and the results of Bennett containing less than 2.7×10^{18} cm^{-3}Fe^{2+} ions, respectively.

To illustrate the effect, consider the linewidth, ΔH_{obs}, of a spin species I, in the presence of fast relaxing spins S. The spins I undergo transitions every $\tau_{obs} \sim h/(g_I \beta \Delta H_{obs})$ on average, as a result of dipolar interactions and spin-lattice relaxation. At low temperatures the spin-lattice relaxation time spins S, τ_S is much longer than τ_{obs}, and these spins contribute to the dipolar broadening of the I resonance line. As the temperature is raised, τ_S decreases. When

τ_s is much shorter than τ_{obs} the spins S make many transitions among their various spin states between each transition of spins I, and their contribution to the dipolar broadening averages to zero. Simple interpolation formulae exist to describe the effect,[6]

$$\left(\frac{1}{\tau_{obs}(T)}\right)^2 = \left(\frac{1}{\tau_{other}(T)}\right)^2 + \left(\frac{1}{\tau_{obs}^{SI}(0)}\right)^2$$
$$\cdot \frac{2}{\pi} \tan^{-1}\left(\frac{\alpha\, t_s\,(T)}{\tau_{obs}^{SI}(T)}\right)$$

in which α is of order unity. More sophisticated forms are possible, with essentially the same physical content, but this will suffice for our purposes.

The model may be verified in several ways. First, all three ions studied should show the decrease in linewidth at comparable temperatures, with only small differences which reflect differences in g-factors and spin. To within the accuracy of measurement the linewidth reductions become appreciable in the same range of temperature, about 20°K. Secondly, this temperature can be estimated by equating observed spin-lattice relaxation rates[7] to τ_{obs}. The spin-lattice relaxation rate is varying very rapidly in the appropriate temperature range, and the differences between the various measured rates are not important. We find the narrowing should become appreciable between 20 and 25°K. Thirdly we may estimate the extent of the linewidth reduction using the theory of reference 2 extended in a simple way to deal with unlike spins on a lattice which is face-centered cubic. The measured concentration of Fe^{2+} is about $(1 \pm 0.5) \times 10^{-19}/cm^3$ (190 ppm). The predicted dipolar broadening from Fe^{2+} alone is comparable with the observed linewidth reductions of 0.6 G (Mn^{2+}), 1.2 G (Fe^{3+}) and 1.7 G (Fe^{1+}). For Fe^{1+} the whole width can be assumed to come from dipolar interactions for a [111] magnetic field.

Bennett[4] recently measured the spin relaxation rates of Fe^{1+} in MgO. He did not find a line broadening on lowering the temperature for Fe^{1+} in samples containing less than 50 ppm Fe^{2+}, i.e., a concentration of less than $2.7 \times 10^{18}/cm^3$. This means roughly an order of magnitude less

than the Fe^{2+} concentration present in our sample As the sensitivity is about 0.05 G and the broadening effect is of the order of 1 G these numbers are consistent. Figure 2 compares his and our results.

Finally, we observe that the only other explanations of the minimum of which we are aware do not appear to explain the observations. The first also invokes a reduction in the dipolar broadening from another spin species. Blume[8] has observed that the populations of the energy levels of these other ions J may change with temperature. If the excited J states are less effective in dipolar broadening than the states of lower energy, narrowing should occur as the temperature is raised. Whilst there may be species present in iron doped MgO with energy levels separated by suitable amounts[9] they do not appear to be present in a sufficient concentration for this mechanism to be comparable with the one we have proposed. Kemple and Stapleton[10] have observed this mechanism of linewidth reduction recently for Ho^{3+} in yttrium ethyl sulphate.

A second explanation, proposed to us informally on several occasions, interprets the minimum as a result of convolving the Gaussian dipolar-broadened lines with the Lorentzian contribution from spin-lattice relaxation; the argument is that the peak—peak separation of the derivative of the convolved line shape should pass through a minimum as the Lorentz contribution increases from zero. We have verified analytically that this explanation is not valid.

In conclusion, the minimum in the electron spin resonance linewidths studied occurs because that part of the dipolar contribution to the width from fast relaxing spins is motionally narrowed when their spin lattice relaxation rate becomes sufficiently fast. This appears to be the first case in which this effect has been verified in electron spin resonance, although analogous phenomena have been seen in nuclear magnetic resonance.[6] As fast-relaxing impurities are strongly coupled to the lattice, they are sensitive to lattice strains and generally have linewidths which are so large that low concentrations of them are hard to detect. It is possible that the existence and extent of minima in the widths of

them are hard to detect. It is possible that the existence and extent of minima in the widths of slowly-relaxing spins may be used to estimate concentrations of fast relaxing ions also present.

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Die Breiten von paramagnetischen Resonanzlinien von Fe^{1+}, Fe^{3+} und Mn^{2+} Ionen in MgO verschmalern sich in Funktion der zunehmenden Temperatur im Helium Bereich. Diese Abnabme resultiert aus der Bewegungsverschmalerung der Linien-breite, welche aus der Dipol-Wechselwirkung mit Fe^{2+} Ionen herrührt. Im gesamten Bereich wird die Relaxationskonstante vergleichbar mit der Frequenzbreite der untersuchten Linien.