Exchange energies of iron group ions in single crystal MgO

We have evaluated the exchange energy J in Fe^{3+}/MgO from the data previously reported in the literature [1] coupled with further measurements of lineshape for single-crystal specimens containing 2300 and 4300 ppm Fe^{3+}, respectively. The lineshapes for the $+\frac{1}{2}$ to $-\frac{1}{2}$ transition in these specimens, derived by integration of derivative plots recorded at 9.1 GHz, are shown in Fig. 1 which illustrates their Lorentzian shape, the lineshape factors defined as the ratio of the derivative peak-to-peak linewidth (ΔH_{ms}) to the integrated linewidth at half height ($\Delta H_{1/2}$), were 0.479 and 0.57, respectively. Furthermore, the values of the moment ratio $M_4^{1/4}/M_2^{1/2}$ (where M_2 and M_4 are the second and fourth moments of the line) were 1.48 and 1.42, respectively. Consequently, having shown that these two lineshapes were Lorentzian, it was considered justifiable to extend this to all the specimens examined in [1] using a shape factor of 0.57. A similar situation has recently been reported by the authors in Cr^{3+}/MgO [2]. On this basis, values of exchange energy J have been derived and the variation of J with iron concentration is shown in Table I.

A plot of J versus concentration shows a linear dependence up to 4300 ppm Fe^{3+} (Fig. 2). If the Fe^{3+} line is extrapolated to a concentration representing 66.6% of available sites occupied by Fe^{3+} (i.e. to the point corresponding to Fe_2O_3), an exchange energy of 8.59×10^{12} Hz is obtained; this compares well with the value of 10.493×10^{12} Hz for Fe^{3+} in α-Fe_2O_3 obtained from measurements of the intensity of esr pair spectra [3]. We have also calculated the values of Weiss constant θ, (by the method described in [2]) and these are also tabulated in Table I. The Weiss constant is linearly dependent on the dopant concentration in a manner similar to that reported both for Cr^{3+}/MgO [2] and also for Co^{2+}/MgO [4].

The collected data for iron chromium and cobalt can be compared with the predictions of the general rules for the behaviour of the exchange energy for different ions in the same crystal lattice. According to Anderson [5] these are, firstly that the exchange energy for a trivalent ion will be greater than that for a divalent ion and secondly

TABLE I Values of exchange energy and Weiss constant for various concentrations of Fe^{3+} in MgO

Iron concentration (ppm)	Exchange energy, J (GHz)	Weiss constant, θ (K)
140	1.80	3.02
310	4.17	7.00
710	9.72	16.33
2,300	26.05	43.77
4,300	57.53	96.65

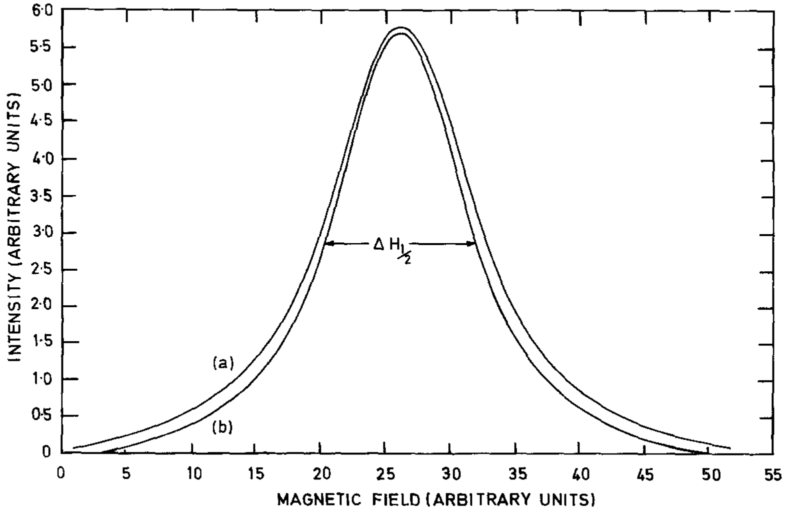

Figure 1 Integrated lineshapes for (a) 2300 ppm Fe, (b) 4300 ppm Fe, 77 K, 9.165 GHz, $\theta_H = 0°$.

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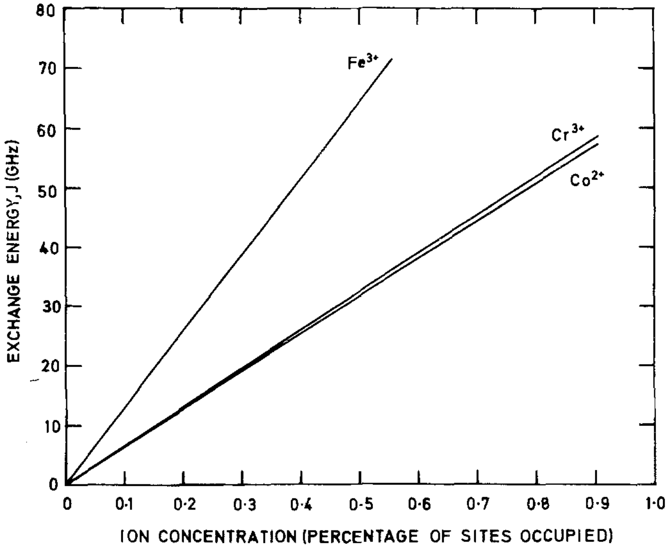

Figure 2 The variation of J with concentration of iron group ions in MgO.

that an ion with a d^5 configuration will have a greater exchange energy than one having a d^3 configuration. Here the comparison has been made by deriving the slopes of the exchange energy-concentration variations for each ion, shown in Fig. 2. The numerical data are given in Table II, and it can be seen that, for any given concentration,

$$J(\mathrm{Fe}^{3+}) > J(\mathrm{Cr}^{3+}) > J(\mathrm{Co}^{2+})$$

and also that the exchange energy for the S-state ion is greater than for the F-state ions.

TABLE II Comparison of data for three iron group ions in MgO

Ion and configuration	Slope Hz (conc.%)$^{-1}$	References
Fe^{3+}, $3d^5$, $^6S_{5/2}$	12.9×10^{10}	This work
Cr^{3+}, $3d^3$, $^4F_{3/2}$	6.57×10^{10}	[2]
Co^{2+}, $3d^7$, $^4F_{3/2}$	6.40×10^{10}	[4]

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J. S. THORP
M. D. HOSSAIN
*Department of Applied Physics and Electronics
University of Durham, UK*