

## DIPOLAR-BROADENING AT ZERO-FIELD

**3.1 Introduction**

The measured linewidth of the magnetic resonance transition is one of the critical parameters which determines the frequency stability and practical accuracy of the frequency reference. In solids, the dominant line broadening mechanism is inhomogeneous dipolar broadening due to the random distribution of spins (*i.e.*, magnetic moments) which causes variations in the local magnetic field throughout the sample.

The theory of dipolar broadening is well established, with the original work by Van Vleck (1948) [1] and Kittel and Abrahams (1953) [2]. The series of papers by de Biasi *et al.* compare theory and experiment for transition metal ions in CaO, MgO, and SrO lattices [2,3,4,5,6,7,8]. The theory presented in [3] takes into account the percentage of exchange coupled pairs. If the exchange coupling is anti-ferromagnetic, the magnetic moment of the pair is zero and does not add to dipolar broadening. At very high concentrations, a different effect is “exchange narrowing” resulting from the rapid diffusion of spins. In this regime, the electrons are delocalized and the hyperfine coupling is no longer observed.

The high-field theory of dipolar broadening assumes that the eigenstates of  $S_z$  are good quantum numbers, which implies that the Zeeman sensitivity of all the transitions is  $2.8 \text{ MHz} / G$ , assuming the electron  $g$ -factor is  $\sim 2$ . As was shown in Chapter 2, the Zeeman sensitivity at zero-field depends on the Landé  $g$ -factor and the quantum number  $m_F$ , and for some transitions the first-order magnetic field sensitivity is zero. As a result, the dipolar linewidths at zero-field vary with the individual transition, and in the magnetic field independent case may not be the dominant broadening mechanism.

### 3.2 Dipolar Broadening of Dilute Paramagnetic Ions at High-Field

The case of  $\text{Cr}^{3+}$  ( $S = 3/2$ ) in magnesium oxide powder is studied in de Biasi (1983) [4], which compares theory and experiment in the high-field case, and includes the effect of exchange coupled pairs. In the case of powders, the results are:

$$\Delta H_{pp} = C_1 A(S) \quad (3.1)$$

The terms in Equation 3.1 are

$$A(S) = \frac{\mu_0 g\beta}{4\pi a^3} \left( \frac{S(S+1)}{1.4 + 0.3(S^2 + S)^{-1}} \right)^{1/2} \quad (3.2)$$

$$C_1 = (\pi\sqrt{7}/15) f_e [S_1(r_c)]^{3/2} [S_2(r_c)]^{1/2} \quad (3.3)$$

$$S_1(r_c) = a^6 \sum_{r_{jk} > r_c} r_{jk}^{-6} \quad (3.4)$$

$$S_2(r_c) = a^{12} \sum_{r_{jk} > r_c} r_{jk}^{-12} \quad (3.5)$$

The variables in Equations 3.2 to 3.5 are the lattice constant is  $a$ , the distance between  $j$  and  $k$  lattice sites  $r_{jk}$ , and the electron spin angular momentum  $S$ . Equation 3.1 calculates the width of the Lorentzian magnetic field distribution to the random distribution of paramagnetic ions in the sample. The summations  $S_1$  and  $S_2$  exclude the radius of exchange coupling. The concentration  $f_e$  is the number of paramagnetic ions which are not exchange coupled. For low concentrations ( $< 1\%$ ), exchange coupling is a minor effect and the width of the magnetic field distribution is linearly proportional to concentration. For magnesium oxide, that lattice constant  $a$  is 4.2112 Å [3],  $g = 1.98$  at high-field and  $S = 3/2$ . The factor  $A(S)$  is therefore (SI units):

$$A(3/2) = 10^{-7} \frac{1.98(9.274 \times 10^{-24})}{(4.2112 \times 10^{-10})^3} 1.592 = 0.0391 \quad (3.6)$$

and for  $S = 5/2$  (e.g.  $\text{Mn}^{++}$ ),

$$A(5/2) = 10^{-7} \frac{1.98(9.274 \times 10^{-24})}{(4.2112 \times 10^{-10})^3} 2.470 = 0.0601 \quad (3.7)$$

The geometric factors  $S_1$  and  $S_2$  are (*c.f.* [3], Table A1), for cubic lattice and assuming the number of the order of each coordination sphere  $n = 5$ , (*i.e.*, the exchange interaction  $n = 5$  nearest neighbor sites), are 0.512 and 0.00219, respectively. Therefore, the factor  $C_1$  is equal to:

$$C_1 = 1.964 f_e (0.512)^{3/2} / (0.00219)^{1/2} = 15.4 f_e \quad (3.8)$$

The expression for the width of the magnetic field distribution is:

$$\Delta H_{pp} = 15.4 f_e \cdot 0.0391 = 0.602 f_e \quad (3.9)$$

where  $f_e$  is the concentration of single paramagnetic ions and the magnetic field units are Tesla.

Therefore, for  $S = 3/2$  ions (*e.g.*,  $\text{V}^{++}$ ) with a concentration of 100 ppm ( $10^{-4}$ ), the calculated dipolar linewidth in MgO powder is 0.602 Gauss. For  $S = 5/2$  ions at 100ppm concentration, the calculated dipolar linewidth is 0.934 Gauss. These calculations can be used to estimate for paramagnetic ion concentration from the measured high-field peak-to-peak linewidths.

### 3.3 Dipolar Broadening at Zero-Field

Figure 1 shows a calculation of the intensities and Zeeman shift for transitions between the  $F = 4$  and  $F = 5$  states of  $V^{++}$  in MgO. The numerical calculation does not take into account variations in the linewidth that results from the variations in the magnetic field sensitivity of individual transitions, but assumes each transition is 100 kHz wide:

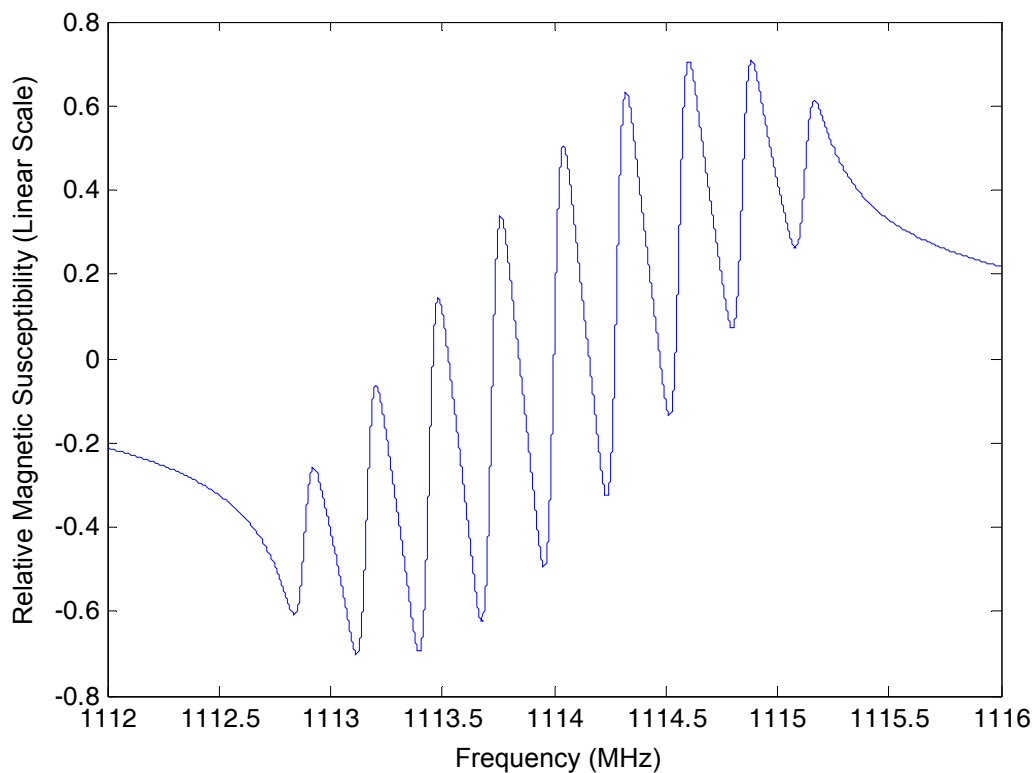


Figure 3.1 Numerically Calculated  $V^{++}/\text{MgO}$  Spectrum Showing Zeeman shift at 1 Gauss

The figure shows that the dispersion spectrum of the  $F = 4$  to  $F = 5$  manifold consists of 9 transition frequencies. The center transition at 1114 MHz is magnetic field independent. For an external field of 1 Gauss, the outermost transitions are shifted by  $\pm 1.12$  MHz, *i.e.*,

$\pm \frac{4}{10} g_S$ , the inner two transitions are shifted by only  $\pm 0.28$  MHz or,  $\pm \frac{1}{10} g_S$ . As a result, the zero-field dipolar linewidths must account for the different Zeeman sensitivities at zero-field. The analysis of the zero-field Zeeman terms was discussed in Chapter 2. Therefore, the dipolar linewidth of the transitions are  $1/10^{\text{th}}$ ,  $1/5^{\text{th}}$ ,  $3/10^{\text{th}}$ , and  $2/5^{\text{th}}$ , the high-field linewidths, and the center transition is independent of dipolar broadening. Assuming the variation in local magnetic field is the same as calculated in Equation 3.9 for the high-field case, and assuming the vanadium concentration is 100 ppm, the zero-field resonance widths are 0, 168 kHz, 336 kHz, 504 kHz, and 672 kHz for  $z$ -polarized transitions.

A more subtle consideration is the modification of the magnetic field distribution width calculated in Equation 3.2. The different Landé  $g$ -factors at zero-field mean the magnetic moment is different for each  $F$ -state. In effect, each group of ions with the same quantum number  $F$  can be considered as a separate species in the analysis, and the overall width of the distribution is the sum of the contribution from each species. Thus, the factor  $g_S$  in Equation 3.2 should be replaced by  $g_F$ , and the electron spin  $S$  by  $F$ :

$$\Delta H = \frac{C_1}{4} \sum_{F=2}^{F=5} A(F) \quad (3.10)$$

and

$$A(F) = \frac{\mu_0}{4\pi} \frac{g_F \beta}{a^3} \left( \frac{F(F+1)}{1.4 + 0.3(F^2 + F)^{-1}} \right)^{1/2} \quad (3.11)$$

Following the calculation shows that for a given vanadium concentration, the width of the dipolar magnetic field distribution at zero-field is a factor of two smaller than at high-field.

An additional consideration is the small crystal field term in the complete Hamiltonian for divalent vanadium in cubic symmetry, Equation 2.1 [9]. The Hamiltonian at zero-field is:

$$H = AI \cdot S + U \left[ S_x^3 I_x + S_y^3 I_y + S_z^3 I_z - \frac{1}{5} (S \cdot I) \{3S(S+1) - 1\} \right] \quad (3.12)$$

Although  $U$  is much less than  $A$ , the additional zero-field splitting represented by the  $S^3$  terms can affect the observed resonance width at zero-field. The measurement of  $U$  and a study of the effects of the term is the subject for future research.

### 3.4 Comparison to Measurement

The article by Bramley (1985) [10] which studied the vanadyl ion at zero-field reports line narrowing due to second-order magnetic field dependent transitions, from 2.3 MHz compared to  $\sim 18$  MHz for transitions with first order magnetic field sensitivity.

The measurement shown below in Figure 3.2 is for a vanadium doped magnesium oxide sample in a static magnetic field of approximately 50 Gauss. The modulation field used in the measurement was approximately 5 Gauss. The measurement validates that for  $V^{++}/MgO$  system, the dipolar linewidth scales with the Zeeman sensitivity. The measured linewidth of the  $m_F = \pm 1$  transitions is half the linewidth of the  $m_F = \pm 2$  transitions, and the  $m_F = \pm 3$  and  $\pm 4$  transitions are seen to be even broader, in accordance with the theory. The magnetic field independent  $m_F = 0$  is barely observed in this particular measurement because of the small modulation field.

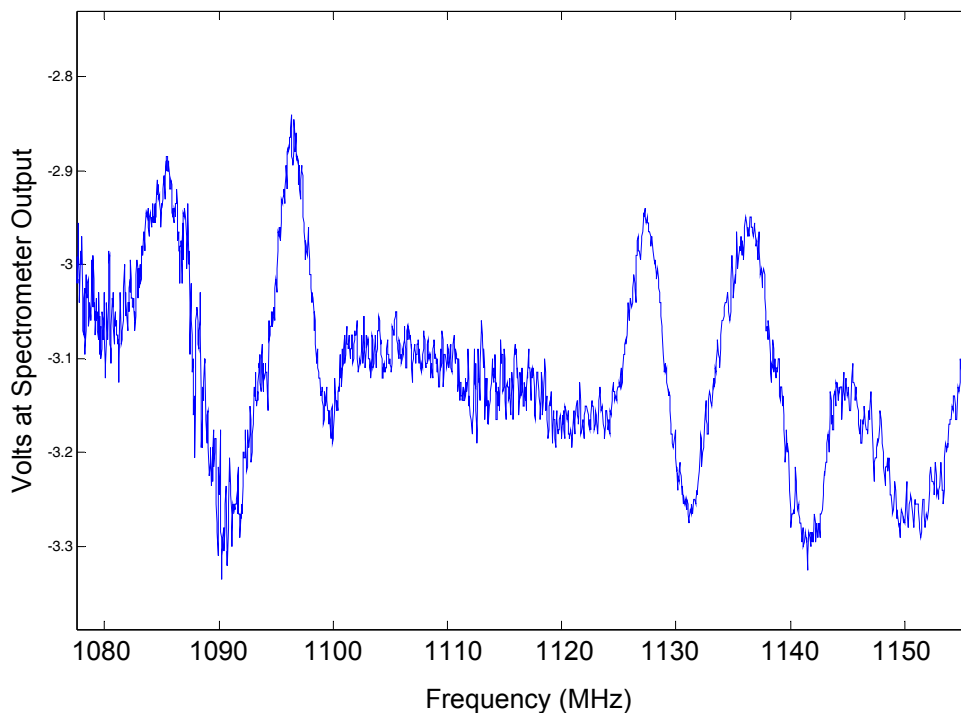


Figure 3.2 Measured V<sup>++</sup>/MgO Spectrum at 50 Gauss Zeeman Field

To resolve the individual transitions, the Zeeman field must be larger than the magnetic field variations in the crystal, *e.g.*, if the random inhomogeneous broadening due to the paramagnetic ions in the crystal is on the order of 1 Gauss, the Zeeman field needs to be several Gauss. This is also a consideration for defining the polarization axis. The magnetic field independent transitions are very insensitive to magnetic fields smaller than the hyperfine constant ( $\sim 70$  Gauss), therefore a modulation field of 100 Gauss or more would be needed to adequately perturb the transition. However, a static field in the range of 50 to 100 Gauss, combined with modulation on the order of 20 Gauss, is one possibility to measure the field independent transition.

A much more interesting technique is to use the “polarization rotation,” *i.e.*, to modulate the quantization axis. As is seen in Figure 2.2 of Chapter 2, the magnetic field independent transition is the most intense transition of the manifold when the RF field is polarized in the direction of the quantization axis, whereas the magnetic field independent transition is the weakest in the perpendicular polarization. Measuring the difference of these intensities by

modulating the quantization axis and hence polarization allow for measured of the magnetic field independent transition using only small modulation field. However, the modulation field significantly larger than internal field distribution causing dipolar broadening, for the two polarizations to be well defined.



## BIBLIOGRAPHY

- [1] J. H. Van Vleck, "The Dipolar Broadening of Magnetic Resonance Lines in Crystals," *Physical Review*, vol. 74, no. 9, pp.1168-1183, Nov. 1948.
- [2] C. Kittel and E. Abrahams, "Dipolar Broadening of Magnetic Resonance Lines in Magnetically Diluted Crystals," *Physical Review*, vol. 90, no. 2, pp. 238-239, Apr. 1953.
- [3] R.S. de Biasi and A A R Fernandes, "The ESR Linewidth of Dilute Solid Solutions," *J. Phys. C: Solid State Phys.*, 16 (1983) 5481-5489.
- [4] R. S. de Biasi and A. A. R. Fernades, "Measurement of Small Concentrations of Cr and Mn in MgO Using Electron Spin Resonance," *Communications of the American Ceramic Society*, September 1984 pp. C-173 – C-175.
- [5] R. S. de Biasi and M. L. N. Grillo, "Influence of Manganese Concentration on the ESR Spectrum of  $Mn^{2+}$  in CaO," *Journal of Alloys and Compounds*, 282, (1999), pp. 5-7.
- [6] R.S. de Biasi, M.L.N. Grillo, "Influence of Manganese Concentration on the ESR Spectrum of  $Mn^{2+}$  in SrO," *Journal of Alloys and Compounds* 290 (1999) 22-24
- [7] R. S. de Biasi, and M. L. N. Grillo, "Influence of Copper Concentration on the ESR Spectrum of  $Cu^{2+}$  in MgO," *Journal of Alloys and Compounds*, 302, 2000, pp. 26-28.
- [8] R. S. de Biasi and M. L. N. Grillo, "Influence of Gadolinium Concentration on the ESR Spectrum of  $Gd^{3+}$  in SrO," *Journal of Alloys and Compounds*, 337, 2002, pp. 30-32.
- [9] R. S. De Biasi, "Influence of the  $S^3$  Term on the EPR Spectrum of  $Cr^{3+}$  in Cubic Symmetry Sites in MgO," *Journal of Magnetic Resonance*, vol. 44, pp. 479-482, 1981.
- [10] Richard Bramley and Steven J. Strach, "Zero-Field EPR of the Vanadyl Ion in Ammonium Sulfate," *J. of Magnetic Resonance*, vol. 61, pp. 245, 1985.