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Abstract. Antiferromagnetic resonance has been observed in single crystals of gadolinium vanadate at frequencies of 0.035, 17, 24 and 34 GHz. At 1.36 K the frequency at zero applied magnetic field is 30.61(2) GHz, and its variation when a field is applied along the c-axis is compared with the predictions of mean field theory. A detailed comparison with a range of magnetic measurements on this model compound shows that overall agreement with mean field theory can only be obtained within about 10%. The variation of the field for resonance has also been determined at a range of angles including 90° from the c-axis.

1. Introduction

Gadolinium vanadate, GdVO₄, is a tetragonal paramagnet with the zircon structure $I4_1/amd$. The dimensions of the unit cell are $a = 0.72126$ nm, $c = 0.63485$ nm; it contains four gadolinium ions, all magnetically equivalent. Detailed magnetic measurements (Cashion et al 1970) on a single crystal show that it becomes a simple antiferromagnet below $T_N = 2.495$ K, with two sub-lattices, magnetized parallel and anti-parallel to the c-axis. Magnetic measurements have also been made by Mangum and Thornton (1972), and the attenuation of ultrasonic waves at 9 GHz has been studied in detail by Page and Rosenberg (1977). In terms of an exchange field B_E and an anisotropy field B_A, values have been determined for (a) the two fields required to reach saturation magnetization:

$$2B_E - B_A \qquad \text{along the } c\text{-axis} \qquad (1)$$
$$2B_E + B_A \qquad \text{normal to the } c\text{-axis} \qquad (2)$$

together with (b) the field for spin-flop:

$$B_{SF} = [B_A(2B_E - B_A)]^{1/2}. \qquad (3)$$

This paper reports a further measurement, the observation of antiferromagnetic resonance in single crystals of gadolinium vanadate. The field corresponding to antiferromagnetic resonance was assumed by Cashion et al to be given by

$$B_{AFR} = [B_A(2B_E + B_A)]^{1/2}$$

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but when an external field B is applied along the c-axis the full expression for the resonance frequency f becomes

$$hf/g\mu_B = [B_A(2B_E + B_A) + (aB/2)^2]^{1/2} \pm B(1 - a/2). \tag{4}$$

On mean field theory, the parameter a = ratio of the principal magnetic susceptibilities, parallel to perpendicular. The ground state of the Gd^{3+} ion is $^8S_{7/2}$, with g = 1.991 (isotropic). The spin Hamiltonian

$$\mathcal{H} = g\mu_B(B \cdot S) + D[S_z^2 - (1/3)S(S + 1)] \tag{5}$$

includes only the most important crystal field splitting term, which makes a contribution to the anisotropy field B_A of the same order as that from dipolar interactions between the gadolinium ions. The latter is calculated to be equivalent to a field of 0.221 T; since D was unknown, Cashion *et al* (1970) assumed a value $(D/g\mu_B) = 0.15$ T to fit their anisotropy field of $B_A = 0.37$ T. Subsequently, values of D have been obtained by electron spin resonance of the Gd^{3+} ion, in three dilute vanadates with the same crystal structure, but slightly different lattice constants (Mehran and Stevens 1982). Interpolation in their figure 6 for the ratio $c/a = 0.880_1$ appropriate to $GdVO_4$, gives $D = 3B_2{}^0 = 0.0513$ cm^{-1}. From this value, the relation (Cashion *et al*)

$$2SD = g\mu_B B_{cf}$$

leads to $B_{cf} = 0.386$ T; crystal field terms of higher order produce differences only of about 5%. This is close to the value of 0.38 T assumed by Mangum and Thornton, and the anisotropy field B_A becomes $0.386 + 0.221 = 0.607$ T, considerably larger than that of Cashion *et al*.

2. Antiferromagnetic resonance

Electron spin resonance using single crystals of $GdVO_4$, at frequencies of about 17, 24 and 34 GHz and temperature 1.36 K, shows a strong signal, ascribed to antiferromagnetic resonance (AFR). Measurements as a function of magnetic field B, applied along the c-axis, have been made using several rectangular parallelepipeds, and for an ellipsoid with approximate dimensions $1.7 \times 0.5 \times 0.4$ mm. These results are shown in figure 1, where the values of the resonance frequency f are plotted for values both above and below that for zero applied field.

The points lie on a straight line; from the slope, $g(1 - a/2) = 1.928$, and hence the value of the parameter a, which should fall to zero at 0 K, is found to be $a = 0.064$ at 1.36 K. With this value, the term $(aB/2)^2$ in equation (2) is negligible, amounting only to $\sim 0.1\%$ at $B = 1$ T; this confirms that no appreciable deviation from a straight line would be expected. An earlier measurement at the much lower frequency of 0.035 GHz shows an intense absorption at $B = 1.06$ T along the c-axis, at 1.6 K. This may be converted to a value for 1.36 K by assuming that it varies as the sub-lattice magnetization m. From the vanadium NMR measurements of Bleaney *et al* (1981, 1982), the reduced value m/m_0 can be represented (up to 1.9 K) by the relation

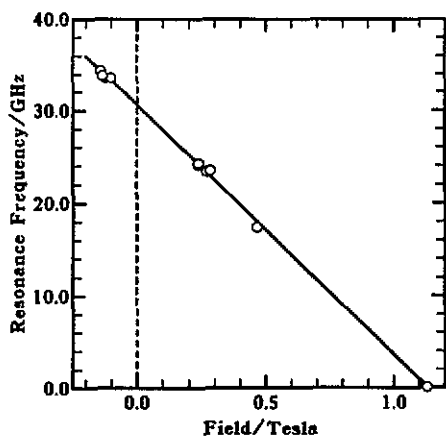$$m/m_0 = 1 - 0.0443T^2 - 0.00492T^4 + \ldots \tag{6}$$

Figure 1. Plot of the measured values of the antiferromagnetic resonance frequency against the field B (in tesla) applied along the c-axis, in single crystals of gadolinium vanadate. Values for frequencies above the the antiferromagnetic resonance frequency in zero field are shown to the left of $B = 0$. The resonance frequency in zero field is 30.61(2) GHz.

from which $m/m_0 = 0.8534$ at 1.6 K and 0.9012 at 1.36 K. Hence the resonance field of 1.06 T at 1.6 K should correspond to 1.12 T at 1.36 K. Combined with the points at the high frequencies, this agrees with the effective g-value of 1.928, and $a = 0.064$. An advantage of the AFR measurement is that the bulk magnetic moment of the specimen is always small, so that demagnetizing corrections can be neglected. This is confirmed by the points in figure 1, which show no systematic deviations between the samples of different shape.

The line widths (peak–peak in the differential of the absorption curve for the ellipsoid) are about 0.1 T at 34 GHz, 0.06 T at 24 GHz, 0.08 T at 17 GHz and 0.05 T at 0.035 GHz. In spite of these line widths, the various samples each give an intercept at $B = 0$ close to 30.6 GHz, corresponding to $B_{AFR} = 1.10$ T at 1.36 K. The results for finite temperature may be extrapolated to $T=0$ K by assuming that they vary as the sub-lattice magnetization m. Division of 30.6 GHz by $m/m_0 = 0.901$ gives 34.0 GHz for $T = 0$ K, equivalent to $B_{AFR} = 1.220$ T. This procedure is open to criticism, because B_A has an appreciable contribution from the the crystal field splitting B_{cf} that does not vary as m/m_0. Also, the relation used by Cashion *et al* is valid only if the crystal field terms are small compared with the magnetic splitting; this is not the case if D is as large as suggested by the ESR measurements on the diluted compounds. Antiferromagnetic resonance has also been observed for the ellipsoid with magnetic field rotated away from the c-axis. At 33.86 GHz and 1.35 K the resonance field rises from 0.134 T to 0.739 T, and at 23.533 GHz and ~1.4 K from 0.283 T along the c-axis to 0.694 T at an angle of 58° from the c-axis. Normal to this axis, the resonance frequency should be given by equation (16) of Keffer and Kittel (1952):

$$(hf/g\mu_B)^2 = 2B_E B_A + B_A{}^2 + B^2/2 \pm (B_E + B_A)B^2/2B_E$$
$$= B_{AFR}{}^2 + (B^2/2)[1 \pm (1 + B_A/B_E)]. \tag{7}$$

From a resonance measurement, $B^2/2 = (0.74)^2/2 = 0.274$ T² at 33.65 GHz. This is higher than the AFR frequency of 30.6 GHz and corresponds to the plus

sign in (7). To fit the measured value of B_{AFR}, the last term $(B^2/2)[2 + B_A/B_E]$ must be only 0.249 T^2; clearly agreement cannot be obtained whatever the value of B_A/B_E. These formulae depend on the assumption that the angle θ between the magnetic moments of each sub-lattice and the c-axis is small, a condition that is not well fulfilled. Figure 3 of Cashion *et al* suggests that at 0.74 T, the magnetization is about 0.25 of its maximum value, for which θ is about 14°.

3. Discussion

There are two experimental quantities that need no correction for the demagnetizing field. One is the frequency at which antiferromagnetic resonance occurs in zero applied field, which gives the value of

$$B_{AFR} = [B_A(2B_E + B_A)]^{1/2}.$$

The other is the field at which spin-flop occurs:

$$B_{SF} = [B_A(2B_E - B_A)]^{1/2}$$

The two measured values, extrapolated to 0 K, are 1.22 T and 1.08 T respectively; these may be combined to give $B_A = 0.401$ T and $B_E = 1.655$ T. Then the values of the fields $2B_E + B_A$ and $2B_E - B_A$, required to reach the saturation moment normal to and along the c-axis respectively, are 3.71 T and 2.90 T, considerably higher than the direct measurements of 2.92 T and 2.18 T (Cashion *et al*).

An alternative is to combine these two last fields with the value of $B_A = 0.607$ T, giving

$$B_{AFR} = [B_A(2B_E + B_A)]^{1/2} = [0.607(2.92)]^{1/2} = 1.33 \text{ T}$$

$$B_{SF} = [B_A(2B_E - B_A)]^{1/2} = [0.607(2.18)]^{1/2} = 1.15 \text{ T}.$$

The former corresponds to an antiferromagnetic resonance frequency of ~ 37.1 GHz at 0 K. Again, these values are somewhat larger than those of Cashion *et al* (extrapolated to 0 K):

$$B_{AFR} = 1.205 \text{T}, (f = 33.6 \text{GHz}) \qquad \text{and} \qquad B_{SF} = 1.08 \text{ T}.$$

In conclusion, the various measurements show that it is difficult to obtain precise overall agreement with the formulae of mean field theory. A further point is that the value of the parameter a, determined from the variation of the frequency with field applied along the c-axis, is only 0.064, much smaller than the ratio 0.37 of the principal susceptibilities, to which it should be equal on mean field theory. The discrepancy cannot be attributed to experimental error in the values of the susceptibility along the c-axis, since these agree well with the variation of the moment, as determined from the nuclear resonance frequency of the vanadium ions (see Bleaney *et al* 1981).

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