EPR and Magnetization of GdGa$_2$

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Paramagnetic resonance and magnetic measurements were performed on powdered samples of GdGa$_2$. The magnetic data indicated ferrimagnetic behavior with $T_c \simeq 181^\circ$ K. Above 250° K the susceptibility obeys the Curie–Weiss law $\chi_g = 2.66_2 \times 10^{-2}/(T - 27.6)$ emu/g–Oe which corresponds to an effective moment of 7.95 Bohr magnetons. Over the range from 190 to 300°K the data obey a Néel type law, $\chi_g^{-1} = 35.95 \ (T - 12.5) - 2.20 \times 10^4/(T - 177)$, which is indicative of ferrimagnetic order. The resonance measurements were performed at 9.013 gHz at 247, 296, and 349° K. The spectra were analyzed with a computerized curve-fitting technique that involves a linear combination of Lorentzian absorption and dispersion susceptibility components. Following demagnetization corrections, the g-factor was found to be 1.983$_2$ while the half-power, half-linewidth was 592.7 Oersteds.

Introduction

Studies of the magnetic properties of the gadolinium ion in various intermetallic compounds involving elements from column IIIA has shown a variety of behaviors, typical of which are: GdB$_6$ is antiferromagnetic (*1*), GdAl$_2$ is ferromagnetic (*2*), and GdIn$_3$ is antiferromagnetic (*3*). In the Gd–Ga system four phases have so far been identified GdGa, GdGa$_2$, Gd$_3$Ga, and Gd$_3$Ga$_2$ (*4*). Among these compounds GdGa has been reported as ferromagnetic (*5*), Gd$_3$Ga$_2$ is antiferromagnetic (*6*), while as reported herein GdGa$_2$ appears to be ferrimagnetic.

The structure of GdGa$_2$ is hexagonal of the AlB$_2$ type. This is a layered structure with alternating planes of Gd and Ga atoms arranged perpendicular to the c-axis. Haszko (*7*) reported lattice constants of $a = 4.219$ Å and $c = 4.135$ Å, with Ga–Ga and Gd–Ga separations of 2.44 and 3.20 Å, respectively. Baenziger (*8*) found similar data with $a = 4.221$ Å and $c = 4.141$ Å.

In this paper we report magnetization data as well as results for the EPR parameters; e.g. g-factor, g-shift, linewidth, and lineshape.

Experimental Details

The magnetic data were obtained with a Faraday balance that has been described in detail elsewhere (*9*). Basically, it consists of a Cahn Model RG electronic balance and a Varian Model 4005 electromagnet. The associated cryogenic apparatus includes features that make it possible to acquire data at temperature intervals of less than 0.25°K on small samples; typically less than 3 mg as in this experiment. Temperatures were determined by two four-terminal resistance thermometers whose calibrations are traceable to the National Bureau of Standards (U.S.A.). The overall system accuracy is better than 0.5% based on calibration against a spectroscopically standardized sample of Gd$_2$O$_3$.

The X-band spectrometer is a conventional, reflection type design that employs a cavity-locked frequency control circuit to maintain klystron frequency to within 5 ppm during a typical 30-min resonance scan. The detection system utilizes a PAR Model HR-8 lock-in amplifier operating at 100 kHz. The modulation field intensity at the sample is approximately 1 Oe peak-to-peak. A gold-plated

TE_{102} rectangular cavity with iris coupling has been designed so that a finger dewar can be inserted through its narrow wall with its cylindrical axis perpendicular to the applied field. The dc field is supplied by a Harvey–Wells Model L-92 electromagnet that has high current stability and adjustable homogeneity. An NMR gaussmeter is used to determine the applied field at the sample to within 0.2 Oe. Nonambient temperature spectra were obtained with chilled xylene (247°K) and heated mineral oil (349°K).

The samples were prepared from gadolinium and gallium metals obtained from Leico Industries, Inc. and Metals Research Limited, respectively. The stated purities were 99.9 and 99.999 %. The samples were prepared in a nonconsumable electrode arc-melting furnace and then homogenized in a vacuum furnace at 0.1 microns for 3 days at 700°C. X-Ray diffraction patterns of the samples showed only lines of the desired $GdGa_2$ phase. The lattice constants were found to be $a = 4.221$ Å and $c = 4.145$ Å in very close agreement with those of Baenziger and Moriarty (8).

Both the magnetization and EPR samples were in the form of finely ground powders of approximately 325 mesh. The EPR samples were loosely packed into capillary tubes of 1 mm diameter. Multiple EPR scans were obtained at each temperature, and with different sample orientations, to help insure the reliability of the data.

Results and Analysis

The inverse mass susceptibility of $GdGa_2$ is shown in Fig. 1. Above 250°K the experimental data can be accurately fitted to a Curie–Weiss law of the form $\chi_g = 2.66_2 \times 10^{-2}/(T - 27.6)$ emu/g-Oe. The corresponding moment is 7.95 Bohr magnetons in very close agreement with that of the free Gd^{3+} ion. Further, the data above 190°K can be fitted to a Néel law of the form

$$\chi_g^{-1} = \frac{(T - 12.5)}{2.78 \times 10^{-2}} - \frac{2.20 \times 10^4}{(T - 177)} \qquad (1)$$

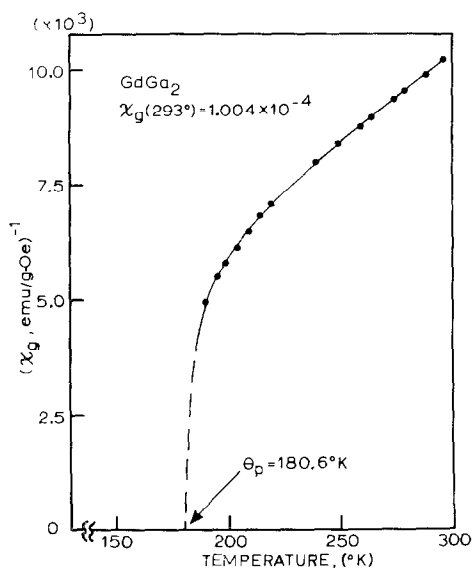which is indicative of ferrimagnetic order below 181°K.

Fig. 1. Inverse mass susceptibility of $GdGa_2$ versus temperature. Solid circles show the experimental data while the curve is a Néel-type equation with empirically adjusted parameters.
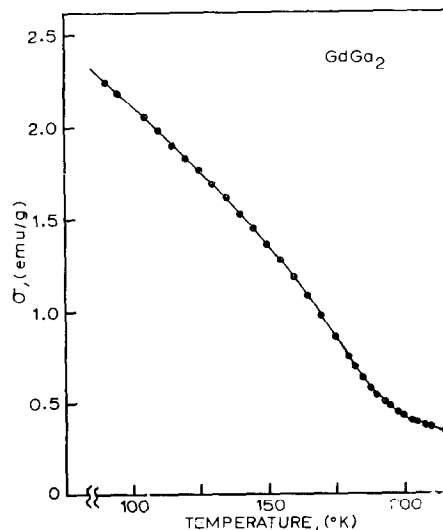

Fig. 2. Magnetization of $GdGa_2$ versus temperature. The applied field was 3230 Oersteds. The ferrimagnetic Curie temperature was determined by several methods to be 181°K.

The specific magnetization is shown in Fig. 2. The inflection point of the curve, as determined from large scale plots of the data,

occurs at 180°K in good agreement with the paramagnetic Curie temperature $\theta_p = 180.6$ K from the Néel law. Further, plots of σ^2 versus T for applied fields of 1360 and 3230 Oe, linearly extrapolated to zero magnetization, yielded ferrimagnetic Curie temperatures of 181.2 and 180.1°K, respectively, in good agreement with the Néel law. The shape of the curve and the small values of magnetization support the existence of ferrimagnetic order in GdGa$_2$; however, it is difficult to understand this type of order arising in GdGa$_2$ with its C32 structure in which all gadolinium sites are crystallographically equivalent. There is a possibility that the small magnetization results from excess gadolinium but this could not explain the relatively high Curie temperature of 180°K nor the shape of the susceptibility data just above T_c. Thus on the basis of the experimental data, ferrimagnetic order seems to exist but confirmation of the ordering pattern must await additional collaborative data.

A typical derivative resonance curve for GdGa$_2$ is shown in Fig. 3. These data were obtained at 296°K with a field sweep rate of 115 Oe/minute and an amplifier time constant of 0.1 seconds. The markers on the curve are the NMR reference field intensities used to calibrate the field axis. Curves of similar quality were obtained at 247 and 345°K.
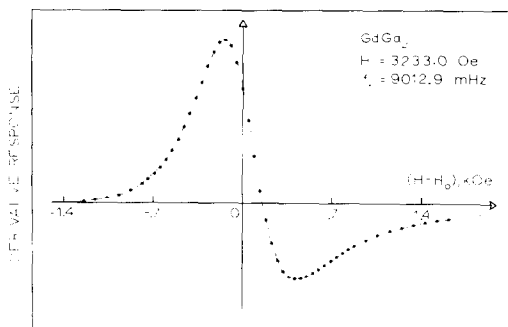
In metallic compounds the power absorbed from an RF field is, to first order, proportional to a linear combination of the real and imaginary components of the susceptibility; i.e.

$$P = K(\chi'' + b\chi') \tag{2}$$

where K is a normalization constant and b is the admixture coefficient. In the case of GdGa$_2$ the lineshapes prove to be Lorentzian; hence, $\chi'' = 1/(1 + x^2)$, $\chi' = x/(1 + x^2)$, $x = (H - H_0)/DH$, H_0 is the resonant field, and DH is the half-width at half-maximum absorption. Thus, an experimental derivative resonance curve should have the form

$$\frac{dP}{dx} = K\left[\frac{b - 2x - bx^2}{(1 + x^2)^2}\right] + m(H - H_0) \tag{3}$$

where m is a parameter to account for possible spectrometer baseline slope.

A programmable calculator, Hewlett–Packard Model 9100A with printer and plotter peripherals, was used to plot Eq. (3) directly onto the experimental resonance curves. It proved to be possible to adjust the parameters K, m, b, and DH so that the two curves were superposed over a field at least twice the linewidth. An example of a typical fit is shown in Fig. 3 in which the solid circles are representative points on a continuous curve that closely overlays the experimental data shown by the solid curve.

Numerous resonance spectra were recorded at 247, 296, and 349°K so that statistically significant data could be obtained. Both the g-factor and the linewidth were found to be temperature dependent. Plots of these parameters versus the magnetization obeyed well-defined linear relationships whose forms were $g = 0.0267\sigma + 1.983_2$ and $DH = -307.2\sigma + 592.7$ (in Oersteds) with least-squares correlation coefficients greater than 0.9995. Extrapolating the g-factor to $\sigma \to 0$, to account for sample demagnetizing effect, we obtain $g = 1.983_2$. The corresponding g-shift, assuming a free Gd^{3+} value of 1.993, is found to be -0.01 which we attribute to s-f exchange interaction. As a rough estimate of the exchange parameter, we find $J(0) = -0.02$ eV from the relation (10) $J(0) = 4NE_F\Delta g/3n$

FIG. 3. Typical EPR derivative spectrum of GdGa$_2$ at 296° K. The solid curve shows the experimental data while the solid circles are representative points on a computer-fitted curve consisting of a linear combination of Lorentzian absorption and dispersion components. The contribution of the dispersion component; i.e. $b = 0.77$, is evidenced by the considerable asymmetry of the curve.

where N is the Gd^{3+} density, n is the conduction electron density (assumed to be $3N$ for $GdGa_2$), and E_F is the free-electron Fermi energy. It remains unclear as to why the linewidth is linearly dependent on the magnetization.

Acknowledgments

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