Pressure Dependence of the Paramagnetic Curie Temperature of Gadolinium†

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The effect of hydrostatic pressure on the paramagnetic Curie temperature Θ, the ferromagnetic Curie temperature T_c, and the magnetic susceptibility in the region of short-range order in gadolinium has been measured to 4.4 kbar. The pressure coefficients together with their standard deviations were determined to be $d\Theta/dP=-1.45\pm0.06°$/kbar and $dT_c/dP=-1.36\pm0.04°$/kbar and are the same to within the experimental uncertainty. This result suggests that for a direct para-to-ferromagnetic transition the two temperatures are of the same physical origin and are determined by the band structure in the paramagnetic region.

I. INTRODUCTION

THE interrelation between the magnitude of the effective exchange interaction and the temperature at which a system orders magnetically is well known. In the simplest molecular-field theories, this can be expressed as

$$J=3k\Theta/2zS(S+1), \qquad (1)$$

where Θ is the paramagnetic Curie temperature and J is the exchange interaction.[1] Theoretical calculations of the dependence of J on interatomic separation[2,3] can be tested by measuring the change of Θ, and thus J, as a function of pressure. The first experiments determining the quantity dT_c/dP were performed by Partick[4] on a number of pure metals and alloys where T_c is the ferromagnetic Curie temperature. His results for Gd were not consistent with the interaction curves existing at the time.[2] Subsequently, a number of experiments have been directed to the determination of the pressure dependence of the ordering temperatures in the rare-earth metals in which Gd has received the most attention.[3,5–12] The Gd results obtained vary from the value of $-1.2°$K/kbar[4] to $-1.72°$K/kbar.[7] These results all refer to the change in the ferromagnetic Curie temperature T_c. Where attempts have been made to interpret the experimental results, the physical origins of T_c and Θ have been treated as being identical.

While the simple relationship between the strength of the exchange interaction and the ordering temperature is a very useful concept, its shortcomings are well known. In particular, at high temperatures the magnetic susceptibility becomes, to a very good approximation, $\chi=C/(T-\Theta)$, where C is the Curie constant. In the simple molecular-field approximation Θ and the ferromagnetic ordering temperature T_c have the same value, while experimentally, particularly in metals, it is observed that $T_c<\Theta$. Between the high-temperature region and ferromagnetic state, there is a region of "short-range order" in which the simple Curie-Weiss law is not obeyed. The difference between Θ and T_c depends on such quantities as the purity and strain of the sample being measured, usually decreasing as the former is increased and the latter decreased.

For the case of Gd, it is generally accepted that the exchange interaction between the half-filled $4f$ states of the ions is via the conduction electrons and not as a consequence of a direct overlap. This indirect exchange interaction, the Rudermann-Kittel-Kasuya-Yosida (RKKY) interaction,[13] depends on the nature of the exchange interaction of the $4f$ electrons with the conduction band and also on the details of the conduction band itself. The result of this theory is that each ion sees an effective exchange interaction. The paramagnetic Curie temperature is given by

$$k\Theta=\tfrac{2}{3}(g_L-1)^2J(J+1)\sum_i J(\mathbf{R}_i), \qquad (2)$$

where g_L is the Lânde g factor, J is the total angular-momentum quantum number and $J(\mathbf{R}_i)$ is the effective exchange interaction between ions. A theoretical calculation of $J(\mathbf{R}_i)$ requires a knowledge of the band structure in the *paramagnetic state*. In the early theories of the RKKY interaction, the conduction bands have

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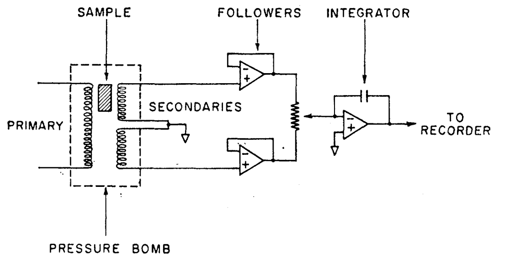

FIG. 1. A simplified schematic of the mutual-inductance bridge coils and integrator. The followers prevent secondary-coil resistance changes, caused by changes in temperature and pressure, from affecting the electronic gain and bridge balance. The bridge is balanced by adjusting the variable resistor in the absence of a sample.

been approximated by spherical bands. From these results, the effective exchange interaction between the Gd ion cores is directly proportional to square of the *s-f* exchange interaction and to the density of states, $N(E_F)$, at the Fermi surface. More recent band-structure calculations have shown that spherical bands are an extremely poor approximation, the Fermi surface being highly warped.[14] In the case of the heavy rare-earth metals, the nature of the ordering is intimately related to the detailed nature of the bands.[15] It is pointed out[14] "that the exchange perturbation of the bands, due to an ordered array of 4*f* moments is so severe that one can obtain only qualitative information starting with the nonmagnetic band structure."

It would therefore seem that an attempt to interpret the results of a dT_c/dP experiment in metals based on a model that is calculated for the paramagnetic state is open to considerable question. The behavior in the short-range-order region, which also points out the difference between Θ and T_c, raises the question of whether or not these quantities are intrinsically the same or whether there is a fundamental difference between them. If there were a basic difference, we would expect the dependences on pressure dT_c/dP and $d\Theta/dP$ to be different. There exist examples where these differences are very pronounced. In Tb the pressure derivatives for the Ferro, Néel, and paramagnetic Curie temperatures have been determined as -1.10, -0.86, and -0.76°K/kbar, respectively.[11] From the same paper, the changes in the Néel and paramagnetic Curie temperatures for Dy are -0.44 and -0.17°K/kbar.

We have chosen to investigate this relation in Gd for several reasons: (1) Its ordering temperature of 293.2°K is experimentally convenient. (2) Gadolinium is the only rare-earth metal to exhibit a para-to-ferromagnetic transition without an intervening antiferromagnetic or spiral spin phase. (3) The theory of exchange in the 4*f* elements is better developed than for the 3*d* series. Finally, Gd is an *S*-state ion and is thus the simplest of the rare-earth metals theoretically.

II. EXPERIMENTAL TECHNIQUES

The susceptibility was measured with a mutual-inductance bridge located inside the beryllium-copper pressure vessel and operated in a modified ballistic mode such that total flux change in the sample was measured electronically. An approach similar to ours and the precautions necessary for its use have been described by Haakana *et al.*[16] Referring to Figs. 1 and 2, we see that the reversal of a dc magnetic field generated by the primary coil produces a flux change through two secondary coils, one of which contains the cylindrical sample. The difference between the secondary voltages is integrated, giving a voltage proportional to the differential flux change and thus to the susceptibility. This can be written as

$$V=\frac{N_s}{RC}\int_0^T\left(\frac{d\Phi_1}{dt}-\frac{d\Phi_2}{dt}\right)dt=\frac{\beta N_s\Delta I}{RC}\chi, \qquad (3)$$

where $(RC)^{-1}$ is the integrator gain, β is a geometrical factor, N_s is the number of turns in each secondary, χ is the sample susceptibility (it is assumed in this equation that $\chi \ll 1$), ΔI is the change in primary current occurring between $T=0$ and $t=\tau \ll T$, and T is any time of sufficient duration for the magnetic flux to diffuse through the sample and adjacent metal apparatus. Whenever T satisfies this condition, the phase-shift problem encountered with metallic samples in ac bridges does not arise. The use of high-input impedance followers is important for the elimination of the effect of the secondary coils dc resistance on the output voltage.

The pressure system was of standard design. Temperature was measured with a thermocouple located inside the pressure bomb. Pressure was measured with a

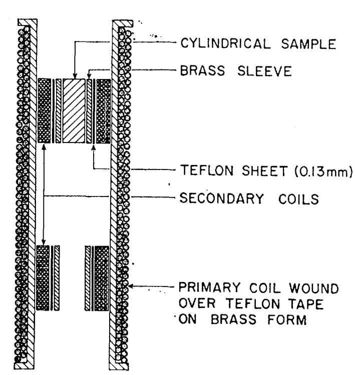

FIG. 2. The mechanical configuration of the mutual-inductance bridge assembly. The coils and sample are supported by a central brass post with suitable spacers (not shown). The entire assembly is located inside the high-pressure bomb.

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manganin gauge located in the intensifier and kept at room temperature. The pressure bomb was heated by a coil of copper tubing clamped tightly around the bomb, heat being supplied by circulating hot DC-704 silicon oil through the coil. The oil heater consisted of a 1 kVA transformer in which the secondary winding had been replaced by a single-shorted turn of $\frac{3}{8}$-in. copper tubing through which the oil was pumped. The tubing from the transformer to the bomb was interrupted with electrically insulating couplings. A temperature controller maintained the circulating oil temperature at a constant value. This system completely eliminates magnetic hum pickup problems and also has the advantage of a fast thermal response time, the heat capacity of the system being essentially just that of the bomb.

Fabrication of suitable coil assemblies, capable of withstanding the high temperatures and pressures, constituted the major experimental difficulty. These problems were minimized by wet-winding the secondary coils with Emerson and Cumming type W66 Epoxy.[17] This process consists of wetting the wire with epoxy before winding it onto the coil and is considered superior to vacuum-potting in that there is no chance of obtaining voids. Best results were obtained by not using a permanent coil form, but instead supporting the two rigid secondary coils with a thin cushion of Teflon, as shown in Fig. 2. Leakage currents were reduced by use of a low-impedance primary wound in a metallic form.

The simple relation between the integrator voltage and the susceptibility, Eq. (3), is valid only in the limit of $\chi \ll 1$. The result of an idealized calculation[18] in which the sample is treated as a prolate spheroid with semi-axes a and c ($a \leq c$) located in a secondary coil or radius d is

$$V \propto \frac{a^2c}{d}\left[\frac{\chi}{3+\chi F(c/a)}\right]G(c/a,d), \tag{4}$$

where V is the integrator output voltage and the functions F and G represent purely geometrical factors. Solving for $1/\chi$ we obtain the result

$$\frac{1}{V} \propto 1/\chi + \text{const.} \tag{5}$$

The important conclusion is that the change in the measured voltage reciprocal is directly proportional to $1/\chi$, the constant not being important since only the relative change in $1/\chi$ is needed for the determination of $d\Theta/dP$. The use of polycrystalline samples means that the ratio c/a is pressure-independent and the effects of anisotropic compressibilities are not important.

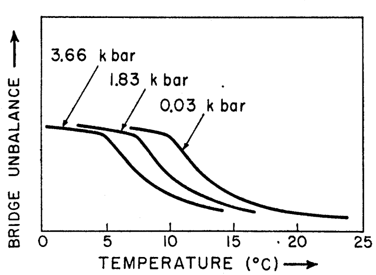

FIG. 3. Typical curves of bridge unbalance near T_c versus temperature at three different pressures. dT_c/dP was determined from 20 such curves.

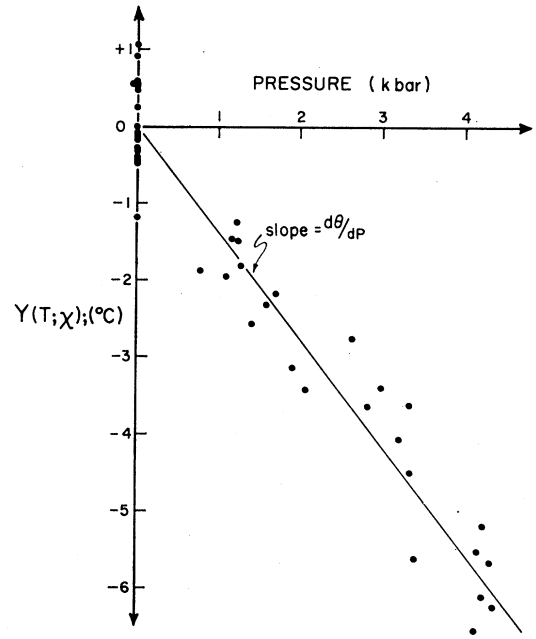

FIG. 4. $Y(T;\chi)$ plotted versus pressure. This quantity, Eq. (6b), is proportional to the change in the paramagnetic Curie temperature Θ.

The 6.35-mm diameter by 15.9 mm long ($\frac{1}{4}\times\frac{5}{8}$ in.) polycrystalline sample of 99.9% purity was annealed in a vacuum furnace. A spectrographic analysis disclosed the following impurities in percent: Fe, 0.013; Mn, 0.040; Ni and Co, not detected (less than 0.009 each). The data were taken as series of voltage versus temperature measurements at constant pressure. The balance conditions were checked before and after each series of measurements. The upper limits on temperature and pressure of 155°C and 5 kbar reflect failure in the secondary coils beyond these limits. In the ferromagnetic transition region, bridge unbalance was plotted continuously as a function of temperature. The results for three isobars are shown in Fig. 3. For this range of temperature, there were no problems associated with coil failure.

[17] Emmerson and Cummings, Inc., 869 Washington St., Canton, Mass.

[18] Robert I. Potter, Ph.D. thesis, University of California, Riverside, 1968 (unpublished). The interested reader is referred to this source for a more extensive description of experimental details and procedures.

III. DATA ANALYSIS AND EXPERIMENTAL RESULTS

The data to be analyzed were divided into three temperature intervals: ferromagnetic, short-range-order, and the high-temperature or Curie-Weiss region. The region of short-range-order is not sharply defined, being given as the region in temperature below which the linear dependence of $(1/\chi)$ on temperature is no longer satisfied and above the ferromagnetic Curie temperature. From an inspection of our results we treat data below 120°C as being in the short-range-order region but do not attach any further significance to this choice. It has been shown that for a particular coil-sample combination, there is a linear relationship between $1/V$, where V is the signal voltage, and $1/\chi$. If we represent the paramagnetic Curie temperature by $\Theta(P)=\Theta_0+\alpha P$, where $\alpha=(d\Theta/dP)_0$, all of the high-temperature data can be represented by the relation

$$1/\chi=(1/C)(T-\Theta_0-\alpha P) \tag{6a}$$

or equivalently by

$$T-\Theta-C/\chi=\alpha P. \tag{6b}$$

The results of a least-squares fit of the data to this relation are shown in Fig. 4.

The analysis of the data in the short-range-order region was made based on the following empirical relationship between the temperature, pressure, and susceptibility:

$$1/\chi=(1/C)[A(T-T'-\alpha'P)+B(T-T'-\alpha'P)^2]. \tag{7a}$$

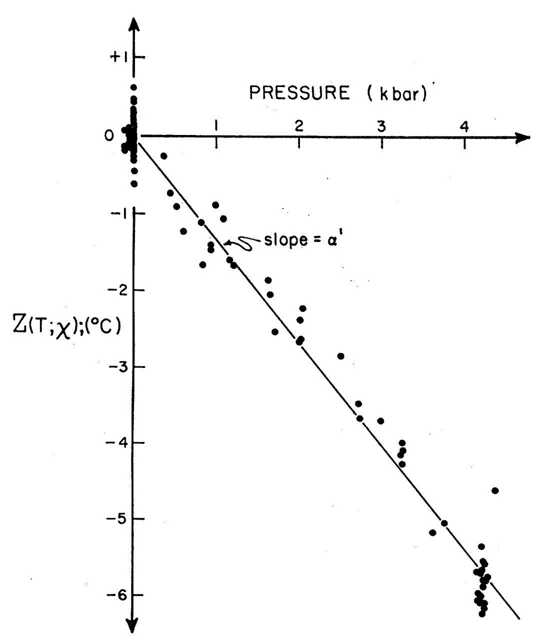

FIG. 5. $Z(T;\chi)$ plotted versus pressure. This quantity, Eq. (7b), represents the change with pressure, of an effective ordering temperature in the region of short-range order as discussed in the text.

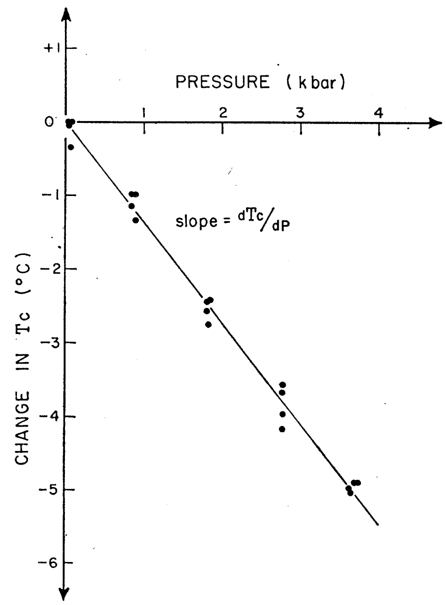

FIG. 6. Change in T_c versus pressure, showing the data and the straight line of slope dT_c/dP that minimizes the sum of the squared deviations.

We emphasize that while this form describes the short-range-order region quite well, it has been introduced empirically and is not based on any theoretical model. The parameter A reflects a different slope in this region and B reflects the curvature. It should be noted that this expression contains T', the intercept as an unknown rather than assuming it to be associated with either T_c or Θ_0. Similarly, we have expressed the dependence on pressure by α' to emphasize that it need not be the same as the coefficient in the Curie-Weiss region. The analysis of the data is simplified by solving for the linear relation between the independent variables P and T and is given by

$$T-T'+(A/2B)\{1-[1+(4B/A^2)(C/\chi)]^{1/2}\}=\alpha'P. \tag{7b}$$

A least-squares fit of the data to this expression was made and the results together with the experimental points are shown in Fig. 5.

The data in the ferromagnetic region were obtained as a continuous function of temperature. Application of pressure was observed to displace the data along the temperature axis but not to substantially change the shape of the curves. The change in the ferromagnetic Curie temperature $(\partial T_c/\partial P)\Delta P$ was determined directly from the temperature by which each curve is displaced with respect to the atmospheric-pressure-reference curve. The data and the least-squares fit to the assumed linear change in T_c with pressure are shown in Fig. 6. The result of the least-squares analysis for each temperature region is presented in Table I as "uncorrected-pressure coefficient and standard deviation." The standard deviation in each pressure coefficient was calculated following standard procedures.[19]

A systematic error arises from the compression of the sample and coil assembly. We have made an estimate of this correction. The details of this calculation are presented in Ref. 15. The result for $d\Theta/dP$ is $-0.065°K/kbar$ and for α', the coefficient in the short-range-order region, is $-0.043°K/kbar$. The uncertainty in this correction is estimated to be less than 25%. The pressure dependence of the g factor in the Curie constant is small and has been neglected. The results for the determined pressure coefficients together with their uncertainties are listed in Table I under "corrected pressure coefficient and total uncertainty."

TABLE I. A summary of the data analysis results. The pressure coefficient of inverse susceptibility in the short-range order region is α'.

	dT_c/dP	α'	$d\theta/dP$
Uncorrected pressure coefficient and standard deviation (°C/kbar),	-1.361 ±0.031	-1.343 ±0.015	-1.382 ±0.055
Correction for compressibility of apparatus and sample, and estimated uncertainty of correction (°C/kbar)	0	-0.043 ±0.011	-0.065 ±0.016
Accuracy of temperature measurement	0.5%		
Accuracy of pressure measurement (at 3–4 kbar)	1.0%		
Corrected pressure coefficient and total uncertainty	-1.36 ±0.04	-1.39 ±0.03	-1.45 ±0.06
The remaining parameters of Eqs. (5) and (6) were determined to be:	$\theta_0=49.4°C$ $A=0.535$ $B=0.00122$ $T'=13.46°C$		

IV. RESULTS AND CONCLUSIONS

The values obtained for the pressure derivatives and the total uncertainties are as follows:

$$dT_c/dP=-1.36\pm0.04°K/kbar\,,$$
$$\alpha'=-1.39\pm0.03°K/kbar\,,$$
$$d\Theta/dP=-1.45\pm0.06°K/kbar\,.$$

The parameter α' was defined in Eq. (7a) and describes the change with pressure of the susceptibility in the region of short-range order. Our results for dT_c/dP are in essential agreement with those of other workers. Bartholin and Bloch[10] quote results of $-1.48°K/kbar$ for polycrystalline samples and $-1.40°K/kbar$ for single crystals. The latter result is obtained with the magnetizing field along either the a or c axis. Of more significance are the relative values of dT_c/dP and $d\Theta/dP$, since the presence of magnetic order severely distorts the Fermi surface. The difference observed in the pressure derivatives of T_c, T_N, and Θ in Tb[11] seems to be a strong indication of the importance of band-structure effects. Results obtained on the same sample and with the same experimental equipment make this comparison more significant than the scatter of absolute values in the literature would indicate.

The primary conclusion to be drawn from this work is that to within the experimental uncertainty, the pressure derivatives of the ferromagnetic and paramagnetic Curie temperatures are the same. The usual assumptions of regarding T_c and Θ as being intrinsically the same, but differing numerically due to short-range-order effects, we feel, have been established experimentally by these results. Thus, we can conclude, in contrast to the case of Tb and Dy, that the dependence on pressure of the susceptibility is a simple displacement of the entire curve to lower temperatures at the rate of $-1.4°C/kbar$.

ACKNOWLEDGMENTS

The authors wish to thank Professor A. W. Lawson for helpful suggestions regarding the pressure equipment and correction of the data for coil-assembly compression, and M. R. MacPherson for interesting discussions and assistance in performing the experiment.

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