

Magnitude of Exchange Interactions in Gadolinium*

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The effective nearest-neighbor exchange interaction J in gadolinium can be deduced from experiment in two ways. From a high-temperature expansion of the susceptibility and the measured value of the Curie temperature T_c one obtains $J=2.9^\circ\text{K}$, while from the low-temperature magnetization curve and simple spin-wave theory one finds $J=1.8^\circ\text{K}$. In order to clarify the reason for this discrepancy the low-temperature spin-wave problem has been analyzed in detail. Contributions to the magnetization from two different spin-wave modes were evaluated up to order $T^{7/2}$ and important corrections arising from zone boundary effects were included. The detailed analysis yields a slightly improved low-temperature value, $J=2.1^\circ\text{K}$. It also demonstrates that the magnetization follows a $T^{3/2}$ law very closely from low temperatures up to about $0.8 T_c$ because of a complicated cancellation of the higher order effects. Finally it is shown qualitatively that the remaining difference between the high- and low-temperature J values can probably be explained by the effect of interactions beyond nearest neighbors and it is suggested that these are on the average more antiferromagnetic than ferromagnetic.

1. INTRODUCTION

THERE are two well-known methods of deducing values of the effective nearest-neighbor exchange interaction J in ferromagnets. One results from fitting spin-wave theory to the experimental magnetization curve at low temperatures. In the second method, an expansion of the partition function¹ or of the susceptibility² above the Curie temperature T_c in powers of J/kT yields a relation between J , T_c and the ionic spin quantum number S . J is then deduced from the measured T_c and a suitable choice for S . Perhaps the best example of such a relation is

$$kT_c/J = (5/96)(z-1)[11S(S+1)-1], \quad (1)$$

which was obtained by Rushbrooke and Wood² who found that it provides a fit to their very precise numerical calculations to within an accuracy of 1%.

For iron, cobalt, and nickel, the low-temperature J values are of the order of 20 to 80% larger³ than values obtained from Eq. (1). However, S values of $1/2$ or 1 used in Eq. (1) can be only qualitatively significant for these metals, and one does not expect to find close agreement between the low- and high-temperature J values. The situation for gadolinium, on the other hand, is rather different. Gadolinium is ferromagnetic up to $T_c=289^\circ\text{K}$, and the saturation magnetization, at 0°K and paramagnetic resonance data⁵ indicate a well-defined value of $S=7/2$. From the measured T_c one

obtains $J=2.9^\circ\text{K}$ from (1). However, the experimental magnetization curve of Elliott, Legvold and Spedding, yields $J=1.8^\circ\text{K}$ on the basis of elementary spin-wave theory⁶ ($T^{3/2}$ term only). Since gadolinium is thought to be well represented by the Heisenberg picture of a ferromagnet, this discrepancy appeared difficult to understand.

Another puzzling feature of the magnetization curve of Elliott *et al.* is that it follows a $T^{3/2}$ law very closely from low temperatures up to about $0.8T_c$. At temperatures approaching T_c one would have expected the higher order terms to become important and lead to large departures from $T^{3/2}$ behavior.

The primary aim of the present investigation was to attempt to explain the difference between the high- and low-temperature J values by a detailed treatment of the spin-wave problem. It had been observed by Keffer³ from molecular field considerations that one might expect to find contributions to the magnetization from $T^{5/2}$ and $T^{7/2}$ terms of the same order of magnitude as the $T^{3/2}$ contribution. Also several people⁷ have noted that since gadolinium is a hexagonal structure with two atoms per unit cell there is the possibility of an appreciable contribution to the magnetization from a second spin-wave mode analogous to the optical mode of lattice vibration theory.

In the next section a spin-wave theory appropriate to gadolinium is described and in Sec. 3 the contributions to the magnetization from terms up to $T^{7/2}$ in both modes are carefully evaluated. From the detailed theory one obtains $J=2.1^\circ\text{K}$ which represents only a slight improvement over the simplified theory. The possibility of explaining the remaining discrepancy by the exchange interactions beyond nearest neighbors is examined in the concluding section.

While only partly successful in resolving the difference between high- and low-temperature J values, the de-

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¹ W. Opechowski, *Physica* **4**, 181 (1937); **6**, 1112 (1939); V. Zehler, *Z. Naturforsch.* **5A**, 344 (1950).

² G. S. Rushbrooke and P. J. Wood, *Mol. Phys.* **1**, 257 (1958).

³ F. Keffer, in *Handbuch der Physik*, edited by S. Flügge, (Springer-Verlag, Berlin, 1963) (to be published).

⁴ J. F. Elliott, S. Legvold, and F. H. Spedding, *Phys. Rev.* **91**, 28 (1953).

⁵ A. F. Kip, *Revs. Modern Phys.* **25**, 229 (1953); M. Peter, D. Shaltiel, J. H. Wernick, H. J. Williams, J. B. Mock, and R. C. Sherwood, *Phys. Rev.* **126**, 1395 (1962).

⁶ J. A. Hofmann, A. Paskin, K. J. Tauer, and R. J. Weiss, *J. Phys. Chem. Solids* **1**, 45 (1956); **15**, 187 (1960).

⁷ F. Keffer (private communication); T. A. Kaplan, *Phys. Rev.* **124**, 329 (1961).

tailed theory does show that the extended $T^{3/2}$ behavior found by Elliott *et al.*, results from a complicated cancellation of higher order effects.

A few words about magnetic anisotropy are in order. The extremely large anisotropy effects found in other rare-earth metals⁸ are due to the inability of the non-spherically symmetrical f -shell charge cloud to rotate because of strong electrostatic interactions with the crystal environment.⁹ However the Gd^{3+} ions, which we imagine embedded in the sea of conduction electrons are in $^8S_{7/2}$ states and thus are spherically symmetric. The anisotropy is therefore much smaller than in the other rare earth metals, although the data of Elliott *et al.*, indicate it to be somewhat greater than in iron. In the absence of more detailed information, it was omitted from the theory which follows.

2. SPIN-WAVE THEORY

We shall begin by developing the theory for a general lattice structure, denoting the positions of unit cells by \mathbf{l} and the positions of the atoms which form a basis of the structure by \mathbf{b} , measured from some origin in the unit cell.¹⁰ Our starting point is the Heisenberg exchange Hamiltonian of the spin system

$$\mathcal{H} = -\frac{1}{2} \sum_{\mathbf{l}\mathbf{b}} \sum_{\mathbf{l}'\mathbf{b}'} 2J_{\mathbf{l}\mathbf{b},\mathbf{l}'\mathbf{b}'} \mathbf{S}_{\mathbf{l}\mathbf{b}} \cdot \mathbf{S}_{\mathbf{l}'\mathbf{b}'}, \quad (2)$$

where $\mathbf{S}_{\mathbf{l}\mathbf{b}}$ is the spin operator of an atom at the site $\mathbf{l}\mathbf{b}$ and $J_{\mathbf{l}\mathbf{b},\mathbf{l}'\mathbf{b}'}$ expresses the exchange interaction between atoms at $\mathbf{l}\mathbf{b}$ and $\mathbf{l}'\mathbf{b}'$. The well-known spin operator substitutions and approximations of the Holstein-Primakoff theory¹¹ lead to the expression

$$\mathcal{H} = C - 2 \sum_{\mathbf{l}\mathbf{b}} \sum_{\mathbf{l}'\mathbf{b}'} J_{\mathbf{l}\mathbf{b},\mathbf{l}'\mathbf{b}'} \times [(S_{\mathbf{b}}S_{\mathbf{b}'})^{\frac{1}{2}} a_{\mathbf{l}\mathbf{b}}^* a_{\mathbf{l}'\mathbf{b}'} - S_{\mathbf{b}'} a_{\mathbf{l}\mathbf{b}}^* a_{\mathbf{l}\mathbf{b}}], \quad (3a)$$

$$C = -\sum_{\mathbf{l}\mathbf{b}} \sum_{\mathbf{l}'\mathbf{b}'} S_{\mathbf{b}} S_{\mathbf{b}'} J_{\mathbf{l}\mathbf{b},\mathbf{l}'\mathbf{b}'}, \quad (3b)$$

where $a_{\mathbf{l}\mathbf{b}}^*$ and $a_{\mathbf{l}\mathbf{b}}$ are the usual spin creation and destruction operators and $S_{\mathbf{b}}$ is the spin quantum number for the basis atom \mathbf{b} .

The transformation to spin waves is now made:

$$\begin{aligned} a_{\mathbf{k}\mathbf{b}} &= (1/N^{\frac{1}{2}}) \sum_{\mathbf{l}} a_{\mathbf{l}\mathbf{b}} e^{i\mathbf{k} \cdot \mathbf{l}}, \\ a_{\mathbf{k}\mathbf{b}}^* &= (1/N^{\frac{1}{2}}) \sum_{\mathbf{l}} a_{\mathbf{l}\mathbf{b}}^* e^{-i\mathbf{k} \cdot \mathbf{l}}, \\ a_{\mathbf{l}\mathbf{b}} &= (1/N^{\frac{1}{2}}) \sum_{\mathbf{k}} a_{\mathbf{k}\mathbf{b}} e^{-i\mathbf{k} \cdot \mathbf{l}}, \\ a_{\mathbf{l}\mathbf{b}}^* &= (1/N^{\frac{1}{2}}) \sum_{\mathbf{k}} a_{\mathbf{k}\mathbf{b}}^* e^{i\mathbf{k} \cdot \mathbf{l}}. \end{aligned} \quad (4)$$

N is the total number of unit cells in the sample. Using the fact that $J_{\mathbf{l}\mathbf{b},\mathbf{l}'\mathbf{b}'}$ depends only on $\rho = \mathbf{l} - \mathbf{l}'$, a result of translational symmetry, the transformation gives

$$\mathcal{H} = C - 2 \sum_{\mathbf{k}} \left\{ \sum_{\mathbf{b}\mathbf{b}'} [(S_{\mathbf{b}}S_{\mathbf{b}'})^{\frac{1}{2}} J_{\mathbf{k}}^{\mathbf{b}\mathbf{b}'} a_{\mathbf{k}\mathbf{b}}^* a_{\mathbf{k}\mathbf{b}'} - S_{\mathbf{b}'} J_0^{\mathbf{b}\mathbf{b}'} a_{\mathbf{k}\mathbf{b}}^* a_{\mathbf{k}\mathbf{b}}] \right\}, \quad (5)$$

⁸ W. E. Henry, Suppl. J. Appl. Phys. **31**, 323S (1960).

⁹ R. J. Elliott, Phys. Rev. **124**, 346 (1961).

¹⁰ Notation and development follows J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960).

¹¹ T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940).

where

$$J_{\mathbf{k}}^{\mathbf{b}\mathbf{b}'} = \sum_{\rho} J_{\mathbf{b}\mathbf{b}'}(\boldsymbol{\rho}) \exp(i\mathbf{k} \cdot \boldsymbol{\rho}). \quad (6)$$

The Hamiltonian (5) must now be diagonalized. The general case of any number of basis atoms has not been attempted. It is at this stage that one should take advantage of any special features of a problem which simplify the diagonalization.

Accordingly, we restrict our spin-wave theory to the case appropriate to gadolinium in which there are two identical ($S_1 = S_2 = S$) atoms per unit cell. The two different atoms in the unit cell are labelled by 1 and 2 and the two independent Bose operators are denoted $a_{\mathbf{k}1}$ and $a_{\mathbf{k}2}$. Since the atoms are identical the various $J_{\mathbf{k}}^{\mathbf{b}\mathbf{b}'}$ of (6) are not all different. We define

$$J_{\mathbf{k}} \equiv J_{\mathbf{k}}^{11} = J_{\mathbf{k}}^{22} \quad \text{and} \quad J_{\mathbf{k}}' \equiv J_{\mathbf{k}}^{12} = (J_{\mathbf{k}}^{21})^*. \quad (7)$$

Then the Hamiltonian (5) for the hexagonal structure of gadolinium is

$$\mathcal{H} = C + \sum_{\mathbf{k}} \{ A_{\mathbf{k}} (a_{\mathbf{k}1}^* a_{\mathbf{k}1} + a_{\mathbf{k}2}^* a_{\mathbf{k}2}) + B_{\mathbf{k}} a_{\mathbf{k}1}^* a_{\mathbf{k}2} + B_{\mathbf{k}}^* a_{\mathbf{k}2}^* a_{\mathbf{k}1} \}, \quad (8)$$

with

$$A_{\mathbf{k}} = 2S(J_0 - J_{\mathbf{k}} + J_0'), \quad (9)$$

$$B_{\mathbf{k}} = -2SJ_{\mathbf{k}}'. \quad (10)$$

The unitary transformation,

$$\begin{aligned} a_{\mathbf{k}1}^* &= (i/\sqrt{2})(c_{\mathbf{k}1}^* - ic_{\mathbf{k}2}^*), \\ a_{\mathbf{k}1} &= (-i/\sqrt{2})(c_{\mathbf{k}1} + ic_{\mathbf{k}2}), \\ a_{\mathbf{k}2}^* &= (1/\sqrt{2})e^{-i\phi}(c_{\mathbf{k}1}^* + ic_{\mathbf{k}2}^*), \\ a_{\mathbf{k}2} &= (1/\sqrt{2})e^{i\phi}(c_{\mathbf{k}1} - ic_{\mathbf{k}2}), \end{aligned}$$

$$\begin{aligned} \phi &= \tan^{-1}\{\text{Re}(B_{\mathbf{k}})/\text{Im}(B_{\mathbf{k}})\} \\ &= \tan^{-1}\{\text{Re}(J_{\mathbf{k}}')/\text{Im}(J_{\mathbf{k}}')\}, \end{aligned} \quad (11)$$

changes \mathcal{H} into the diagonal form

$$\mathcal{H} = C + \sum_{\mathbf{k}} (A_{\mathbf{k}} - |B_{\mathbf{k}}|) c_{\mathbf{k}1}^* c_{\mathbf{k}1} + \sum_{\mathbf{k}} (A_{\mathbf{k}} + |B_{\mathbf{k}}|) c_{\mathbf{k}2}^* c_{\mathbf{k}2}. \quad (12)$$

Thus there are two different spin-wave modes whose excitation energies are

$$\epsilon_{\mathbf{k}}^{(1)} = 2S(J_0 - J_{\mathbf{k}} + J_0' - |J_{\mathbf{k}}'|), \quad (13a)$$

$$\epsilon_{\mathbf{k}}^{(2)} = 2S(J_0 - J_{\mathbf{k}} + J_0' + |J_{\mathbf{k}}'|). \quad (13b)$$

Let us assume that the exchange interaction is important between nearest neighbors only. (We shall be led to re-examine this assumption later.) The sums over $\boldsymbol{\rho}$ in (6) and (7) are confined to nearest neighbors, the exchange interaction being expressed by J if they are in the same hexagonal plane and by J' if they are in

different hexagonal planes. Then we can write

$$J_k = 2J \{ \cos[\frac{1}{2}k_x a + (\sqrt{3}/2)k_y a] + \cos[\frac{1}{2}k_x a - (\sqrt{3}/2)k_y a] + \cos k_x a \}, \quad (14)$$

$$|J_k'| = 2J' \cos \frac{k_z c}{2} \left\{ 1 + 4 \cos \frac{k_x a}{2} \times \left[\cos \left(\frac{\sqrt{3}}{2} k_y a \right) + \cos \left(\frac{k_x a}{2} \right) \right] \right\}^{\frac{1}{2}}. \quad (15)$$

From (14) and (15) it can be seen that $\epsilon_k^{(1)}$ is a minimum when $k_x = k_y = k_z = 0$ and $\epsilon_k^{(2)}$ is a minimum when $k_x = k_y = 0$, $k_z = \pm 2\pi/c$. In analogy with the description of lattice vibrations the former is said to describe an acoustic spin-wave mode, the latter an optical spin-wave mode. It is to be noted from (15), however, that under the transformation $k_z' = k_z \pm 2\pi/c$, the dispersion relations $\epsilon_k^{(1)}$ and $\epsilon_k^{(2)}$ become interchanged.

The calculation of the magnetization in the next section makes use of expansions of $\epsilon_k^{(1)}$ and $\epsilon_k^{(2)}$ about their minima inside the first Brillouin zone. It is convenient to make the substitutions

$$\lambda^2 = (k_x^2 + k_y^2)a^2, \quad (16)$$

$$\mu_1 = k_z c/2, \quad \text{acoustic mode}$$

$$\mu_2 = \pi/2 - k_z c/2, \quad \text{optical mode } (k_z \geq 0). \quad (17)$$

Then expanding in power series

$$(J_0 - J_k)/6J = \frac{1}{4}\lambda^2 - \frac{1}{64}\lambda^4 + \frac{1}{1920}\lambda^6, \quad (18)$$

$$(J_0' - |J_k'|)/6J' = \frac{1}{12}\lambda^2 + \frac{1}{2}\mu_1^2 - \frac{1}{576}\lambda^4 - \frac{1}{24}\lambda^2\mu_1^2 - \frac{1}{24}\mu_1^4 + \frac{1}{34560}\lambda^6 + \frac{1}{1152}\lambda^4\mu_1^2 + \frac{1}{288}\lambda^2\mu_1^4 + \frac{1}{720}\mu_1^6, \quad (19a)$$

acoustic mode

$$(J_0' + |J_k'|)/6J' = 1 + \mu_2 - \frac{1}{12}\lambda^2\mu_2 - \frac{1}{6}\mu_2^3 + \frac{1}{576}\lambda^4\mu_2 + \frac{1}{72}\lambda^2\mu_2^3 + \frac{1}{120}\mu_2^5, \quad (19b)$$

optical mode ($k_z \geq 0$).

[The terms in λ^6 in (18) and (19a) have been obtained by approximating

$$11k_x^6 + 15k_x^4k_y^2 + 45k_x^2k_y^4 + 9k_y^6 = 12\lambda^6/a^6.]$$

As the structure of gadolinium is very nearly close packed¹² ($c/a = 1.590$) it should be a good approximation to set $J' = J$. Our theory then involves only one parameter J . Defining

$$\theta = kT/12JS, \quad (20)$$

one obtains the following series expansions of the dispersion relations:

$$\epsilon_k^{(1)}/kT = \theta^{-1} \left(\frac{1}{3}\lambda^2 + \frac{1}{2}\mu_1^2 - \frac{5}{288}\lambda^4 - \frac{1}{24}\lambda^2\mu_1^2 - \frac{1}{24}\mu_1^4 + \frac{19}{34560}\lambda^6 + \frac{1}{1152}\lambda^4\mu_1^2 + \frac{1}{288}\lambda^2\mu_1^4 + \frac{1}{720}\mu_1^6 \right), \quad (21a)$$

$$\epsilon_k^{(2)}/kT = \theta^{-1} \left(1 + \mu_2 + \frac{1}{4}\lambda^2 - \frac{1}{12}\lambda^2\mu_2 - \frac{1}{6}\mu_2^3 - \frac{1}{64}\lambda^4 + \frac{1}{576}\lambda^4\mu_2 + \frac{1}{72}\lambda^2\mu_2^3 + \frac{1}{120}\mu_2^5 \right). \quad (21b)$$

3. CALCULATION OF THE MAGNETIZATION

As a result of the excitation of spin-waves in both modes the magnetization decreases as a function of temperature. Let n_1 and n_2 be the number of spin waves per unit volume at temperature T in the acoustic and optical modes, respectively. In either mode n_i is given by the Bose-Einstein integral

$$n_i = \frac{1}{(2\pi)^3} \int d\mathbf{k} [\exp(\epsilon_k^{(i)}/kT) - 1]^{-1}, \quad (22)$$

$$= \frac{1}{(2\pi)^3} \sum_{p=1}^{\infty} \int d\mathbf{k} \exp(-p\epsilon_k^{(i)}/kT).$$

Equation (21) shows that $\epsilon_k^{(i)}/kT$ involves a single parameter, our reduced temperature θ . It is convenient to define

$$m_i(\theta) = (g\mu_B n_i / M_0) = (1/2NS)n_i = (\sqrt{3}a^2c/4S)n_i, \quad (23)$$

and write the magnetization per unit volume $M(\theta)$ as

$$M(\theta)/M_0 = 1 - m_1(\theta) - m_2(\theta). \quad (24)$$

Here M_0 is the saturation magnetization per unit volume at absolute zero. The expressions (22) to (24) for the magnetization are based on the standard method¹¹ of calculation using the partition function.

The integral in (22) extends over the first Brillouin zone in order to capture the correct number of \mathbf{k} states. However, it is usually found that a negligible error is introduced if the integrations over k_x , k_y , and k_z are

¹² J. R. Banister, S. Legvold, and F. H. Spedding, Phys. Rev. **94**, 1140 (1954).

taken to infinity instead of to the zone boundary. For a hexagonal structure this is true regarding the k_x and k_y integrations, but the integration over k_z would be appreciably in error if it were taken to infinity instead of to the zone boundary at $k_z = \pm\pi/c$. Therefore, noticing from (14) and (15) that the $\epsilon_k^{(i)}$ are even functions of k_z , and making the transformations (16) and (17), we are lead to approximate $m_i(\theta)$ for each mode by

$$m_i(\theta) = \frac{\sqrt{3}}{4\pi^2 S} \sum_{p=1}^{\infty} \int_0^{\infty} d\lambda \lambda \int_0^{\pi/2} d\mu_i \exp(-p\epsilon_k^{(i)}/kT). \quad (25)$$

It remains to substitute the expressions (21) into (25) and work out approximate values for the integrals. Following standard methods,³ the exponential is broken into the product of two exponentials, the first including up to second-order terms in λ and μ_i . The second exponential containing the higher order terms is then expanded as a power series and the evaluation of $m_i(\theta)$ proceeds term by term.

Let us illustrate this for the acoustic mode. The contribution to $m_1(\theta)$ from the term $c_{nm}\theta^{-1}\lambda^{2n}\mu^{2m}$ ($n+m>1$) in (21a) is

$$\frac{\sqrt{3}}{4\pi^2 S} (-c_{nm}) \sum_{p=1}^{\infty} \frac{p}{\theta} \int_0^{\infty} \lambda^{2n+1} \exp(-p\lambda^2/3\theta) d\lambda \times \int_0^{\pi/2} \mu_1^{2m} \exp(-p\mu_1^2/2\theta) d\mu_1. \quad (26)$$

With the substitutions

$$I_m(x) = \int_x^{\infty} t^{2m} e^{-t^2} dt, \quad (27)$$

$$\mu_0 = (\frac{1}{2}p\theta^{-1})^{1/2}\pi/2, \quad (28)$$

the expression (26) becomes

$$\frac{\sqrt{3}}{4\pi^2 S} (-c_{nm}) 3^{n+1/2} m^{-1/2} n! \theta^{n+m+1/2} \zeta(n+m+\frac{1}{2}) I_m(0) \times \left\{ 1 - \frac{1}{\zeta(n+m+\frac{1}{2}) I_m(0)} \sum_{p=1}^{\infty} p^{-(n+m+1/2)} I_m(\mu_0) \right\}. \quad (29)$$

The summation inside the brackets, which arises from carrying the integration over k_z to the zone boundary, is rapidly convergent and is easily evaluated from a table of the error function. It should be noted that these correction terms are zero at $\theta=0$, becoming increasingly important as the temperature increases. When all the terms in (21a) are considered in this way and are added together, one obtains contributions to $m_1(\theta)$ which are essentially like $\theta^{3/2}$, $\theta^{5/2}$, and $\theta^{7/2}$, modified slightly by the zone boundary corrections. These are listed in Table I.

The treatment of the optical mode is similar in principle. However, the presence of the energy gap in

TABLE I. Contributions to $M(\theta)/M_0$ from the various terms. The θ -dependent "zone boundary corrections" are included in each term.

θ^{-1}	$\theta^{3/2}$ term	Acoustic mode		$m_1(\theta)$	Optical mode		$m_2(\theta)$
		$\theta^{5/2}$ term	$\theta^{7/2}$ term		θ^2 term	θ^3 term	
3.0	0.0118	0.0011	-0.0001	0.0128	0.0001	0.0000	0.0001
2.0	0.0215	0.0030	-0.0004	0.0241	0.0008	0.0001	0.0009
1.4	0.0362	0.0072	-0.0012	0.0422	0.0030	0.0005	0.0035
1.0	0.0585	0.0157	-0.0038	0.0704	0.0082	0.0014	0.0096
0.8	0.0801	0.0260	-0.0079	0.0982	0.0146	0.0027	0.0173
0.6	0.1191	0.0489	-0.0198	0.1482	0.0288	0.0053	0.0341
0.4	0.2056	0.1152	-0.0711	0.2497	0.0674	0.0129	0.0803

(21b) leads to expressions involving the Bose-Einstein integral function

$$F(s, t) = \sum_{p=1}^{\infty} p^{-s} e^{-p/t}. \quad (30)$$

It is convenient to introduce $\theta' = \theta/(1+\pi/2)$. From the terms up to third order in λ and μ in (21b) one obtains contributions to $m_2(\theta)$ varying essentially as θ^2 and θ^3 ;

$$m_2(\theta) = (\sqrt{3}/4\pi^2 S) 2\theta^2 [F(2, \theta) - F(2, \theta')] + (\sqrt{3}/4\pi^2 S) (2/3)\theta^3 [F(3, \theta) - F(3, \theta')] - (\pi/2)\theta^{-1} F(2, \theta'). \quad (31)$$

These also are listed in Table I.

We have now succeeded in calculating the magnetization per unit volume as a function of the parameter θ as in (24). From this form it is easy to find it as a function of T by taking $S=7/2$ and choosing a value of J . Somewhat surprisingly it is found that if $J \sim 2^\circ\text{K}$, and $M(T)/M_0$ is plotted against $T^{3/2}$ over a temperature range extending nearly to the Curie temperature, the result is very nearly a straight line, in agreement with the unexpected behavior found by Elliott, Legvold and Spedding. The slope of the experimental curve is fitted with $J=2.1^\circ\text{K}$.

It appears, then, that the various contributions to $M(T)$ from higher order terms of the acoustic and optical modes and the important temperature-dependent "zone boundary corrections" add together to give a verisimilitude of $T^{3/2}$ behavior, as shown in Fig. 1. However, there still remains a significant difference between the low- and high-temperature J values.

Note added in proof. The theory of Kasuya (see reference 14) takes into account exchange interactions between all neighbors. In a cubic crystal he finds that the coefficient of the $T^{5/2}$ term of the magnetization is greatly reduced relative to that obtained in a nearest-neighbor-only theory. Thus it is likely that the excellent $T^{3/2}$ behavior of the experimental results is due to the combined effect of Kasuya's result and the crystal structure considerations of the present paper.

4. THE EFFECT OF INTERACTIONS BETWEEN MORE DISTANT PAIRS OF NEIGHBORS

Both the preceding theory and the theory of Rushbrooke and Wood² which leads to Eq. (1) treat the

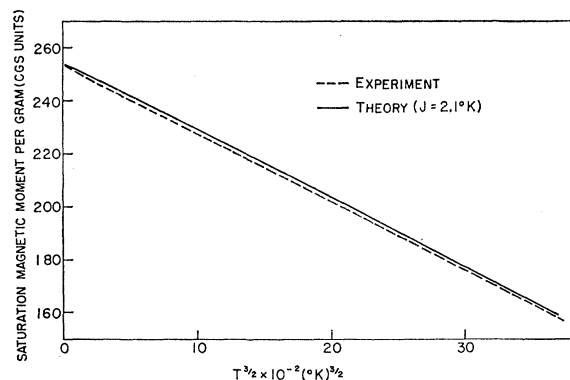


FIG. 1. Comparison between the experimental magnetization curve of gadolinium obtained by Elliott, Legvold, and Spedding and that resulting from the detailed spin-wave theory with $J = 2.1^{\circ}\text{K}$.

exchange interactions between nearest-neighbor pairs only. In this section we examine qualitatively how these two theories might be affected by interactions between pairs of more distant neighbors. Instead of a single parameter J_1 for nearest-neighbor pairs there will be additional quantities J_2, J_3 , etc., expressing the strength of the exchange coupling between second, third, and farther neighbors.

Some information about the J_n 's can be obtained from a brief examination of the exchange coupling mechanism itself. In the rare-earth metals this is thought¹³ to be of the indirect exchange type which passes via the conduction electrons.¹⁴ Let the exchange interaction between a conduction electron of spin \mathbf{s} and an ion of spin \mathbf{S} be $-\kappa \mathbf{s} \cdot \mathbf{S}$. Since the Gd ions are in 8S states, spin-orbit effects do not arise. Then the indirect exchange coupling formula of Yosida¹⁴ can be used to give J as a function of the distance R between two ions,

$$J(R) = -\frac{9\pi}{2} n_0^2 \frac{\kappa^2}{E_F} \frac{2k_F R \cos(2k_F R) - \sin(2k_F R)}{(2k_F R)^4}. \quad (32)$$

Here n_0 is the number of conduction electrons per atom, E_F is the Fermi energy, and k_F is the corresponding value of k . Because this equation was derived assuming κ to be momentum independent and assuming free conduction electrons, its value is open to question. However, the oscillating character of Eq. (32) as a function of R is almost certainly a realistic feature of the indirect exchange mechanism, and it is this which is of interest in the present discussion. If J_1 is positive, as it must be

for strong ferromagnetic coupling, then (32) shows that J_2 and other J_n 's are likely to be negative. It is quite plausible that in gadolinium the coupling between atoms beyond nearest neighbors is on average more antiferromagnetic than ferromagnetic.

Let us now consider the effect on the high- and low-temperature J_1 values resulting from an antiferromagnetic interaction $J_2 = -\alpha J_1$ between second-nearest neighbors. As in Secs. 2 and 3 let J stand for the exchange interaction in a nearest-neighbor-only theory.

Rather than speculating on how Eq. (1) might be altered by the presence of second-nearest neighbors, we shall use the molecular field theory expression for the transition temperature of a ferrimagnet or antiferromagnet³ which suggests that Jz_1 be replaced by $J_1 z_1 + J_2 z_2$, z_n being the number of n th neighbors. Hence, for small α the relative change in the high-temperature nearest-neighbor exchange interaction is approximately

$$(J_1 - J/J) = \alpha(z_2/z_1) = \alpha/2. \quad (33)$$

The spin-wave theory is altered by extending the sums over \mathbf{q} in (6) to second neighbors. When the series expansions (18) and (19a) are recalculated, it is found that to second order in λ and μ the only effect on the dispersion relation (21a) for the acoustic mode is to replace J in (20) by $J_1 + J_2$. (Such a simple replacement does not hold for higher order terms or for the lowest order terms of the optical mode.) Hence the approximate spin-wave theory result corresponding to (33) is

$$(J_1 - J)/J = \alpha. \quad (34)$$

Equations (33) and (34) show that the high- and low-temperature nearest-neighbor exchange interactions are affected in different ways. For example, Eq. (32) suggests that α might be approximately 0.2. This would lead to an increase in the low-temperature J value from 2.1 to 2.5 $^{\circ}\text{K}$, while the high-temperature J value would increase from 2.9 to 3.2 $^{\circ}\text{K}$.

While the preceding discussion is admittedly rather crude, it illustrates in a qualitative way how interactions beyond nearest neighbors might go some distance towards accounting for the remaining discrepancy between the high- and low-temperature J values for gadolinium. It is well known that the interaction (32) is long range, and, therefore, the number of J_n 's which play an effective role is probably at least five and likely more.

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¹³ P. G. deGennes, *Compt. rend.* **247**, 1836 (1958).

¹⁴ T. Kasuya, *Progr. Theoret. Phys. (Kyoto)*, **16**, 45 (1956); K. Yosida, *Phys. Rev.* **106**, 893 (1957).