

## Application of Spin-Wave Theory to EuS†

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Magnetization data for EuS powder in zero field and at liquid-helium temperatures has been obtained by nuclear magnetic resonance of both the  $\text{Eu}^{151}$  and  $\text{Eu}^{153}$  nuclei. These data are considered simultaneously with those for the specific heat of EuS powder obtained by McCollum and Callaway in order to provide a more definitive application of the spin-wave theory to this material. The theory is that given by Holstein and Primakoff and special attention is given to the effects of magnetic dipolar coupling on the spin-wave energy and moment. The calculation was carried out by summation over the exact Brillouin zone. Values of the nearest-neighbor exchange interaction  $J_1$  and second-neighbor exchange  $J_2$ , as well as an effective field  $H$  which *simultaneously* produced reasonable agreement between calculation and experiment are  $J_1 = 0.20 \pm 0.01^\circ\text{K}$ ,  $J_2 = -0.08 \mp 0.02^\circ\text{K}$  and  $H = 4.0 \pm 0.2$  kOe. These values are fairly consistent with other parameters known for EuS.

### I. INTRODUCTION

AN unprecedented opportunity to test the Heisenberg model of ferromagnetism has been provided by the recent discovery of ferromagnetism in EuO, EuS and EuSe as well as antiferromagnetism in EuTe.<sup>1</sup> As *a priori* evidence for the validity of the model we may cite the ionic nature of these compounds and the  $^8S$  ground state of the  $\text{Eu}^{++}$  ion. The test of the model is greatly simplified for these cases because of the simple (NaCl) crystal structure. Furthermore, the Curie points, at least for the oxide and the sulfide, are sufficiently high that the predictions of the low temperature spin-wave theory as well as the high-temperature effective field theories may be compared for the same material.

The ferromagnetism of  $\text{GdCl}_3$ <sup>2</sup> and  $\text{CrBr}_3$ <sup>3</sup> have recently been discussed in terms of the Heisenberg model. For the former, the Curie point is only  $2.2^\circ\text{K}$ , and molecular field theory alone is invoked to describe its magnetic behavior. The Curie point of  $\text{CrBr}_3$  is  $37^\circ\text{K}$ , and spin-wave theory has been applied to the analysis of temperature dependence of its magnetization in the liquid-helium temperature range.<sup>4</sup> However, the description is complicated by the layered hexagonal structure of the material and no comparison between the high-temperature and low-temperature results has been made.

Detailed studies have been made of the "high-temperature" behavior of the europium compounds. The saturation moments, as functions of temperature and

field, have been compared with the molecular field theory predictions<sup>5</sup> and were found to fit the Brillouin function of spin  $\frac{7}{2}$  rather well. In the paramagnetic region the effective moment in Bohr magnetons per  $\text{Eu}^{++}$  ion, as determined by applying the Curie-Weiss law to the susceptibility, is close to the theoretical value 7.94. The transition temperature and paramagnetic Curie points have been determined by magnetic measurements and, for EuS, also by location of the specific heat anomaly.<sup>6</sup> The results are reasonably consistent and indicate the existence of two important exchange interactions; a positive exchange  $J_1$  between nearest neighbors on the face-centered cubic  $\text{Eu}^{++}$  lattice and a superexchange interaction  $J_2$  between second-neighbor  $\text{Eu}^{++}$  ions which is antiferromagnetic. Finally, Calhoun and Overmeyer<sup>7</sup> determined  $J_1$  to be positive by observing the paramagnetic resonance of exchange coupled pairs of  $\text{Eu}^{++}$  ions in CaO containing a few percent EuO.

In the temperature region far below the transition temperature the behavior of a Heisenberg ferromagnetic is known to be described by spin-wave theory. In order to test this theory for EuS, McCollum and Callaway have measured the specific heat of EuS powder between 1 and  $4^\circ\text{K}$ .<sup>8</sup> The entire specific heat in this region may be regarded as magnetic, and they attempted to fit their data to two forms of the spin-wave result. They found  $J_1$  to be positive and  $|J_2/J_1| \ll 1$ , but the sign of  $J_2$  remained uncertain.

We report here nuclear magnetic resonance measurements on the  $\text{Eu}^{151}$  and  $\text{Eu}^{153}$  nuclei in EuS powder between 1.9 and  $4.2^\circ\text{K}$ . Since the resonance frequencies are expected to be proportional to the magnetization, these measurements constitute determinations thereof. With both sets of data at hand it is possible, for the first

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<sup>1</sup> B. T. Matthias, R. M. Bozorth, and J. H. Van Vleck, *Phys. Rev. Letters* **7**, 160 (1961); R. L. Wild and R. D. Archer, *Bull. Am. Phys. Soc.* **7**, 440 (1962); T. R. McGuire, B. E. Argyle, M. W. Shafer, and J. S. Smart, *Appl. Phys. Letters* **1**, 17 (1962); S. van Houten, *Physics Letters* **2**, 215 (1962); G. Busch, P. Junod, M. Risi, and O. Vogt, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and The Physical Society, London, 1962), p. 727.

<sup>2</sup> W. P. Wolf, M. J. M. Leask, B. Magnum, and A. F. G. Wyatt, *J. Phys. Soc. Japan* **17**, Suppl. B1, 487 (1961).

<sup>3</sup> I. Tsubokawa, *J. Phys. Soc. Japan* **15**, 1664 (1960).

<sup>4</sup> A. C. Gossard, V. Jaccarino, and J. P. Remeika, *Phys. Rev. Letters* **7**, 122 (1961).

<sup>5</sup> U. Enz, J. F. Fast, S. van Houten, and J. Smit, *Philips Res. Rept.* **17**, 451 (1962).

<sup>6</sup> V. L. Moruzzi and D. T. Teaney (private communication).

<sup>7</sup> B. A. Calhoun and J. Overmeyer, Ninth Annual Conference on Magnetism and Magnetic Materials, *J. Appl. Phys.*, Suppl. (to be published).

<sup>8</sup> D. C. McCollum and J. Callaway, *Phys. Rev. Letters* **9**, 337 (1962); J. Callaway and D. C. McCollum, *Phys. Rev.* **130**, 1741 (1963).

time, to attempt a simultaneous comparison of the temperature dependence of two "independent" properties of the "same" material<sup>9</sup> with spin-wave theory. It is a feature of the work reported here that the spin-wave theory is used, again for the first time, in an exact form. In particular, the effects of magnetic dipolar coupling on the spin-wave spectrum and on the moment per spin-wave are included. The latter effect was first calculated by Holstein and Primakoff<sup>10</sup> and also treated in connection with the pseudodipolar-coupling model of anisotropy,<sup>11</sup> but it has not, to our knowledge, been seriously considered in connection with experiment until now. The numerical calculations were carried out by summation over the Brillouin zone.

It is appropriate for us to note here that Callaway and McCollum have suggested that simultaneous consideration of the specific heat and magnetization would produce more definitive results as regards the fundamental interactions in EuS. This does, in fact, turn out to be the case. The nuclear magnetic resonance experiment and its results are discussed in Sec. II. The specific heat results are also given in Sec. II. In Sec. III the necessary spin-wave results are briefly presented. In Sec. IV the simultaneous fit to spin-wave theory is presented and finally, in Sec. V we review the present knowledge of the magnetic properties of EuS comparing the high- and low-temperature results. In an appendix we discuss quantitatively the temperature regime in which the usual temperature series accurately describes the spin-wave result for the magnetization. It turns out that, for the simple cubic lattice with nearest-neighbor exchange only, the series is valid only if  $T < [2/3(S+1)]\theta$  ( $\theta$  is the paramagnetic Curie point), and that for practical purposes the series may be terminated at  $T^{7/2}$ .

## II. EXPERIMENTAL RESULTS

### Magnetization

The nuclear-resonance experiment on a ferromagnetic material is a measure of the magnetization via the hyperfine interaction

$$H = \mathbf{A} \cdot \mathbf{S}, \quad (1)$$

where  $\mathbf{I}$  is the nuclear spin and  $\mathbf{S}$  the ionic spin. If  $\mathbf{S}$  is replaced by its average value  $\langle S \rangle$  and since  $\Delta m_I = \pm 1$ , the interaction is measured by

$$g_N \beta_N H_A = A \langle S \rangle = h\nu_A, \quad (2)$$

where  $H_A$  is the hyperfine field and  $\nu_A$  the resonant frequency in that field. In EuS only the divalent europium has an ionic moment so that the magnetization of the

material is given by

$$\dot{M} = N_{\text{Eu}} g \beta \langle S \rangle, \quad (3)$$

so that

$$h\nu_A = A (M/N_{\text{Eu}} g \beta). \quad (4)$$

Since the hyperfine field is not the only field acting on the nucleus the observed frequency is not truly a measure of this interaction alone. The experiment, however, is done in zero external field and on multidomain particles so that the average demagnetizing field is also zero. The only other source of field at the nucleus is the dipole field at a site due to the rest of the crystal. Exact calculation of this field requires knowledge of the particle shape which is not available. Using the Lorentz field approximation, however, it is possible to evaluate the dipole field. Since the lattice is nearly cubic the contribution of the local dipoles may be neglected, and only the Lorentz field  $\frac{4}{3}\pi M$  is left as a correction to the hyperfine field. Since both the hyperfine field and the Lorentz field are linear in  $M$ , the resonant frequency of the nucleus is also linear in  $M$ :

$$h\nu_r = h\nu_A + h\nu_L = M[(A/Ng\beta) + \frac{4}{3}\pi]. \quad (5)$$

$A$  is a measure of the Fermi contact interaction and may be expected to vary as the lattice expansion of the material. But since the temperature range covered in the measurements is so narrow, no correction was made for a change in  $A$ . Furthermore, divalent europium is in a  $^8S_{7/2}$  ground state so the ionic  $g$  factor is 2.00 and temperature-independent. Thus, in EuS the frequency of the nuclear resonance as the temperature is varied is taken to be proportional to the sample magnetization.

The material used in the experiment was taken from the sample used by Teaney and Moruzzi<sup>6</sup> in their specific heat study of the magnetic transition. They find the Curie temperature to be 16.3°K. B. E. Argyle, at this laboratory, finds the Curie temperature of the same sample from magnetization measurements to be 16.5°K. T. R. McGuire, also at this laboratory, has made extensive studies of the magnetic properties of the same sample above and below the Curie temperature. Parameters which he obtains from the high temperature susceptibility are  $C_m = 7.34$ ,  $\mu_{\text{eff}} = 7.59$  and  $\theta \approx 19^\circ\text{K}$  using a Curie-Weiss theory. The moment per  $\text{Eu}^{2+}$  ion at 4.2°K is  $6.26\mu_B$ , assuming all ions to be  $\text{Eu}^{2+}$  and taking the x-ray density. Each of these parameters is some 5 to 8% lower than is expected for stoichiometric EuS. The most probable source of the discrepancy is the dilution of the lattice by  $\text{Eu}^{3+}$  ions.

The resonance experiments were done in two spectrometers, one a modified grid dip meter, the other a transmission line bridge. In both cases the Dewar system was within the circuitry so that only the sample was at low temperatures. The temperature was measured by determining the helium overpressure and comparing this with the 1958 pressure-temperature scale. Fre-

<sup>9</sup> The two properties are "independent" only in the sense that they are given by different functions of the same spin-wave spectrum. On the other hand, the two samples are only nominally the same, having been produced quite independently.

<sup>10</sup> T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940).

<sup>11</sup> S. H. Charap, Phys. Rev. **119**, 1538 (1960).

quencies were measured with a Hewlett-Packard counter.

Naturally occurring europium consists of two isotopes,  $\text{Eu}^{151}$  and  $\text{Eu}^{153}$ , each about 50% abundant and each with a nuclear moment. We expect, and find, strong resonance signals from each isotope. Parameters which are determined by the nuclear resonance experiment and which may be directly compared with other experiments [electron paramagnetic resonance (EPR) and ENDOR] are  $A^{151}$ ,  $A^{153}$ , the ratio  $A^{153}/A^{151}$  and the quadrupole splitting. Baker and Williams<sup>12</sup> have determined (ENDOR) the ratio  $A^{153}/A^{151}$  for  $\text{Eu}^{2+}$  in  $\text{CaF}_2$  as 0.4439, while our NMR result for this ratio is 0.4438 at 4.2°K. Shuskus<sup>13</sup> has determined (EPR) values for  $A^{151}$  and  $A^{153}$  for  $\text{Eu}^{2+}$  in  $\text{CaO}$ ,  $\text{SrCl}_2$ , and  $\text{CaF}_2$ . These values, together with NMR results for EuS are contained in Table I. In all cases the agreement among the various experiments is excellent.

The resonance of the isotope  $\text{Eu}^{153}$  was studied in somewhat more detail than that of  $\text{Eu}^{151}$  since the lower frequency,  $\sim 150$  Mc/sec, permitted the use of more sensitive apparatus. A derivative trace of this resonance in zero applied field is shown in Fig. 1. Upon the application of a field of 1.8 kOe perpendicular to the rf field, the intensity decreased and the spectrum shifted up by about 50 kc/sec. Were the resonance due to nuclei within the bulk of the material rather than those in the domain walls, the spectrum should have shifted down by 0.86 Mc/sec assuming that the hyperfine interaction is negative.<sup>12</sup> The lack of a significant frequency shift on application of a dc field indicates that the spectrum is from nuclei within the domain walls. Fig. 1 shows five definite peaks equally spaced in frequency which indicates a quadrupole splitting and which agrees with the nuclear spin value  $I = \frac{5}{2}$ .

Baker and Williams<sup>12</sup> have studied the quadrupole interaction of  $\text{Eu}^{2+}$  in  $\text{CaF}_2$  by means of the ENDOR technique. They find that  $e^2Qqh^{-1} = 2.0$  Mc/sec for  $\text{Eu}^{153}$  in this case. This is explained by the admixture of  $^6P$  and  $^6D$  excited states into the  $^8S$  ground state of the ion. If this were the cause of the observed splitting in EuS, then it must be a strictly local effect and not in any way con-

TABLE I. Values of the hyperfine constants of  $\text{Eu}^{151}$  and  $\text{Eu}^{153}$  as determined by EPR<sup>a</sup> for  $\text{Eu}^{2+}$  ions in  $\text{CaO}$ ,  $\text{SrCl}_2$ , and  $\text{CaF}_2$ , and by NMR for  $\text{Eu}^{2+}$  ions in EuS.<sup>b</sup>

	$A^{151}$ ( $10^{-4}$ cm <sup>-1</sup> )	$A^{153}$ ( $10^{-4}$ cm <sup>-1</sup> )	$T$ (°K)
CaO	30.16	13.46	4.02
CaF <sub>2</sub>	34.07	15.1	290
SrCl <sub>2</sub>	34.1	15.5	290
EuS	29.83	14.44	4.2

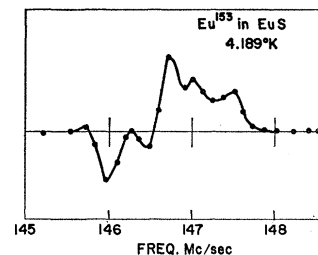
<sup>a</sup> A. Shuskus, Phys. Rev. **127**, 2022 (1962).

<sup>b</sup> Present work.

<sup>12</sup> J. M. Baker and F. I. B. Williams, Proc. Roy. Soc. (London) **A267**, 283 (1962).

<sup>13</sup> A. Shuskus, Phys. Rev. **127**, 2022 (1962).

FIG. 1. Derivative of absorption versus frequency for  $\text{Eu}^{153}$  in EuS. The line is nearly saturated.



nected to the lattice, in which case the five-line quadrupole spectrum results from the superposition of five separate wall-enhanced resonances. We would then deduce that the quadrupole splitting of  $\text{Eu}^{153}$  in EuS is 3.1 Mc/sec which is in reasonable agreement with Baker and Williams' result.

We may also calculate the magnetocrystalline-anisotropy field by measuring the change of intensity of the resonance upon application of the dc field. The formula used is the expression for the domain wall enhancement<sup>14</sup>  $\xi = H_N(H_0 + H_K)^{-1}$ . A six-fold change in  $\xi$  is observed when the applied field is changed by  $1.8 \times 10^8$  Oe. Using this value and the value of the hyperfine field,  $H_N = 340 \times 10^8$  Oe we calculate  $H_K$  as  $55 \times 10^8$  Oe. This value is at least an order of magnitude too large.

We have analyzed the quadrupole spectrum expected from a nuclear resonance in a domain wall when there is an axial electric field fixed with respect to the crystal. Depending upon the crystallographic plane which contains the domain wall and upon the choice of magnetic easy axis in the domain and the axis of electric field a distribution of absorption intensity with frequency results which contains singularities associated with the zeros in the slope of the frequency for resonance as a function of spin direction.<sup>15</sup> In particular, only if the magnetic easy axis in the domain coincides with the axis of electric field and if the domain wall is in a (110) plane, assuming only 180° walls, does the intensity distribution have five singularities. The spectrometer is sensitive to the derivative of intensity with frequency and thus it would plot five peaks from such a distribution. Were this the case we could not directly apply the enhancement expression to the calculation of the anisotropy without further knowledge of relaxation times and field gradients which are not available. On this basis the quadrupole splitting is twice that previously computed or 6.2 Mc/sec.

In any case the spectrum observed for  $\text{Eu}^{153}$  indicates a quadrupole splitting of the line.

Figure 2 is a plot of the resonant frequency of the central line of the  $\text{Eu}^{153}$  spectrum versus  $T^{3/2}$ . The solid curve is obtained by using the series expansion,

$$\nu = \nu_0 [1 - aT^{3/2}(\text{gap corr}) - bT^{5/2}(\text{gap corr})] \quad (6)$$

and obtaining a least-squares fit of the data. While this

<sup>14</sup> P. G. deGennes, P. A. Pincus, F. Hartmann-Boutron, and J. M. Winter, Phys. Rev. **129**, 1105 (1963).

<sup>15</sup> For an example of a similar calculation for dipolar fields see E. L. Boyd and J. C. Slonczewski, J. Appl. Phys. **33**, 1077 (1962).

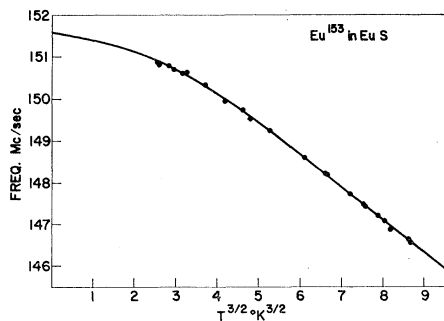


FIG. 2. NMR frequency versus  $T^{3/2}$  for  $\text{Eu}^{153}$  in  $\text{EuS}$ . The solid curve is a least-squares fit of the series expansion which results from simple spin-wave theory.

equation is not strictly applicable to the case of  $\text{EuS}$ , it is what would result from a simple spin-wave theory and gives a value of  $\nu_0 = 151.6$  Mc/sec.

Figure 3 is similar to Fig. 2 except that the isotope is now  $\text{Eu}^{151}$ ; it yields  $\nu_0 = 343.0$  Mc/sec. The loaded transmission line used for this study was not sensitive enough to resolve the quadrupole splitting of the resonance.

With an extrapolated value of  $\nu_0$ , the frequency at  $0^\circ\text{K}$  obtained from the solid curves of Figs. 2 and 3, a new normalized plot  $[\nu(T) - \nu_0]/\nu_0$  is made. This is shown in Fig. 4. The normalized data points lie on the same curve. This is a good internal check of the data. It also shows that frequency pulling by nuclear spin waves as discussed by de Gennes *et al.*,<sup>14</sup> is not a factor in the comparison with the magnetization.

### Specific Heat

The data taken by McCollum and Callaway<sup>8</sup> of low temperature specific heat of  $\text{EuS}$  cover the same temperature range as the nuclear resonance data. These data are included for the comparison with spin-wave theory. They are plotted in Fig. 5. In view of the linewidth obtained in the NMR study the measurement of  $M$  versus  $T$  and  $C/R$  versus  $T$  are of comparable precision (0.1%  $C/R$  versus  $T$  and 0.03%  $M$  versus  $T$ ).

The materials used were prepared by M. W. Shafer at this laboratory and by Wild and Archer<sup>1</sup> for the specific

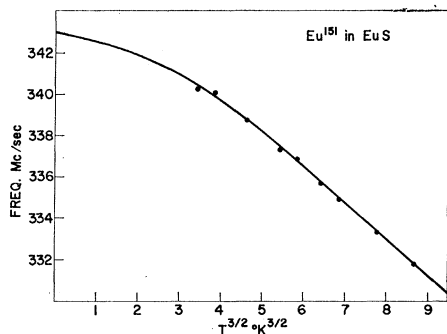


FIG. 3. NMR frequency versus  $T^{3/2}$  for  $\text{Eu}^{151}$  in  $\text{EuS}$ . The solid curve is a least-squares fit of the series expansion which results from simple spin-wave theory.

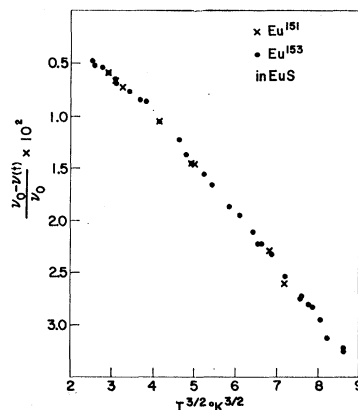


FIG. 4. The reduced frequency  $(\nu(T) - \nu_0)/\nu_0$  versus  $T^{3/2}$  for  $\text{EuS}$ . The value of  $\nu_0$  is taken from the solid curve in Figs. 2 and 3.

heat sample by essentially the same technique. The Curie temperatures were 16.3 and  $17^\circ\text{K}$ , respectively. It is probable that the  $\text{Eu}^{2+}$  content was about the same in both cases. Thus, the measurements of  $M$  versus  $T$  and  $C/R$  versus  $T$ , while made on different samples of the same material, may be compared.

### III. SPIN-WAVE THEORY

All of the theory which we require is contained in the famous paper of Holstein and Primakoff.<sup>10</sup> The results to be used are stated below, and we discuss the possibility of making the usual approximations leading to the results normally presented as those of spin-wave theory.

The deviation due to spin-wave excitation at temperature  $T$  of the magnetization  $M(T)$  from its value at absolute zero is given by:

$$\frac{M(0) - M(T)}{M(0)} = \frac{1}{g\beta NS} \sum_{\mathbf{k}} \mu_{\mathbf{k}} \langle n_{\mathbf{k}} \rangle, \quad (7)$$

where  $N$  is the density of magnetic ions,  $\mu_{\mathbf{k}}$  is the moment associated with a spin-wave vector  $\mathbf{k}$  ( $= g\beta$  in the absence of dipolar coupling;  $g$  is the spectroscopic splitting factor, and  $\beta$  the Bohr magneton) and  $\langle n_{\mathbf{k}} \rangle$  denotes the Bose distribution function (number of spin waves)

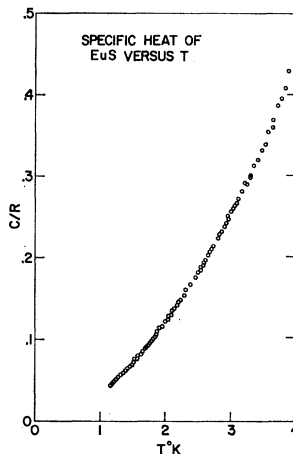


FIG. 5. Specific heat versus temperature for  $\text{EuS}$ . This figure was supplied by Dr. McCollum of the University of California at Riverside.

over the spin-wave energies  $e_{\mathbf{k}}$ ;

$$\langle n_{\mathbf{k}} \rangle = [\exp(e_{\mathbf{k}}/k_B T) - 1]^{-1}. \quad (8)$$

Here  $k_B$  is Boltzmann's constant, and  $S$  is the spin per magnetic ion. The specific heat associated with the excitation of spin waves is

$$\begin{aligned} \frac{C}{R} &= \frac{1}{N k_B} \sum_{\mathbf{k}} e_{\mathbf{k}} \frac{\partial}{\partial T} \langle n_{\mathbf{k}} \rangle \\ &= \frac{1}{N} \sum_{\mathbf{k}} \left( \frac{e_{\mathbf{k}}}{k_B T} \right)^2 \frac{\exp(e_{\mathbf{k}}/k_B T)}{[\exp(e_{\mathbf{k}}/k_B T) - 1]^2}. \end{aligned} \quad (9)$$

The Hamiltonian  $H$  involves the exchange which we restrict to all nearest-neighbor (nn) and next-nearest-neighbor (nnn) pairs  $\langle i, j \rangle$ ;

$$H_{\text{ex}} = -2J_1 \sum_{\langle i, j \rangle \text{nn}} \mathbf{S}_i \cdot \mathbf{S}_j - 2J_2 \sum_{\langle i, j \rangle \text{nnn}} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (10)$$

with  $\mathbf{S}_i$  the spin operator associated with the site  $i$ . For a system governed by this exchange the spin-wave energies are given by

$$\begin{aligned} \epsilon_{\mathbf{k}} &= 2SJ_1 \sum_{\mathbf{l}_1} [1 - \exp(i\mathbf{k} \cdot \mathbf{l}_1)] \\ &\quad + 2SJ_2 \sum_{\mathbf{l}_2} [1 - \exp(i\mathbf{k} \cdot \mathbf{l}_2)], \end{aligned} \quad (11)$$

where  $\mathbf{l}_1$  and  $\mathbf{l}_2$  denote, respectively, the set of  $Z_1$  nearest-neighbor and  $Z_2$  next-nearest-neighbor vectors of the magnetic lattice. While the experiments are performed on unmagnetized powder samples, the individual domains are understood to be magnetized according to local conditions of anisotropy, interdomain fields and the magnetic dipolar coupling within the domain. These effects are represented in the Hamiltonian by a Zeeman energy term

$$H_z = -g\beta H \sum_i S_{iz}, \quad (12)$$

and the dipolar interaction between all pairs  $\langle i, j \rangle$

$$H_d = \sum_{\langle i, j \rangle} \frac{(g\beta)^2}{r_{ij}^3} \left\{ \mathbf{S}_i \cdot \mathbf{S}_j - 3 \frac{(\mathbf{S}_i \cdot \mathbf{r}_{ij})(\mathbf{S}_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} \right\}. \quad (13)$$

Here  $H$  is the component along the domain magnetization direction  $z$  of the field acting on the domain, and  $\mathbf{r}_{ij}$  is the separation of the pair of sites  $i, j$ . Each domain is assumed to be uniformly magnetized and the demagnetizing field resulting from Eq. (13) will be included, along with an effective anisotropy field and the interdomain field in  $H$ .

The spin-wave spectrum for a nearly saturated magnetic domain governed by the Hamiltonian  $H = H_{\text{ex}} + H_z + H_d$  was first calculated by Holstein and Primakoff.<sup>10</sup> Under the assumption that certain dipole sums may be replaced by integrals, they found

$$\epsilon_{\mathbf{k}} = (\epsilon_{\mathbf{k}} + g\beta H) \{1 + \phi_{\mathbf{k}} \sin^2 \theta_{\mathbf{k}}\}^{1/2}, \quad (14)$$

where  $\epsilon_{\mathbf{k}}$  is given by Eq. (11),

$$\phi_{\mathbf{k}} = g\beta 4\pi M / (\epsilon_{\mathbf{k}} + g\beta H), \quad (15)$$

and  $\theta_{\mathbf{k}}$  is the angle between the wave vector  $\mathbf{k}$  of the spin wave and the magnetization  $\mathbf{M}$ . The reduction in moment associated with the excitation of a spin wave is

$$\mu_{\mathbf{k}} = \frac{\partial}{\partial H} \epsilon_{\mathbf{k}} = g\beta \frac{1 + \frac{1}{2} \phi_{\mathbf{k}} \sin^2 \theta_{\mathbf{k}}}{[1 + \phi_{\mathbf{k}} \sin^2 \theta_{\mathbf{k}}]^{1/2}}, \quad (16)$$

which differs from  $g\beta$  only beyond the first order in the dipolar interaction. For application to experiment it is almost habitual to expand the radicals appearing in Eqs. (14) and (16) keeping only the leading term in  $\phi_{\mathbf{k}}$ . Physically, this involves the assumption that the energy of spin waves excited in the experiment is largely given by the exchange and Zeeman terms; the dipolar interaction being only a small perturbation. Immediately, one then has  $\mu_{\mathbf{k}} = g\beta$ . Under this approximation it is also valid to calculate thermodynamic properties neglecting the variation of spin-wave energy with the angle of propagation  $\theta_{\mathbf{k}}$ ; i.e., replace  $\sin^2 \theta_{\mathbf{k}}$  by its average value,  $\frac{2}{3}$ . Then  $\langle n_{\mathbf{k}} \rangle$  is calculated using the dispersion law

$$e_{\mathbf{k}} = \epsilon_{\mathbf{k}} + g\beta(H + \frac{4}{3}\pi M), \quad (17)$$

so that the effect of the dipolar coupling on the spin-wave spectrum is represented by the demagnetizing field (included in  $H$ ) and the Lorentz local field correction  $\frac{4}{3}\pi M$ . It is further assumed that the spin-wave exchange energy, already taken to be large compared to  $g\beta 4\pi M \sin^2 \theta_{\mathbf{k}}$ , is small compared to that corresponding to the Brillouin zone boundary. In that case it is appropriate to expand  $\epsilon_{\mathbf{k}}$  in powers of  $\mathbf{k}$ , keeping only the leading terms, and also to convert the sum on  $\mathbf{k}$  to integrals, extending the range of integration to  $|k| = \infty$ . The result of this procedure is the well-known spin-wave theory in which the magnetization and specific heat vary as  $T^{3/2}$ ; leading corrections due to the periodicity of the lattice appear as terms proportional to  $T^{5/2}$  and, because of the gap in the spectrum  $g\beta(H + \frac{4}{3}\pi M)$  the coefficients have a temperature as well as field dependence.<sup>16</sup>

For EuS in the helium temperature range, none of the procedure described below Eq. (16) is applicable. From the previous work on this material it is known that  $g\beta 4\pi M / k_B \approx 2^\circ\text{K}$ , so that the expansion of the radical is not valid for many of the spin-waves excited. Furthermore the exchange, as measured by  $2S(J_1 + J_2)$ , corresponds to about  $1^\circ\text{K}$ . We include, in the appendix, an unpublished calculation due to Tanaka and Glass<sup>17</sup> for the simple cubic lattice and nearest-neighbor exchange only, and show that the power series in  $T$  is valid only for  $4SJ_1/k_B T > \approx 1.5$ . It is reasonable to expect that a similar criterion will obtain for the face-centered cubic lattice. Therefore, we conclude that the results indicated

<sup>16</sup> For an application of this form of the theory, see B. E. Argyle, S. H. Charap, and E. W. Pugh, Phys. Rev. **132**, 2051 (1963).

<sup>17</sup> T. Tanaka and S. J. Glass (to be published).

by the equations of this section must be used without approximation in the present context.

#### IV. RESULTS

The expressions needed for a complete calculation of specific heat and magnetization in the circumstance that spin-wave excitation is dominant are given in Sec. III. The formulas may be parametrized as follows:

$$\begin{aligned} \mathcal{J} &= 2SJ_1/k_B, \\ \mathcal{P} &= -J_2/J_1, \\ \mathfrak{M} &= g\beta 4\pi M/2SJ_1, \\ \mathfrak{C} &= g\beta H/2SJ_1, \end{aligned} \quad (18)$$

so that a choice of values for these four quantities completely specifies a material as regards its magnetic behavior. It is not our purpose to find those parameters which separately produce best fits to the magnetization and specific heat data. Previous attempts have resulted in rather good fits over a broad range of microscopic parameters despite the fact that the formulas used to produce these are not quite correct. Considering the deficiencies of the available samples of EuS, it was not expected that a least square analysis based on the correct spin-wave formulas would yield a much narrower range of possibilities. The following procedure was adopted: Values were assigned to  $\mathcal{P}$ ,  $\mathfrak{M}$ , and  $\mathfrak{C}$ , and specific heat and magnetization were calculated numerically on an IBM 7094 computer for an appropriate range of values of  $\mathcal{J}/T$ . By comparison with the experimental results we determine values of  $\mathcal{J}/T$  corresponding to the various temperatures of experimental measurement. For the magnetization 29 experimental points between 1.890 and 4.219°K were used. For the specific heat twelve points at equal temperature intervals between 1.25 and 4.00°K were read off the graph. In this way the value of  $\mathcal{J}$  required to fit each experimental point for given  $\mathcal{P}$ ,  $\mathfrak{M}$ , and  $\mathfrak{C}$  is determined. If the latter parameters are fortunately chosen it is expected that the set of  $\mathcal{J}$  values so obtained will be a reasonably consistent set.

In every case  $\mathfrak{M}$  was chosen to reflect a value of  $4\pi M \approx 14$  kOe. This value is based on the result of the magnetic moment measurement ( $\approx 194$  emu/g) converted to a magnetization value through the x-ray density (5.7 g/cc). As indicated in Sec. II, this magnetization is smaller than the theoretical value and the value of NS on the right-hand side of Eq. (7) must be reduced appropriately for the calculation. The same correction does not apply to Eq. (9) since the measured specific heat is normalized to the stoichiometric density of  $\text{Eu}^{2+}$  ions. Values of  $\mathfrak{C}$  were chosen to correspond to field increments of the order of 500 Oe and it turned out not to be meaningful to examine values of  $\mathcal{P}$  in smaller increments than 0.05.

If attention is restricted to the magnetization alone, it is impossible to determine  $\mathcal{J}$ ,  $\mathcal{P}$ , or  $\mathfrak{C}$  although a relation among these is established. At all values of  $\mathcal{P}$  which

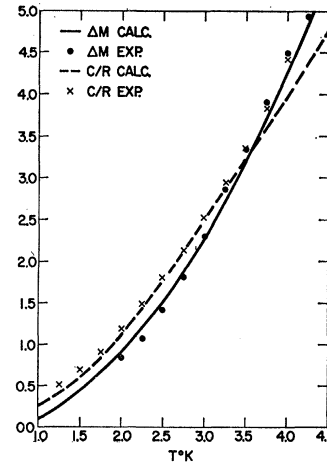


FIG. 6. Comparison of experimental values of  $M_0 - M(T)$  for  $\text{Eu}^{153}$  in units of  $10^6 M_0/\nu_0$  and  $C/R$  (in units of  $10^{-1}$  J/mole-deg) with calculated values of the two using  $J_1/k_B = 0.21^\circ\text{K}$ ,  $\mathcal{P} = 0.4$ , and  $H = 4$  kOe.

were considered ( $-0.3 \leq \mathcal{P} \leq 0.6$ ), a value of  $\mathfrak{C} (\geq 0)$  was found which produced a very consistent set of  $\mathcal{J}$  values (rms deviations  $\approx 1\%$ ) over the measured temperature range. If, on the other hand, attention is restricted to specific heat alone, good fits (rms deviations of  $\mathcal{J} < 4\%$  though never less than  $2.6\%$ ) are obtained for  $0.2 < \mathcal{P} < 0.6$  for certain values of  $\mathfrak{C}$ . Within this range acceptable fits to specific heat and magnetization occurred simultaneously for the following parameters:

$$\begin{aligned} \mathcal{P} &= 0.3; H \approx 2 \text{ kOe}; J_1/k_B = 0.19^\circ\text{K}, \\ \mathcal{P} &= 0.4; H \approx 4 \text{ kOe}; J_1/k_B = 0.20^\circ\text{K}, \\ \mathcal{P} &= 0.5; H \approx 6 \text{ kOe}; J_1/k_B = 0.21^\circ\text{K}, \end{aligned}$$

with rms deviations in  $J_1$  of about  $3\%$ . Figure 6 is a plot of  $\nu_0 - \nu(T)$  and  $C/R$  as calculated for  $\mathcal{P} = 0.4$  with a number of experimental points included for comparison. The fit is observed to be fair, as would be expected from the discussion above. Our result may be stated as

$$\begin{aligned} J_1/k_B &= 0.20 \pm 0.01^\circ\text{K}, \\ J_2/k_B &= -(0.08 \pm 0.02^\circ\text{K}), \end{aligned}$$

and

$$H = 4 \pm 2 \text{ kOe},$$

where a degree of correlation in the uncertainties attached to these quantities should be recognized. These results will be discussed in relation to other evidence on the properties of EuS in the next section.

#### V. DISCUSSION

Although the cubic europium compounds, EuO, EuS, EuSe, and EuTe are expected to be the very nearly ideal physical manifestation of the Heisenberg model, the available specimens are far from perfect. Nevertheless, the various studies of the magnetic behavior of EuS do present us with reasonably consistent picture based on that model.

We begin by deriving from the present results some numbers of interest. The exchange energy associated

with the ground state is

$$-NS^2(J_1Z_1+J_2Z_2)=-NS^2J_1Z_1(1-\frac{1}{2}p). \quad (19)$$

The remaining magnetic effects which have been represented above by an effective magnetic field contribute to the ground state an energy

$$-\alpha HM, \quad (20)$$

where  $\alpha$  is a number between  $\frac{1}{2}$  and 1. The value of  $\alpha$  depends upon the relative strength of those contributions whose origin is in internal interactions such as the dipolar fields ( $\alpha=\frac{1}{2}$ ) and those which have the nature of one-ion effects ( $\alpha=1$ ). This ground-state energy is measured by integrating the magnetic specific heat from  $T=0$  to  $T=\infty$ . We have the energy per ion

$$\int_0^\infty \frac{C_m(T)}{R} dT = Z_1 S^2 \frac{J_1}{k_B} (1-\frac{1}{2}p) + \alpha \frac{HM}{Nk_B}, \quad (21)$$

which takes on a range of values of about 24–27°K according to our results. The Curie point  $T_c$  is calculated by combining the Rushbrooke and Wood empirical formula for nearest-neighbor exchange only

$$(k_B T_c / J_1)_{p=0} = 99, \quad (Z_1 = 12, s = \frac{7}{2}) \quad (22)$$

with the molecular field result for the variation of the Curie point as second-neighbor exchange is "turned on"

$$\left(\frac{k_B T_c}{J_1}\right)_p = (1-\frac{1}{2}p) \left(\frac{k_B T_c}{J_1}\right)_{p=0} \quad (23)$$

to give

$$(T_c)_p = 99(1-\frac{1}{2}p) \left(\frac{J_1}{k_B}\right)_p. \quad (24)$$

Our parameters give for EuS,

$$T_c = 15.8 \pm 0.6^\circ\text{K}. \quad (25)$$

The paramagnetic Curie point is given by

$$\theta = \frac{2}{3}S(S+1)(Z_1J_1+Z_2J_2) = 126(J_1/k_B) \times (1-\frac{1}{2}p) = 20.1 \pm 0.8^\circ\text{K}. \quad (26)$$

Experimentally the Curie point of EuS has been determined by location of the specific heat anomaly. Moruzzi and Teaney<sup>6</sup> find  $T_c=16.3^\circ\text{K}$  in this way, and also

$$\int_0^\infty \frac{C_m(T)}{R} dT = 31 \pm 3^\circ\text{K}. \quad (27)$$

This last result was found by subtracting from the observed behavior a lattice term proportional to  $T^3$  and assuming that  $C_m \approx T^{-2}$  far beyond the transition. The Curie point has also been determined from magnetic measurements by Argyle, who found  $T_c=16.5^\circ\text{K}$ . All of these results were obtained for the material used in the NMR experiment. The Curie point of the material used by Callaway and McCollum<sup>8</sup> was measured by Archer

and Wild<sup>1</sup> as  $T_c=17 \pm 1^\circ\text{K}$ . The paramagnetic Curie point is  $\approx 19^\circ\text{K}$ .

Finally, by comparing the transition temperatures and paramagnetic Curie points of EuO, EuS, EuSe, and EuTe (the telluride is antiferromagnetic), McGuire and co-workers<sup>18</sup> have speculated on the values of  $J_1$  and  $J_2$ . Our results tend to confirm their picture of the variation of the interaction strengths in this series of compounds. Values for  $J_1$  and  $J_2$  have been deduced from the specific heat data by Callaway and McCollum<sup>8</sup> and recently by Low.<sup>19</sup> Both estimates involve integration over the exact Brillouin zone and neglect of all magnetic effects. Callaway and McCollum have  $J_1/k_B=0.172 \pm 0.019^\circ\text{K}$  and  $J_2/k_B=-0.012 \pm 0.032^\circ\text{K}$ . Low, who took into account the renormalization of spin-wave energies by an iteration procedure, found that the lower temperature part of the curve is fitted with  $J_1=0.20^\circ\text{K}$  and  $J_2=-0.07^\circ\text{K}$ , while the higher temperature part deviates from his calculated values in much the same way as in our Fig. 6. Although the calculated and measured values of the integrated specific heat are not reconciled, it would appear that no very serious discrepancies have yet come to light. The magnitudes of  $J_1$  and  $J_2$  may presumably be calculated from first principles. However, the extremely large effective field ( $H \approx 3000-4000$  Oe), which has already been indicated by the large fields required to saturate the EuS powder,<sup>1</sup> is not explained. Magnetocrystalline anisotropy should be small in view of the fact that divalent europium has an  $S$  ground state (the magnetic dipolar coupling will account for  $K_1/M \approx 100$  Oe).

#### ACKNOWLEDGMENTS

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#### APPENDIX. MAGNETIZATION OF A SIMPLE CUBIC LATTICE

We present an exact calculation, first performed by Tanaka and Glass<sup>17</sup> for the magnetization of a simple cubic lattice with nearest-neighbor exchange in the spin-wave region. The result is expressed in closed forms in terms of a Bessel function of imaginary argument.<sup>20</sup>

The dispersion law is

$$\epsilon_k = 4SJ(3 - \cos k_x a - \cos k_y a - \cos k_z a). \quad (A1)$$

<sup>18</sup> T. R. McGuire, B. E. Argyle, M. W. Shafer, and J. S. Smart, *J. Appl. Phys.* **34**, 1345 (1963).

<sup>19</sup> G. G. Low, (unpublished).

<sup>20</sup> All of the Bessel function properties used here are stated by E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (The Macmillan Company, New York, 1943), p. 373.

where the cube edges have length  $a$  and lie along the  $x$ ,  $y$ , and  $z$  directions. The fractional deviation of the moment from saturation at temperature  $T$  is

$$\frac{M(0) - M(T)}{M(0)} = \frac{a^3}{(2\pi)^3 S} \sum_{n=1}^{\infty} \int d^3k \exp(-n\epsilon_k/k_B T). \quad (\text{A2})$$

In obtaining this result the Bose-Einstein function has expanded in powers of  $\exp(-\epsilon_k/k_B T)$  and the sum over the Brillouin zone has been replaced by an integral with limits  $-\pi \leq k_x a \leq \pi$ ,  $-\pi \leq k_y a \leq \pi$ ,  $-\pi \leq k_z a \leq \pi$ . We define  $g = 2SJ/k_B T$  and  $K_i = k_i a$  ( $i = x, y, z$ ) and find

$$\frac{M(0) - M(T)}{M(0)} = \frac{1}{(2\pi)^3 S} \sum_{n=1}^{\infty} \times [\exp(-n2g) \int_{-\pi}^{\pi} dK \exp(n2g \cos K)]^3 \quad (\text{A3})$$

$$= \frac{1}{S} \sum_{n=1}^{\infty} [\exp(-n2g) I_0(n2g)]^3, \quad (\text{A4})$$

where

$$I_0(z) = J_0(iz) = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{z \cos \theta} d\theta \quad (\text{A5})$$

is a Bessel function of the first kind.

While Eq. (A4) represents the exact solution, it is of interest to examine this result for low temperatures, i.e., large  $g$ . The Bessel function possesses an asymptotic expansion for large  $z$

$$I_0(z) \sim \left[ \frac{e^z}{(2\pi z)^{1/2}} \right] \left[ 1 + \sum_{r=1}^{\infty} \frac{1^2 \times 3^2 \cdots (2r-1)^2}{r! 2^3 r z^r} \right] \\ = \frac{e^z}{(2\pi z)^{1/2}} \sum_{r=1}^{\infty} \frac{[\Gamma(r + \frac{1}{2})]^2}{\pi r! (2z)^r}. \quad (\text{A6})$$

Insertion of this series into the result, Eq. (A4), reproduces the well-known series in half-integer powers of  $T$ , which is known to be correct at low temperatures. As the temperature is increased and terms beyond  $T^{3/2}$  begin to become important, as noted by Callaway and McColl-

um,<sup>8</sup> it is quite likely that the series itself may be in error. The usual derivation of the series involves a calculation in which the finite size of the Brillouin zone is neglected, and as the temperature is increased this approximation tends to lose its validity.

We now proceed to make use of the preceding analysis to investigate the range of usefulness of the temperature series result. The asymptotic expansion (A6) is, of course, a nonconvergent series. The difference between the function itself and the sum of the first  $p+1$  terms is of the order of the term given by  $r=p+1$ . In general, for finite  $z$  this difference decreases as  $p$  is increased, reaches a minimum at  $p=p_0$ , and then increases without limit as  $p \rightarrow \infty$ . As  $z$  is decreased in magnitude  $p_0$  becomes progressively smaller. Thus, as  $z$  is decreased the number of terms to be used to represent  $I_0(z)$  is also decreased until, finally, for  $z \approx 1$  the expression must be abandoned entirely. We have investigated the behavior of the asymptotic expansion by comparison with tabulated values<sup>21</sup> of  $I_0(z)$ . At  $z=1.5$  the first three terms yield  $I_0$  to within about 1%. While the error resulting from using these terms for  $z > 1.5$  is less than 1%, for  $z < 1.5$  the error is greater and its dependence on  $z$  introduces a spurious slope.

For calculation of the magnetization the argument  $z$  is  $n2g$  and it is clear that for all values of  $g$  there is a value of  $n$  large enough that  $n2g \gg 1$ . However, the  $n=1$  term contributes of the order of one-half of the entire sum. Therefore, we conclude that the temperature series may be used only if  $2g > 1.5$ , and in that case that it may be terminated at  $T^{7/2}$  with no greater error than  $\approx 1.5\%$ . We note that since the paramagnetic Curie point is given by

$$k_B \theta = 4S(S+1)J, \quad (\text{A7})$$

the criterion for use of the temperature series is

$$T < \frac{2}{3} [\theta / (S+1)]. \quad (\text{A8})$$

This criterion is simply a reflection of the fact that the Curie temperature is of the order of  $S+1$  times the temperature required to excite spin-waves near the edge of the Brillouin zone.

<sup>21</sup> E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, Inc., New York, 1945), p. 226.