

## Modified Callen Decoupling in the Green's-Function Theory of the Heisenberg Ferromagnet with Application to the Europium Chalcogenides†

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We present a first-order Green's-function analysis of the Heisenberg ferromagnet based on a decoupling scheme which produces excellent agreement with exact results. We believe this to be the most reliable simple method available for the calculation of Curie temperatures or of other statistical properties. Explicit polynomial expressions for the Curie temperatures of Heisenberg ferromagnets with nearest-neighbor and next-nearest-neighbor exchange are given for the three cubic lattices. The theory predicts a  $k$ -dependent renormalization of the magnon energies for non-nearest-neighbor models. In the case of nearest-neighbor and next-nearest-neighbor exchange, it suggests an antiferromagnetic-ferromagnetic transition for a certain narrow range of the ratio of the exchange constants. The method is illustrated by application to the europium chalcogenides. It is shown that the empirical paramagnetic and ferromagnetic Curie temperatures are inconsistent with the assumption of first- and second-neighbor exchange only. The inclusion of magnetic dipole interactions removes the contradiction between theory and experiment and allows the determination of the ratio  $J_2/J_1$ . This ratio is found to be about 0.7 for EuO and  $-0.1$  for EuS.

### I. INTRODUCTION

Some years ago Callen<sup>1</sup> presented a simple method for the decoupling of the Green's-function equations for a Heisenberg ferromagnet. His purpose was to improve the accuracy beyond the random phase approximation (RPA)<sup>2,3</sup> while retaining a conveniently practical theory. Such a theory could be the working model for a wide variety of theoretical investigations in ferromagnets, wherever a knowledge of the basic magnetization process would be required. The purpose of this paper is to improve and extend the Callen theory, with a particular interest in the application to the europium chalcogenides. By a simple modification of the Callen decoupling (CD) excellent agreement with the Padé approximant<sup>4-7</sup> predictions of the Curie temperatures was achieved, and agreement maintained with Dyson's low-temperature expansion.<sup>8</sup> The resulting theory is as simple and convenient as RPA, but very much more accurate. Furthermore, the author believes that where Padé results are not available the method provides the most reliable simple estimates of the Curie temperatures.

The application of the results of this theory to the case of the europium chalcogenides has been considered. It has been found that the measured ferromagnetic<sup>9,10</sup> and paramagnetic<sup>11,12</sup> Curie temperatures are inconsistent with the assumption of first- and second-nearest-neighbor exchange only. The inclusion of the magnetic dipole interactions in the Hamiltonian removes the contradiction between theory and experiment and allows the determination of the ratio of the exchange constants ( $\gamma = J_2/J_1$ ) through a knowledge of the ratio of the ferromagnetic to the paramagnetic Curie temperature. The

ratio of the exchange constants is found to be approximately 0.7 for EuO and  $-0.1$  for EuS, in contrast to previous estimates of  $-0.1$  for EuO and  $-0.5$  for EuS.<sup>11</sup>

The theory predicts a  $k$ -dependent renormalization of the magnon energies for non-nearest-neighbor models. In the case of nearest-neighbor and next-nearest-neighbor exchange, it suggests an antiferromagnetic-ferromagnetic transition for a certain narrow range of the ratio of the exchange constants.

For convenience in future work, we have calculated explicit polynomial expansions for the Curie temperatures of Heisenberg ferromagnets with first- and second-nearest-neighbor exchange for the three cubic lattices

### II. DECOUPLING METHOD

The well-known exposition of the basic Green's-function analysis<sup>1</sup> shall not be repeated here. Callen terminated the infinite hierarchy of equations of motion at the first order by invoking the decoupling approximation

$$\langle\langle S_g^z S_f^z; B \rangle\rangle \rightarrow \langle S_g^z \rangle \langle\langle S_f^z; B \rangle\rangle - \alpha \langle S_g^z S_f^z \rangle \langle\langle S_g^z; B \rangle\rangle, \quad g \neq f \quad (1)$$

and by choosing

$$\alpha = (1/2S^2) \langle S^z \rangle. \quad (2)$$

We may compare the results of this theory with other theories by noting that the molecular field approximation (MFA)<sup>13</sup> for nearest-neighbor exchange predicts Curie temperatures given by

$$k T_c^{\text{MFA}} = \frac{2}{3} S(S+1) J_z \quad (3)$$

and that the RPA<sup>3</sup> result is then just

$$T_c^{\text{RPA}} = T_c^{\text{MFA}} / F(-1), \quad (4)$$

where

$$F(-1) = \frac{1}{N} \sum_k \frac{J(0)}{J(0) - J(k)}. \quad (5)$$

The CD<sup>1</sup> then predicts

$$T_c^{\text{CD}} = T_c^{\text{RPA}} \left\{ 1 + \frac{1}{3}(1 + 1/S)[1 - F^{-1}(-1)] \right\}. \quad (6)$$

The CD predictions of Curie temperatures are in good agreement with the Padé approximant results for high-spin values and especially in the limit of infinite spin, but are relatively unsatisfactory for low spins.

In a careful analysis of known results, and a comparison with existing theories, Tahir-Kheli<sup>14</sup> observed that the known Padé approximant results were reproduced remarkably accurately<sup>15</sup> by a formula which can be written as

$$T_c^{\text{TK}} = T_c^{\text{RPA}} \left\{ 1 + \frac{1}{3}(1 - 1/S)[1 - F^{-1}(-1)] \right\}. \quad (7)$$

He proposed a means of superposing these results onto a Green's-function analysis, albeit by a somewhat *ad hoc* procedure which was not a direct-decoupling approximation.

The essential key to our method is to note that the preliminary choice of  $\alpha$  as

$$\alpha = \frac{1}{2S^2} \frac{S-1}{S+1} \langle S^z \rangle \quad (8)$$

gives precisely the Curie temperatures of Eq. (7).

In the low-temperature region, Eq. (8) predicts the correct terms in  $T^{3/2}$ ,  $T^{5/2}$ , and  $T^{7/2}$  for the expansion of the magnetization. Unfortunately, however, it also introduces a spurious  $T^3$  term for general spin, and it predicts an inaccurate coefficient for the  $T^4$  term. To correct these shortcomings, one can include in  $\alpha$  an additional term to ensure that  $\alpha \rightarrow 1/2S$  as  $\langle S^z \rangle \rightarrow S$  [in agreement with Eq. (2) in the low-temperature limit] while preserving the same Curie temperatures as Eq. (7). In particular, we amend Eq. (7) to define the modified Callen decoupling (MCD). We have

$$\alpha = \frac{1}{2S^2} \frac{S-1}{S+1} \langle S^z \rangle + \frac{1}{S(S+1)} \left( \frac{\langle S^z \rangle}{S} \right)^3. \quad (8')$$

The choice of the exponent in the last term of Eq. (8) reflects the work of Copeland and Gersch.<sup>16</sup> For  $S=1$ , the first term of Eq. (8) vanishes and our expression for  $\alpha$  coincides with theirs. They noted that unless the exponent was equal to or greater than 3, the magnetization would be double valued. This observation leads us to the choice of a cubic rather than quadratic dependence on the magnetization for the second term of Eq. (8).

It is easily corroborated that this choice of  $\alpha$  does eliminate the  $T^3$  term in the magnetization, and that it restores the coefficient of the  $T^4$  term

to that calculated by Dyson in the Born approximation. Furthermore, the first two terms of the high-temperature expansion of the susceptibility are reproduced exactly and the third is reproduced approximately (as in RPA and CD).

### III. EXTENSION BEYOND NEAREST-NEIGHBOR MODELS

Now that we have established a decoupling scheme for the case of nearest-neighbor interactions, we proceed to extend it to investigate more general cases. We first define a shell of neighbors of some "central site" as the set of sites which are mapped onto a given site by operations of the point group of the crystal. Then we can again simplify the Green's-function equations. Indexing the shells by " $j$ ," we find the magnon energy to be

$$E(\vec{k}) = \mu_B H + 2 \langle S^z \rangle \sum_j [J_j(0) - J_j(\vec{k})] [1 + 2\alpha f_j], \quad (9)$$

where

$$J_j(\vec{k}) = J_j \sum_{\Delta_j} e^{i\Delta_j \cdot \vec{k}}. \quad (10)$$

The  $\vec{\Delta}_j$  are the vectors connecting the central site to the members of the  $j$ th shell and

$$f_j = \frac{1}{NJ_j(0)} \sum_k J_j(\vec{k}) [e^{-E(k)/kT} - 1]^{-1}. \quad (11)$$

Together with the other equations of the Green's-function method, these form a set of simultaneous equations which can be solved self-consistently for the magnetization and for other quantities of interest.

It is interesting and important to note that many theories, including RPA- and Callen-type decouplings restricted to nearest-neighbor models, predict energy spectra similar to the simple spin-wave spectrum, but with a  $k$ -dependent renormalization factor  $R$ :

$$E(\vec{k}) = \mu_B H + 2SR[J(0) - J(\vec{k})]. \quad (12)$$

However, MCD does not predict a spectrum of this form for models with more than nearest-neighbor interactions. Instead, we can refer the result of MCD to a simple spin-wave spectrum by introducing a distinct renormalization factor  $R_j$  for each shell which interacts with the central site. Thus, we can rewrite Eq. (9) as

$$E(k) = \mu_B H + 2S \sum_j R_j [J_j(0) - J_j(\vec{k})], \quad (13)$$

where

$$R_j = (\langle S^z \rangle / S) [1 + 2\alpha f_j]. \quad (14)$$

Owing to the differing temperature and magnetic field dependences of the  $f_j$ 's, the renormalization factors of different shells also exhibit different functional dependences on temperature and magnetic field. These reflect the fact that the correlations between two spins depends on the distance be-

TABLE I. Coefficients of an expansion of  $kT_c/J_1$  in powers of  $\gamma$  for a sc crystal in the range  $0 < \gamma < 1$ .

$S$	$a_0$	$a_1$	$a_2$	$a_3$
0.5	1.758	5.640	-0.8345	0.2973
1.0	5.286	15.47	-1.933	0.6832
1.5	10.29	29.29	-3.469	1.227
2.0	16.76	47.10	-5.434	1.925
2.5	24.70	68.89	-7.825	2.774
3.0	34.11	94.66	-10.64	3.776
3.5	44.99	124.4	-13.89	4.930
$\infty$	2.945 <sup>a</sup>	7.975 <sup>a</sup>	-0.8527 <sup>a</sup>	0.3039 <sup>a</sup>

<sup>a</sup>The values listed for  $S = \infty$  refer to an expansion of  $kT_c/J_1 S^2$  in powers of  $\gamma$ .

tween the spins. As a result of the form of Eq. (13), the magnon spectrum will change shape ( $k$  dependence) as well as magnitude as a function of the temperature and applied magnetic field.

One of the more dramatic effects of the  $k$ -dependent renormalization is the possibility of a change of the character of the energy spectrum from ferromagnetic (lowest energy is  $\mu_B H$  and is located at  $k=0$ ) to antiferromagnetic (lowest energy is less than  $\mu_B H$  and is located at some  $k \neq 0$ ).

#### IV. NEAREST- AND NEXT-NEAREST-NEIGHBOR EXCHANGE MODEL

We consider the specific predictions of the MCD theory for the case of nearest-neighbor and next-nearest-neighbor exchange. This is the simplest case exhibiting the change in the  $k$  dependence of the magnon spectrum. Furthermore, this case provides the basis for the application of the theory to the europium chalcogenides.

Using MCD, we have calculated  $kT_c/J_1$  as a function of  $\gamma = J_2/J_1$  for all spins and for each of the three cubic lattices. Agreement with Padé approximant work is again within the accuracy of the Padé results.

The Curie-temperature results are so useful for application to materials of current interest that we have empirically fitted the results of the numerical

TABLE II. Coefficients of an expansion of  $kT_c/J_1$  in powers of  $\gamma$  for a sc crystal in the range  $-0.15 < \gamma < 0$ .

$S$	$a_0$	$a_1$	$a_2$	$a_3$
0.5	1.754	5.827	-1.089	11.22
1.0	5.277	15.92	-2.398	25.86
1.5	10.27	30.13	-4.180	47.76
2.0	16.73	48.44	-6.444	76.16
2.5	24.66	70.84	-9.187	111.0
3.0	34.06	97.34	-12.41	152.2
3.5	44.93	127.9	-16.11	199.8
$\infty$	2.941 <sup>a</sup>	8.199 <sup>a</sup>	-0.9592 <sup>a</sup>	12.74 <sup>a</sup>

<sup>a</sup>The values listed for  $S = \infty$  refer to an expansion of  $kT_c/J_1 S^2$  in powers of  $\gamma$ .

TABLE III. Coefficients of an expansion of  $kT_c/J_1$  in powers of  $\gamma$  for a bcc crystal in the range  $0 < \gamma < 1$ .

$S$	$a_0$	$a_1$	$a_2$
0.5	2.603	2.445	-0.1065
1.0	7.660	6.871	-0.2393
1.5	14.81	13.11	-0.4225
2.0	24.06	21.15	-0.6555
2.5	35.40	30.99	-0.9382
3.0	48.84	42.65	-1.271
3.5	64.37	56.11	-1.653
$\infty$	4.194 <sup>a</sup>	3.617 <sup>a</sup>	-0.0994 <sup>a</sup>

<sup>a</sup>The values listed for  $S = \infty$  refer to an expansion of  $kT_c/J_1 S^2$  in powers of  $\gamma$ .

calculation to simple polynomials in  $\gamma$  of the form

$$kT_c/J_1 = a_0 + a_1\gamma + a_2\gamma^2 + a_3\gamma^3. \quad (15)$$

The coefficients obtained in this way are given in Tables I-VI. Curie temperatures calculated from these tables agree with the Padé approximant results<sup>4-7</sup> to within 1% in the domains indicated, with the exception noted in Ref. 15.

The criteria for the stability of the ferromagnetic ground state can be obtained from simple spin-wave theory. If  $J_1 > 0$ , the ferromagnetic ground state is stable when  $\gamma$  is greater than a critical value  $\gamma^*$ . This critical ratio of the exchange constants is lattice dependent, but spin independent. For the cubic lattices, it is given by

$$\gamma^* = \begin{cases} -1, & \text{fcc} \\ -\frac{2}{3}, & \text{bcc} \\ -\frac{1}{4}, & \text{simple cubic} \end{cases} \quad (16)$$

which agrees with the results of RPA, MFA, CD, and MCD.

MCD and RPA differ qualitatively in the forms which they predict for the curve of  $kT_c/J_1$  vs  $\gamma$  (except for  $S=1$ , when the curves are identical). For all spins, RPA predicts an infinite slope at  $\gamma^*$  and no solution to the equations for the phase boundary for  $\gamma < \gamma^*$ .

TABLE IV. Coefficients of an expansion of  $kT_c/J_1$  in powers of  $\gamma$  for a bcc crystal in the range  $-0.4 < \gamma < 0$ .

$S$	$a_0$	$a_1$	$a_2$	$a_3$
0.5	2.601	2.488	-0.1390	0.3960
1.0	7.657	6.958	-0.3328	0.7011
1.5	14.81	13.25	-0.5993	1.138
2.0	24.05	21.37	-0.9389	1.690
2.5	35.39	31.31	-1.352	2.355
3.0	48.82	43.08	-1.838	3.132
3.5	64.35	56.66	-2.397	4.020
$\infty$	4.192 <sup>a</sup>	3.649 <sup>a</sup>	-0.1467 <sup>a</sup>	0.2228 <sup>a</sup>

<sup>a</sup>The values listed for  $S = \infty$  refer to an expansion of  $kT_c/J_1 S^2$  in powers of  $\gamma$ .

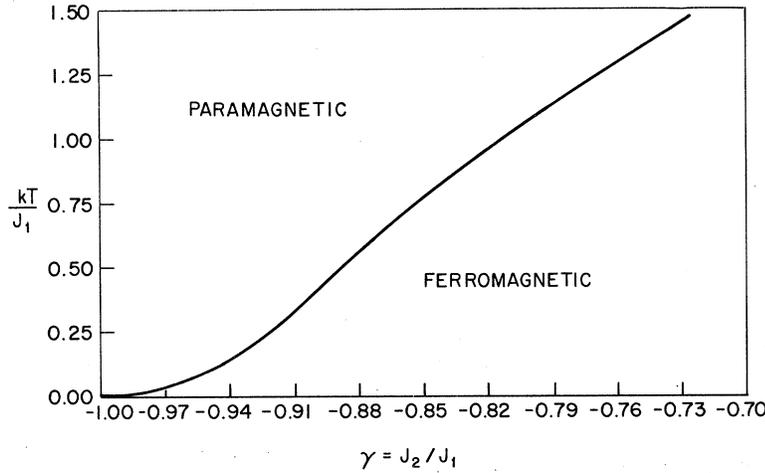


FIG. 1. MCD phase diagram for  $S = \frac{1}{2}$  (fcc). y axis:  $kT/J_1$ ; x axis:  $\gamma = J_2/J_1$ .

For  $S = \frac{1}{2}$ , MCD predicts a phase boundary of the form indicated in Fig. 1. Near  $\gamma = \gamma^*$ , the boundary which separates the ferromagnetic ( $F$ ) and paramagnetic ( $P$ ) regions has a small positive slope and a positive second derivative.

For  $S > 1$ , the situation differs even more sharply from the predictions of RPA. The MCD equations now have solutions for a certain range of values of  $\gamma$  which are less than the critical ratio  $\gamma^*$ . The situation is illustrated in Fig. 2. In this phase diagram, the solid curve which bounds the ferromagnetic region is calculated from the MCD theory. The dashed line is only a schematic suggestion of the boundary between the paramagnetic and anti-ferromagnetic (AF) regions. For values of  $\gamma$  just below  $\gamma^*$ , MCD indicates a paramagnetic-ferromagnetic-antiferromagnetic sequence of transitions as the temperature is decreased. This behavior is plausible in terms of the renormalization of spin waves as previously discussed. The MCD magnon spectrum retains a form characteristic of a ferromagnet to the right of the  $kT_c/J_1$  curve even in the limit  $H \rightarrow 0$ .

The behavior of the ferromagnetic Curie temperature for values of  $\gamma$  between zero and infinity is also

interesting. In this region there is qualitative agreement between the various Green's-function theories. We shall consider the ratio of the ferromagnetic Curie temperature to the paramagnetic Curie temperature  $\theta$ . It has been shown that the paramagnetic Curie temperature is given exactly by the molecular field result.<sup>17</sup> We have

$$k\theta = kT_c^{\text{MFA}} = \frac{2}{3} S(S+1)(J_1 z_1 + J_2 z_2). \quad (17)$$

By plotting  $T_c/\theta$  against  $\gamma/(1+\gamma)$  we compress the region from zero to infinity between the limits of zero and one. The resultant curve for the fcc lattice for  $S = \frac{1}{2}$  in the MCD approximation is shown by the solid line in Fig. 3.

From one point of view, MFA consists of the assumption that the interaction between a site and one of its neighbors is equivalent to the average of such interactions between a site and all other sites in the system. This clearly overestimates the energy of all excitations whose wavelength is greater than the true range of interaction between sites. MFA will consequently overestimate the ferromagnetic Curie temperatures of all systems with a finite range of interaction. On the other hand, the more sites which interact with a given site the more accurate

TABLE V. Coefficients of an expansion of  $kT_c/J_1$  in powers of  $\gamma$  for a fcc crystal in the range  $0 < \gamma < 1$ .

$S$	$a_0$	$a_1$	$a_2$
0.5	4.084	2.991	-0.2100
1.0	11.91	8.0744	-0.4631
1.5	22.96	15.21	-0.8127
2.0	37.24	24.38	-1.257
2.5	54.75	35.61	-1.797
3.0	75.50	48.88	-2.430
3.5	99.47	64.20	-3.158
$\infty$	6.467 <sup>a</sup>	4.097 <sup>a</sup>	-0.1891 <sup>a</sup>

<sup>a</sup>The values listed for  $S = \infty$  refer to an expansion of  $kT_c/J_1 S^2$  in powers of  $\gamma$ .

TABLE VI. Coefficients of an expansion of  $kT_c/J_1$  in powers of  $\gamma$  for a fcc crystal in the range  $-0.5 < \gamma < 0$ .

$S$	$a_0$	$a_1$	$a_2$	$a_3$
0.5	4.081	3.061	-0.2984	0.5177
1.0	11.90	8.221	-0.6600	1.003
1.5	22.95	15.46	-1.154	1.737
2.0	37.22	24.79	-1.780	2.682
2.5	54.73	36.18	-2.539	3.835
3.0	75.46	49.66	-3.431	5.193
3.5	99.42	65.21	-4.456	6.756
$\infty$	6.464 <sup>a</sup>	4.158 <sup>a</sup>	-0.2653 <sup>a</sup>	0.4092 <sup>a</sup>

<sup>a</sup>The values listed for  $S = \infty$  refer to an expansion of  $kT_c/J_1 S^2$  in powers of  $\gamma$ .

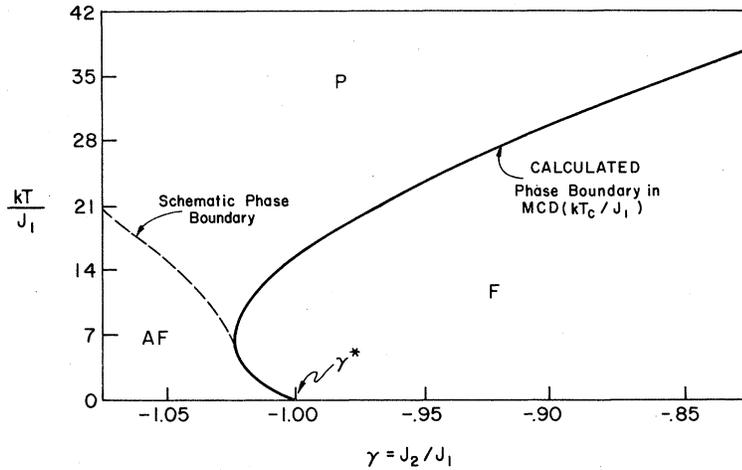


FIG. 2. MCD phase diagram for  $S = \frac{1}{2}$  (fcc). y axis:  $kT/J_1$ ; x axis:  $\gamma = J_2/J_1$ .

MFA is expected to be. For nearest-neighbor exchange models we would expect the ratio  $T_c/\theta$  to be most nearly equal to one for the lattice with the most nearest neighbors. Hence, the fcc lattice should have the largest value of  $T_c/\theta$  for cubic lattices and the simple cubic (sc) lattice should have the smallest. This is in agreement with the RPA, CD, and MCD theories as well as the Padé approximant calculations.

On this basis, several features of Fig. 3 can be readily understood. Since the second-nearest-neighbors in an fcc lattice generate an sc lattice, the value of  $T_c/\theta$  for the fcc lattice at  $\gamma/(1+\gamma) = 1$  ( $J_1/J_2 = 0$ ) must equal  $T_c/\theta$  for the sc lattice. From the discussion of the preceding paragraph, the value of  $T_c/\theta$  for  $\gamma/(1+\gamma) = 1$  should then be less than the corresponding value at  $\gamma/(1+\gamma) = 0$ . By a similar argument, we would expect to find that when the two exchange constants are roughly equal, the value of  $T_c/\theta$  is higher than at either end of the curve.

The region near  $\gamma/(1+\gamma) = 1$  is especially interesting due to the infinite slope of the curve at that point. This is a general effect which does not depend on the particular lattice. A discussion of the physical origin of this effect is presented in the Appendix.

#### V. APPLICATION OF MCD TO EUROPIUM CHALCOGENIDES

The first step toward the application of the theory of the Heisenberg model to the ferromagnetic europium chalcogenides, EuO and EuS, is to determine the appropriate values of the exchange constants.

McGuire and Shafer<sup>11</sup> estimated the values of the exchange constants for all four of the europium chalcogenides on the basis of the MFA. They began with EuTe, which is an antiferromagnet with type-II order.<sup>18</sup> According to MFA, the Néel temperature of a type-II fcc antiferromagnet is independent of  $J_1$ . The experimental value of the Néel temperature then gave a direct estimate of  $J_2$ .

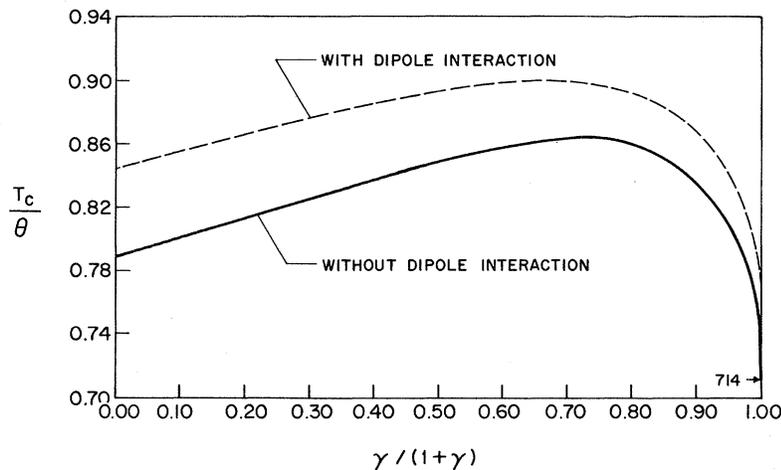


FIG. 3. Dependence of the ratio of Curie temperatures ( $T_c/\theta$ ) on the exchange constants for  $S = \frac{1}{2}$  (fcc). y axis:  $T_c/\theta$ ; x axis:  $\gamma/(1+\gamma)$ .

TABLE VII. Exchange constants resulting from the method of McGuire and Shafer (Ref. 11).

Substance	$\gamma = J_2/J_1$	$J_1/k_B$	$J_2/k_B$
EuO	-0.098	0.634	-0.062
EuS	-0.486	0.199	-0.097
EuSe	-0.854	0.125	-0.106
EuTe	-8.36	0.014	-0.124

The assumption was then made, for lack of other information, that the value of  $J_2$  in EuO is half that in EuTe and that it varies linearly with the lattice constant. These assumptions enabled the calculation of  $J_2$  for EuS and EuSe.

The paramagnetic Curie temperatures, which are given correctly by MFA as previously noted, were then used to determine the values of  $J_1$  for each compound. The experimental values of the ferromagnetic Curie temperatures were not used and the effect of the magnetic dipole interaction was neglected. Table VII gives the results of applying this procedure to current experimental values.

We shall attempt to improve upon these estimates by considering the theoretical dependence of  $T_c/\theta$  on  $\gamma$  and by comparing it to the experimental results. A difficulty which we shall encounter is that  $T_c/\theta$  varies slowly as a function of  $\gamma$  in the region of interest. This slow variation makes  $\gamma$  quite sensitive to the measured values of  $T_c$  and  $\theta$ .

Although the ferromagnetic Curie temperatures are known to a high accuracy, there is considerable uncertainty about the paramagnetic Curie temperatures. For EuS,  $\theta$  is given only to the nearest degree.<sup>11</sup> For EuO, the situation is much worse. Values of 77,<sup>19</sup> 80,<sup>20</sup> and 76 °K<sup>11</sup> have been reported. Most recently, Menyuk *et al.*<sup>12</sup> published data which, when analyzed in the usual way,<sup>21</sup> indicate that  $\theta = 81$  °K. Table VIII lists values of  $T_c/\theta$  corresponding to values of  $\theta$  lying in the range of reported experimental results.

As seen in Fig. 3, the maximum theoretical value of  $T_c/\theta$  is 0.862 for an fcc lattice and for  $S = \frac{7}{2}$ . This corresponds to a value of  $\gamma \approx 2.15$ . As shown in Table VIII, only the results of Menyuk *et al.*<sup>12</sup> ( $\theta = 81$  °K for EuO) correspond to a value of  $T_c/\theta$  which is below this maximum. All other reported results correspond to values of  $T_c/\theta$  which are greater than 0.862. These values are therefore inconsistent with a Heisenberg Hamiltonian which includes only first- and second-nearest-neighbor exchange.

Fortunately, the discrepancy between the theoretical and experimental results is removed if we include the effect of the magnetic dipole interaction.<sup>22</sup> This effect represents an energy of the order of 1 °K. It is significant in the europium chalcogenides because of their low Curie tempera-

tures ( $T_c$  is 69.19 °K for EuO<sup>9</sup> and 16.5 °K for EuS<sup>10</sup>).

The long range of the magnetic dipole interaction allows it to be treated in the MFA. The variation of  $T_c/\theta$  with  $\gamma/(1+\gamma)$ , appropriate to EuO, is shown by the dashed curve in Fig. 3. This curve is shifted upwards from the solid curve which was drawn for the case of no dipole interactions. It now intersects the experimental values of  $T_c/\theta$ . The only qualitative change in the curve occurs away from the region which is relevant to the europium chalcogenides;  $\partial(T_c/\theta)/\partial(\gamma/(1+\gamma))$  is no longer infinite at  $\gamma/(1+\gamma) = 1$ . The values of  $\gamma$ , predicted by this theory, are given as a function of possible values of  $\theta$  in Table VIII.

For EuO, plausible values of  $\gamma$  range from 0.1 to 1.8; this is in contrast to the negative value obtained by the method of McGuire and Shafer.<sup>11</sup> We might also note that Menyuk *et al.*<sup>12</sup> concluded that  $\gamma = 0.5 \pm 0.2$  on the basis of their careful consideration of a complete high-temperature expansion, but neglected the dipolar interaction. This value lies within the range of values listed in Table VIII.

For EuS, the situation is simpler. There is only one reported experimental value for  $\theta$ , namely,  $\theta = 19$  °K. This leads to  $\gamma = -0.113$ .<sup>23</sup> This should be contrasted to the value of -0.5 based on the work of McGuire and Shafer.<sup>11</sup>

In conclusion, we note that all the values of  $\gamma$  obtained by our analysis for both EuO and EuS are significantly greater than those obtained by the method of McGuire and Shafer.<sup>11</sup>

#### ACKNOWLEDGMENT

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#### APPENDIX

This appendix discusses the physical origin of the infinite derivative of  $T_c/\theta$  with respect to  $\gamma/(1+\gamma)$  at the point  $\gamma/(1+\gamma) = 1$ . This is shown for the fcc lattice and  $S = \frac{7}{2}$  in the solid curve in Fig.

TABLE VIII. Exchange constants resulting from the ratio of the Curie temperatures when the analysis includes the effect of the magnetic dipole interaction.

Substance	$\theta$	$T_c/\theta$	$\gamma = J_2/J_1$	$J_1/k_B$	$J_2/k_B$
EuO	77	0.899	1.80	0.315	0.567
	78	0.887	0.792	0.434	0.344
	79	0.876	0.459	0.499	0.229
	80	0.865	0.254	0.552	0.140
	81	0.854	0.105	0.598	0.063
EuS	18.5	0.892	0.137	0.130	0.018
	19	0.868	-0.113	0.151	-0.017
	19.5	0.846	-0.288	0.171	-0.049

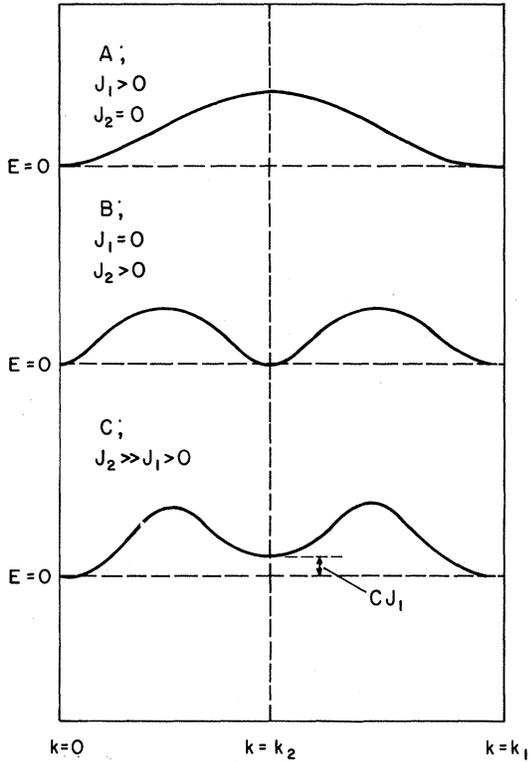


FIG. 4. Excitation spectrum for various exchange constants.

3. The divergence of the derivative is not peculiar to either the lattice or the spin. It will be shown to be a general result.

We first note that

$$\frac{\partial(T_c/\theta)}{\partial(J_1/J_2)} = -\left(\frac{\gamma}{1+\gamma}\right)^2 \frac{\partial(T_c/\theta)}{\partial(\gamma/1+\gamma)}, \quad (\text{A1})$$

so that a divergence of either derivative, at  $\gamma = \infty$ , implies the divergence of the other. We therefore consider the divergence of  $\partial(T_c/\theta)/\partial(J_1/J_2)$  at  $J_1 = 0$ .

Let us first consider the situation when  $J_1$  is positive and  $J_2 = 0$ . Curve A in Fig. 4 indicates schematically the energy spectrum of the ferromagnet in the extended zone scheme from  $k=0$  to a neighboring reciprocal-lattice point  $k=k_1$ . The Brillouin-zone boundary lies halfway between these points, by definition. The quadratic nature of the energy spectrum at  $k=0$  leads to a square-root Van Hove singularity in the density of states at zero energy.

Now let us consider the situation when  $J_2$  is positive and  $J_1 = 0$ . The lattice can then be regarded as being composed of interpenetrating sublattices generated by the second-nearest neighbors. When the nearest-neighbor exchange constant vanishes these sublattices are completely independent. Thus,

each sublattice is a nearest-neighbor ferromagnet with an exchange constant  $J_2$ .

Consider a point in reciprocal space which corresponds to a uniform phase within each sublattice, but a nonzero phase difference between sublattices. Such a point would be found on the boundary of the first Brillouin zone. It is shown schematically in Fig. 4 at  $k=k_2$ . When the sublattices are independent, this point is degenerate with the point at  $k=0$ . This is another way of saying that  $k_2$  is a reciprocal-lattice vector of the sublattice. This will be reflected in the energy spectrum indicated schematically in curve B in Fig. 4. The point at  $k=k_2$  will also contribute a square-root Van Hove singularity at zero energy, superimposed on the singularity which arises from the point at  $k=0$ .

Now let  $J_1$  be nonzero, but much less than  $J_2$ . This allows the sublattices to interact weakly, lifting the degeneracy between the points  $k=0$  and  $k=k_2$ . Since there is a fixed nonzero phase difference between the sublattices at the point  $k=k_2$ , there will be a nonzero contribution to the energy at this point. This energy "gap" at the point  $k=k_2$  will be proportional to  $J_1$  to lowest order. The new spectrum is shown schematically in curve C in Fig. 4.

The two Van Hove singularities are now separated. The one arising from the point  $k=0$  remains at zero energy while the one arising from the point  $k=k_2$  is displaced by an energy  $CJ_1$ . The resultant density of states at low energy is shown schematically in Fig. 5.

At nonzero temperatures, the energy spectrum will be renormalized due to thermal fluctuations. To lowest order, this renormalization just multiplies the energy at the point  $k=k_2$  by a factor proportional to the maximum magnon energy,  $E_{\text{max}}$ .

Specifically, we note that the derivative of the density of states with respect to  $J_1$ , for  $J_1 = 0$ , evaluated at zero energy, is infinite. This divergence is the source of the primary divergence which we seek to explain, as we will show below.

For temperatures just below  $T_c$ , the magnetization is inversely proportional to the number of

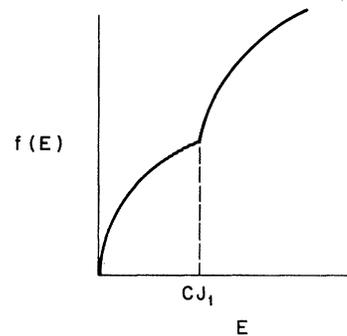


FIG. 5. Density of states at low energy.

magnons  $\Phi$ . We have

$$\langle S^z \rangle \approx \frac{1}{3} S(S+1) \Phi^{-1}. \quad (\text{A2})$$

The number of magnons is given by the integral of the density of states and the Bose factor. In terms of a renormalized energy variable

$$x = E/E_{\max}, \quad (\text{A3})$$

we can write this as

$$\Phi = \int_0^1 f(x) (e^{\beta x} - 1)^{-1} dx. \quad (\text{A4})$$

At the critical temperature, the maximum magnon energy goes to zero. We can then expand the Bose factor. The number of magnons is given in this limit by

$$\Phi = \beta^{-1} E_{\max}^{-1} \int_0^1 x^{-1} f(x) dx. \quad (\text{A5})$$

The integral is simply a generalization of  $F(-1)$ , which was defined in Eq. (5). It is always convergent because of the square-root Van Hove singularity at zero energy.

From Eqs. (A2) and (A5), we see that the ferromagnetic Curie temperature is determined by the expression

$$kT_c = \frac{1}{3} S(S+1) \left( \int_0^1 x^{-1} f(x) dx \right)^{-1} \lim_{\langle S^z \rangle \rightarrow 0} \left( \frac{E_{\max}}{\langle S^z \rangle} \right), \quad (\text{A6})$$

so that  $T_c$  is inversely proportional to the integral.

The previously mentioned divergence of the derivative of the density of states leads to an infinite derivative of the integral with respect to  $J_1$  at the point  $J_1=0$ . This, in turn, gives the infinite derivative of  $T_c/\theta$  with respect to  $J_1/J_2$  for  $J_1/J_2=0$ .

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(Ref. 6) for  $S=\frac{1}{2}$ . They claim an error of less than 0.1%, while the predictions of Eq. (8) for  $S=\frac{1}{2}$  differ from their results by 5, 3, and 2% for the sc, bcc, and fcc lattices.

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<sup>21</sup>Menyuk and Schafer did not analyze their data in this manner. They based their analysis on a high-temperature expansion of the inverse magnetic susceptibility, including terms beyond the usual linear approximation. However, they did not include the magnetic dipole interaction. Their analysis led them to the conclusion that  $\theta=84.05^\circ\text{K}$ .

<sup>22</sup>The value  $76^\circ\text{K}$  for the paramagnetic Curie temperature is still inconsistent with the theory even with the inclusion of the magnetic dipole interaction.

<sup>23</sup>Table VIII also contains values for  $\gamma$  which correspond to  $\theta=18.5^\circ\text{K}$  and  $\theta=19.5^\circ\text{K}$  to indicate the sensitivity to variations in the experimental values of  $\theta$ .