Cluster Approximation for Ferromagnets with First- and Second-Neighbor Exchange, with Application to the Europium Chalcogenides*

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The two-particle cluster approximation of Strieb, Callen, and Horwitz is extended to ferromagnets and paramagnets with nearest- and next-nearest-neighbor exchange, with particular reference to EuO, EuS, EuSe, and EuTe. Curie temperatures, magnetization curves for general values of the applied field, susceptibility, spin-correlation functions, energy, and specific-heat curves are calculated. Using the values of the exchange constants of EuS obtained from low-temperature spin-wave analysis (and no adjustable constants) we find excellent agreement with the observed Curie temperature, very close agreement with the observed "paramagnetic Curie temperature," and very good agreement with the λ-like discontinuity in the specific heat near the Curie temperature. The magnetization data for arbitrary applied fields and the susceptibility data in the paramagnetic region also can be fit closely with these values of the exchange constants. To explore the sensitivity of the theory to the exchange constants, the results of the cluster approximation are given for various ratios of the first- and second-neighbor exchange constants, including the special case of vanishing second-neighbor exchange (in this latter case the approximation generalizes the constant-coupling approximation to arbitrary spin). We find that all the presently measured magnetic properties are rather insensitive to the particular choice of exchange constants, provided that these are chosen to be consistent with the observed Curie temperature; measurement of the spin-correlation functions, however, would provide a sensitive criterion for the choice of exchange constants.

1. INTRODUCTION

A VARIETY of methods existf or the statistical-mechanical analysis of a ferromagnet: some rigorous in restricted temperature regions (spin-wave theory, Opechowski series expansion), some approximate, powerful, and relatively complex (diagrammatic series summations, Green function methods), and some whose chief advantage is simplicity (small-cluster approximations). The simplest of the latter class, the Weiss molecular field theory, is in fact the work-horse of magnetism, providing a convenient and qualitatively reasonable theory of those properties (such as the magnetization) which are the sum of single-spin contributions. However, those properties which depend on two-spin interactions, or spin correlations, are beyond the reach of the Weiss theory. The various small-cluster approximations (Oguchi two-spin cluster, Bethe-Peierls-Weiss method) attempt to extend the Weiss theory, but they characteristically exhibit internal inconsistencies, such as the anti-Curie temperature of the Bethe-Peierls-Weiss theory. However, the "constant coupling" approximation of Kasteleijn and van Kranendonk[1] (which can be viewed as a two-spin cluster approximation defined for systems with nearest-neighbor interaction only) is distinct among the cluster approximations in that it is at least self-consistent. And in fact this method is widely used as the most convenient

simple theory of correlation-dependent properties of nearest-neighbor systems.

A rigorous cluster expansion for the Heisenberg ferromagnet has been derived recently[2] by Strieb, Callen, and Horwitz (SCH). The leading term of the SCH series is the Weiss molecular field, and the two-spin cluster term becomes identical to the constant-coupling approximation for the special case of nearest-neighbor interaction. However, whereas the constant-coupling approximation is restricted to nearest-neighbor interaction, the SCH two-spin cluster approximation provides a simple, convenient procedure applicable to arbitrary types of exchange interactions. In this paper we evaluate and study the SCH two-spin cluster approximation for the physically interesting case of ferromagnets with nearest- and next-nearest-neighbor exchange.

The Heisenberg model with first- and second-neighbor exchange is of particular interest because of the applicability of this model to the europium chalcogenide series (EuO, EuS, EuSe, EuTe). These salts are simple insulators with the Eu ions on a face-centered cubic lattice. The nearest-neighbor exchange is positive whereas the next-nearest-neighbor exchange is probably negative throughout the series. The oxide and sulfide are ferromagnetic, whereas the negative second-neighbor interaction dominates in the telluride. In the selenide the balance is so close that a small applied field

[1] P. W. Kasteleijn and J. van Kranendonk, Physica 22, 317 (1956).

[2] B. Strieb, H. B. Callen, and G. Horwitz, Phys. Rev. 130, 1798 (1963).

induces ferromagnetic ordering, although the zero-field ordering is still uncertain.[3]

When applied to the oxide and sulfide the two-particle cluster approximation gives magnetization curves below T_c and susceptibility curves above, specific-heat curves through the λ-like anomaly at T_c, the ferromagnetic Curie temperature T_c, and the "paramagnetic Curie temperature" θ. For the selenide it provides magnetization curves in the presence of ferromagnetically aligning fields below T_N, and for the selenide and telluride it gives susceptibility curves, Néel temperatures T_N, and "paramagnetic Néel temperatures" θ. In addition the theory provides spin-correlation functions for the analysis of neutron scattering, magnetostriction, or the magnetic contribution to the thermal expansion coefficient.[3a]

A considerable amount of experimental data on the europium chalcogenides is available, as well as a few pertinent theoretical investigations. Matthias, Bozorth, and Van Vleck[4] have measured the susceptibility of EuO. Busch, Junod, Risi, and Vogt[5] have measured magnetization and susceptibility of the sulfide, selenide and telluride, and McGuire, Argyle, Shafer and Smart[5] have measured the susceptibility of these materials. The magnetization of EuS for various applied fields has been measured by Enz, Fast, van Houten, and Smit[6] and by Argyle[7]; it agrees quite closely with the prediction of molecular field theory. The specific heat of EuS has been measured at low temperatures by McCollum and Callaway[8] and over a broad temperature range by Moruzzi and Teaney,[9] who find a pronounced λ-like discontinuity at the Curie temperature.

Boyd[10] has made accurate NMR measurements of the magnetization of EuS at liquid-helium temperature, and Charap and Boyd[10] have attempted to evaluate the exchange constants of this material by fitting spin-wave theory to the magnetization[10] and specific-heat[8] data. In agreement with the spin-wave analysis of McCollum and Callaway,[8] Charap and Boyd find a broad range of exchange constants to be compatible with the observed behavior. A particular pair of values,

selected by Charap and Boyd as the most plausible, will be referred to henceforth as the "spin-wave values of the exchange constants of EuS." Wojtowicz[11] then showed that these values give reasonable agreement with the observed high-temperature specific heat[9] when used in his extension of the high-temperature series expansion. Furthermore, the suggested[5] exchange constants of EuO are roughly consistent with those obtained by Calhoun and Overmeyer[12] in their measurements of paramagnetic resonance of Eu^{2+} pairs in CaO and SrO.

The relationship of the Curie temperature to the exchange constants has been studied by a Green function method by Tahir-Kheli and Jarrett,[13] and we shall find fairly close agreement with their results.

We briefly summarize the general formulation of the SCH two-spin cluster approximation in Sec. 2. As an illustration of the method we evaluate it in Sec. 3 for nearest-neighbor interactions, thereby obtaining the constant coupling approximation for general spin (which, to our knowledge, has not been given in the literature). Curie temperature, magnetization curves, susceptibility curves, and the spin-correlation functions are evaluated and given graphically. In Sec. 4 we then particularize the two-spin cluster approximation to nearest- and next-nearest-neighbor interactions and we calculate the Curie temperature as a function of J_1 and J_2 (the two exchange constants). We find the predicted Curie temperature of EuS is in excellent agreement with experiment[7,14] if we use the exchange constants obtained from the low-temperature spin-wave analysis.[10] Similarly the "paramagnetic Curie temperature" is in very good agreement with that obtained by extrapolation of the measured reciprocal susceptibility curves.[5] The magnetization data for arbitrary applied fields[6,7] and the susceptibility data[5] above T_c can be fit closely with the Charap-Boyd exchange constants, although the number of ions in the nonstoichiometric sample here provides an adjustable parameter. In Sec. 5 we explore the sensitivity of the results to changes in J_1 and J_2. We find that there is a considerable range of values of J_1 and J_2 which produce very good and substantially equivalent agreement with the presently available experimental data.

We conclude that the two-particle cluster approximation provides a convenient and successful theory of the ferromagnetic europium chalcogenides throughout the entire temperature range. It applies as well to the antiferromagnetic europium chalcogenides above their Néel temperatures, and below their Néel temperatures when they are ferromagnetically aligned by an external

[3] S. Pickart (private communication).

[3a] *Note added in proof.* Subsequent investigations have shown that the cluster theory also gives the celebrated ⅓-power law for the magnetization below T_c. This work will be reported in the 1965 J. Appl. Phys. Suppl., Proceedings of the Decennial Conference on Magnetism and Magnetic Materials.

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[5] G. Busch, P. Junod, M. Risi, and O. Vogt, *Report of the International Conference on the Physics of Semiconductors, Exeter, 1962* (The Institute of Physics and the Physical Society, London, 1962). T. R. McGuire, B. E. Argyle, M. W. Shafer, and J. S. Smart, J. Appl. Phys. **34**, 1345 (1963).

[6] J. Enz, J. F. Fast, S. van Houten, and J. Smit, Phillips Res. Rept. **17**, 451 (1962).

[7] B. E. Argyle (unpublished).

[8] D. C. McCollum, Jr. and J. Callaway, Phys. Rev. Letters **9**, 376 (1962). J. Callaway and D. C. McCollum, Jr., Phys. Rev. **130**, 1741 (1963).

[9] V. L. Moruzzi and D. T. Teaney, Solid State Comm. **1**, 127 (1963).

[10] S. H. Charap and E. L. Boyd, Phys. Rev. **133**, A811 (1964).

[11] P. J. Wojtowicz, J. Appl. Phys. **35** (Part 2), 991 (1964).

[12] B. A. Calhoun and J. Overmeyer, J. Appl. Phys. **35** (Part 2), 898 (1964).

[13] R. A. Tahir-Kheli and H. Jarrett, Phys. Rev. **135**, A1096 (1964).

[14] P. Heller and G. B. Benedek, Phys. Rev. Letters **8**, 428 (1962); International Conference on Magnetism, Nottingham U. K., September, 1964 (unpublished).

field. Application to the antiferromagnetic phase will be given separately. However, the presently measured magnetic properties are rather insensitive to the particular choice of exchange constants, provided that these are chosen to be consistent with the observed Curie temperatures. Measurement of the spin-correlation functions near the Curie temperature would provide a sensitive criterion for the choice of exchange constants.

2. THE CLUSTER SERIES

We briefly summarize, without proof, the structure of the SCH cluster expansion. As an introduction to the more general case we then exhibit the constant coupling approximation as the two-spin cluster result for nearest-neighbor interactions.

The Hamiltonian of the system is

$$\mathcal{3C} = -\mu H \sum_i S_i{}^z - 2 \sum_{(i,j)} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \qquad (1)$$

Strieb, Callen, and Horwitz replace the operator $S_i{}^z$ by a spin-deviation operator $\sigma_i \equiv \bar{S} - S_i{}^z$ where $\bar{S}$ is a parameter later to be determined variationally. They treat those terms that are linear in σ_i as the unperturbed portion of the Hamiltonian, expanding the free energy in powers of the remaining perturbation. Resummation of the infinite subseries of terms involving not more than two spins constitutes the two-spin cluster result, and similarly for larger clusters. After the summation to desired order the parameter $\bar{S}$ is determined to minimize the free energy. The power of the method lies to a considerable extent in this variation procedure, which corresponds to a diagrammatic vertex renormalization; the "two-spin cluster" diagrams in fact contain much more extensive classes of "bare" diagrams, or of diagrams with "undressed" vertices.

The *result* of the method is simply stated in terms of an effective one-spin unnormalized density operator $\tilde{\rho}_i$ defined by

$$\tilde{\rho}_i \equiv \exp[\beta(\mu H + 2J_0 \bar{S}) S_i{}^z], \qquad (2)$$

where $\beta = 1/k_B T$ and

$$J_0 \equiv \sum_j J_{ij}. \qquad (3)$$

Then SCH show that the two-spin approximation to the free energy is the sum of a zero-order contribution F_0 and a term $F_2{}'$ arising explicitly from two-spin terms;

$$F_2 = F_0 + F_2{}', \qquad (4)$$

where the zero-order contribution is

$$F_0 = N J_0 \bar{S}^2 - \beta^{-1} N \ln \operatorname{tr}_i \tilde{\rho}_i. \qquad (5)$$

Here N is the number of spins in the system and tr_i denotes a trace taken over the states of the single spin i. The two-spin correction is

$$F_2{}' = -\beta^{-1}$$
$$\times \sum_{(i,j)} \ln \langle \exp\{2\beta J_{ij}[\mathbf{S}_i \cdot \mathbf{S}_j - \bar{S}(S_i{}^z + S_j{}^z) + \bar{S}^2]\}\rangle_0, \qquad (6)$$

where $\langle\ \rangle_0$ denotes the average taken with respect to the density operator $\tilde{\rho}_i \tilde{\rho}_j$,

$$\langle \mathcal{O} \rangle_0 \equiv \operatorname{tr}_i \operatorname{tr}_j \mathcal{O} \tilde{\rho}_i \tilde{\rho}_j / \operatorname{tr}_i \operatorname{tr}_j \tilde{\rho}_i \tilde{\rho}_j \qquad (7)$$

and the summation in Eq. (6) ranges over all spin pairs in the system. $\bar{S}$ is determined by minimization of F_2.

To illustrate the method consider first the zero-order approximation. Then the free energy is given by F_0 [Eq. (5)] above, but it remains to evaluate $\bar{S}$ by minimizing F_0. Evaluation of the trace in Eq. (5) is elementary, and minimizing with respect to $\bar{S}$ gives

$$\bar{S} = (1/N)(\partial F_0/\partial(\mu H)) = \langle S^z \rangle$$
$$= S B_S(\beta \mu H S + 2\beta J_0 S \bar{S}), \qquad (8)$$

where $B_S(x)$ is the Brillouin function. Thus the method achieves the Weiss result in zero order.

3. NEAREST-NEIGHBOR INTERACTIONS; CONSTANT COUPLING

As a second illustration we evaluate the two-spin result for a model in which all spins are equivalent and only nearest neighbors interact. Let $2J$ be the strength of the interaction between neighbors and let z be the number of nearest neighbors. The number of interacting pairs (ij) is then $\frac{1}{2}Nz$, and the free energy F_2 becomes

$$-\beta F_2 = -(z-1)N \ln \operatorname{tr}_1 \tilde{\rho}_1$$
$$+ \tfrac{1}{2}Nz \ln \operatorname{tr}_1 \operatorname{tr}_2 \exp\{2\beta J \mathbf{S}_1 \cdot \mathbf{S}_2$$
$$+ \beta[\mu H + 2(z-1)J\bar{S}](S_1{}^z + S_2{}^z)\}. \qquad (9)$$

To evaluate $\bar{S}$ we differentiate F_2 with respect to $\bar{S}$ and equate to zero; the resulting equation can be written in the heuristically-appealing form

$$\operatorname{tr}_1 S_1{}^z \tilde{\rho}_1 / \operatorname{tr}_1 \tilde{\rho}_1 = \operatorname{tr}_1 \operatorname{tr}_2 S_1{}^z \tilde{\rho}_{12} / \operatorname{tr}_1 \operatorname{tr}_2 \tilde{\rho}_{12}, \qquad (10)$$

where

$$\tilde{\rho}_{12} \equiv \exp\{2\beta J \mathbf{S}_1 \cdot \mathbf{S}_2$$
$$+ \beta[\mu H + 2(z-1)J\bar{S}](S_1{}^z + S_2{}^z)\}. \qquad (11)$$

Furthermore, differentiation of F_2 with respect to H gives the magnetization as

$$\langle S^z \rangle = \operatorname{tr}_1 \operatorname{tr}_2 S_1{}^z \tilde{\rho}_{12} / \operatorname{tr}_1 \operatorname{tr}_2 \tilde{\rho}_{12}. \qquad (12)$$

Equations (10)–(12), together with the definition (2) of $\tilde{\rho}_1$, constitute the self-contained solution. The quantity $\tilde{\rho}_{12}$ can be looked on as an effective two-particle density operator, and the quantity in the square brackets in Eq. (11) can be viewed as an effective two-spin Hamiltonian. It can, in fact, be visualized as the Hamiltonian corresponding to two interacting spins surrounded by a medium in which all other spins are "frozen" with $S^z = \bar{S}$. The relation determining the parameter $\bar{S}$ is equivalent to the requirement [Eq. (10)] that the effective single-spin density operator $\tilde{\rho}_1$ and the effective two-spin density operator $\tilde{\rho}_{12}$ give the same magnetization. $\bar{S}$ is *not* the magnetization.

Kasteleijn and van Kranendonk[1] postulated the form of $\tilde{\rho}_{12}$ as given in Eq. (11) on the basis of certain

necessary restrictions on its form for the specific case of spin $\frac{1}{2}$, plus a liberal measure of intuition. For spin greater than $\frac{1}{2}$ the constant-coupling argument is less clear, and although Kasteleijn and van Kranendonk mentioned this general case in passing, we known of no reference in which the method is given explicitly for general spin, or in which its results are described. We therefore believe it useful to present them here.

The calculation of the constant-coupling equations (10)–(12) is most conveniently carried out by replacing βJ, $\beta\tilde{S}$, and $\beta\mu H$ by the parameters

$$x \equiv e^{-\beta J/2}, \quad y \equiv e^{-2\beta(z-1)J\tilde{S}}, \quad w \equiv e^{-\beta\mu H}, \quad (13)$$

whence

$$-\beta F_2 = -(z-1)N \ln Z_1 + \tfrac{1}{2} N z \ln Z_{12}, \quad (14)$$

where

$$Z_1 \equiv \mathrm{tr}_1 \tilde{\rho}_1 = \mathrm{tr}_1 [y^{z/(z-1)} w]^{S_1{}^z} \quad (15)$$

and

$$Z_{12} \equiv \mathrm{tr}_1 \mathrm{tr}_2 \tilde{\rho}_{12} = \mathrm{tr}_1 \mathrm{tr}_2 [x^{-4\mathbf{S}_1 \cdot \mathbf{S}_2} (wy)^{(S_1{}^z + S_2{}^z)}]. \quad (16)$$

The single-spin sum in Eq. (15) is identical to that calculated in Eq. (8), giving

$$\langle S^z \rangle = -\frac{\partial \ln Z_1}{\partial \ln w} = SB_S\left(-S \ln w - \frac{zS}{z-1} \ln y\right), \quad (17)$$

whereas the two-spin traces required for Z_{12} are best evaluated in the spaces in which $R^2 \equiv (\mathbf{S}_1 + \mathbf{S}_2)^2$ and $R_z \equiv (S_1{}^z + S_2{}^z)$ are diagonal:

$$Z_{12} = \frac{x^{4S(S+1)}}{1-yw} \sum_{R=0}^{2S} \frac{x^{-2R(R+1)}}{(yw)^R} + \frac{x^{4S(S+1)}}{1-(yw)^{-1}} \sum_{R=0}^{2S} \frac{(yw)^R}{x^{2R(R+1)}}. \quad (18)$$

$\tilde{S}$ or y is eliminated by equating $\langle S^z \rangle$, from Eq. (17), to the magnetization calculated from Z_{12};

$$\langle S^z \rangle = -\tfrac{1}{2}(\partial \ln Z_{12}/\partial \ln(yw)). \quad (19)$$

Magnetization curves for $S = \frac{1}{2}, 1, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$, and for $z = 12$ (e.g., face-centered cubic, hexagonal close-packed) have been calculated on the NOL-7090 computer and are shown in Fig. 1.

The Curie temperature is determined by the equation

$$\sum_{R=0}^{2S} x^{-2R(R+1)}(2R+1)[(z-1)R(R+1) - 2zS(S+1)] = 0 \quad (20)$$

as has been shown by Kasteleijn and van Kranendonk, and as we shall demonstrate in the following section.

The scalar correlation function $\langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle$ is given by

$$\langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle = \frac{\partial \ln F_2}{\partial(2\beta J)} = -\frac{1}{4} \frac{\partial \ln Z_{12}}{\partial \ln x}. \quad (21)$$

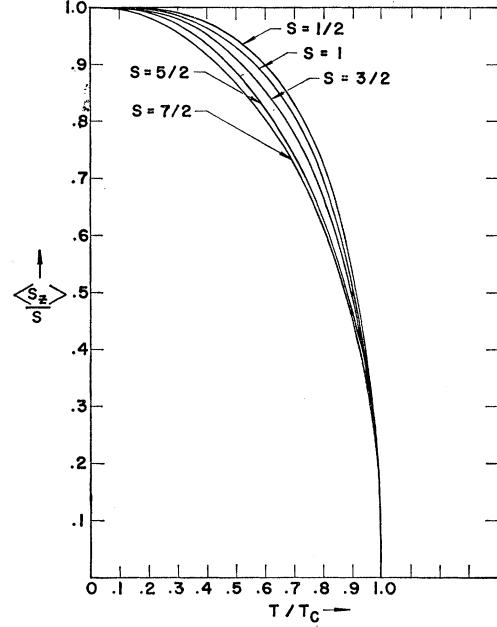We have also evaluated this quantity for several spin values, with $z = 12$; the results are shown in Fig. 2.

FIG. 1. Magnetization versus T/T_c for nearest-neighbor exchange (constant coupling), for various spin values.

4. TWO-SPIN CLUSTER WITH FIRST- AND SECOND-NEIGHBOR EXCHANGE

We now turn to a model in which all spins are crystallographically equivalent and in which an exchange interaction exists between nearest and next-nearest neighbors. Let $2J_1$ be the strength of the nearest-neighbor interaction, and $2J_2$ be the strength of the next-nearest-neighbor interaction. Also let z_1 and z_2 be the numbers of such neighbors, respectively. Then Eq. (6) contributes $\frac{1}{2}Nz_1$ nearest-neighbor terms and $\frac{1}{2}Nz_2$ next-nearest-neighbor terms, which, when added to the zero-order contribution (5), give

$$-\beta F_2 = -(z_1 + z_2 - 1)N \ln \mathrm{tr}_1 \tilde{\rho}_1$$
$$+ \tfrac{1}{2} N z_1 \ln \mathrm{tr}_1 \mathrm{tr}_2 \tilde{\rho}_{12} + \tfrac{1}{2} N z_2 \ln \mathrm{tr}_1 \mathrm{tr}_3 \tilde{\rho}_{13}, \quad (22)$$

where

$$\tilde{\rho}_{12} \equiv \exp\{2\beta J_1 \mathbf{S}_1 \cdot \mathbf{S}_2$$
$$+ \beta[\mu H + 2(z_1 - 1)J_1 \tilde{S} + 2z_2 J_2 \tilde{S}](S_1{}^z + S_2{}^z)\}, \quad (23)$$

$$\tilde{\rho}_{13} \equiv \exp\{2\beta J_2 \mathbf{S}_1 \cdot \mathbf{S}_3$$
$$+ \beta[\mu H + 2z_1 J_1 \tilde{S} + 2(z_2 - 1)J_2 \tilde{S}](S_1{}^z + S_3{}^z)\}. \quad (24)$$

Again $\tilde{S}$ is determined by minimizing F_2, giving the condition

$$(z_1 + z_2 - 1)J_0 \langle S^z \rangle_1 = z_1(J_0 - J_1)\langle S^z \rangle_{12}$$
$$+ z_2(J_0 - J_2)\langle S^z \rangle_{13}, \quad (25)$$

where

$$J_0 = z_1 J_1 + z_2 J_2, \quad (26)$$

and where

$$\langle \Theta \rangle_1 \equiv \mathrm{tr}_1 \Theta \tilde{\rho}_1 / \mathrm{tr}_1 \tilde{\rho}_1, \quad \langle \Theta \rangle_{12} \equiv \mathrm{tr}_1 \mathrm{tr}_2 \Theta \tilde{\rho}_{12} / \mathrm{tr}_1 \mathrm{tr}_2 \tilde{\rho}_{12} \quad (27)$$

and similarly for $\langle \Theta \rangle_{13}$.

Equation (22) completely characterizes the two-spin cluster approximation, with $\bar{S}$ to be determined by Eq. (25). The simple heuristic interpretation of the constant-coupling approximation is not maintained in this more general case, although the formal simplicity of the method remains. In particular, it must be stressed that $\bar{\rho}_1$, $\bar{\rho}_{12}$, and $\bar{\rho}_{13}$ are purely formal, and none of these can be interpreted as a true density operator, as will become increasingly clear.

To evaluate the results of the approximation we again introduce the variables

$$x_1 \equiv e^{-\beta J_1/2}, \qquad x_2 \equiv e^{-\beta J_2/2} \tag{28}$$

$$y_1 \equiv e^{-2\beta J_1(z_1-1)\bar{S}}, \qquad y_2 \equiv e^{-2\beta J_2(z_2-1)\bar{S}} \tag{29}$$

$$w \equiv e^{-\beta \mu H}, \tag{30}$$

and the notations

$$Z_1 \equiv \mathrm{tr}_1\bar{\rho}_1 = \mathrm{tr}_1(y_1^{z_1/(z_1-1)}y_2^{z_2/(z_2-1)}w)^{S_1^z}, \tag{31}$$

$$\begin{aligned}Z_{12} &\equiv \mathrm{tr}_1\mathrm{tr}_2\bar{\rho}_{12} \\ &= \mathrm{tr}_1\mathrm{tr}_2 x_1^{-4\mathbf{S}_1\cdot\mathbf{S}_2}(wy_1y_2^{z_2/(z_2-1)})^{(S_1^z+S_2^z)}, \end{aligned} \tag{32}$$

$$\begin{aligned}Z_{13} &\equiv \mathrm{tr}_1\mathrm{tr}_3\bar{\rho}_{13} \\ &= \mathrm{tr}_1\mathrm{tr}_3 x_2^{-4\mathbf{S}_1\cdot\mathbf{S}_3}(wy_1^{z_1/(z_1-1)}y_2)^{(S_1^z+S_3^z)}. \end{aligned} \tag{33}$$

The single-ion expectation value of S_1^z, which is *not* equal to the actual magnetization, is defined by

$$\begin{aligned}\langle S^z\rangle_1 &\equiv \langle S_1^z\rangle_1 \equiv -\frac{\partial \ln Z_1}{\partial \ln w} \\ &= SB_S\left\{-S\ln w - \frac{z_1 S}{z_1-1}\ln y_1 - \frac{z_2 S}{z_2-1}\ln y_2\right\}, \end{aligned} \tag{34}$$

and the two-ion expectation values of S^z are similarly defined by

$$\langle S^z\rangle_{12} = \tfrac{1}{2}\langle S_1^z + S_2^z\rangle_{12} = -\frac{1}{2}\frac{\partial \ln Z_{12}}{\partial \ln(wy_1y_2^{z_2/(z_2-1)})}, \tag{35}$$

$$\langle S^z\rangle_{13} = \tfrac{1}{2}\langle S_1^z + S_3^z\rangle_{13} = -\frac{1}{2}\frac{\partial \ln Z_{13}}{\partial \ln(wy_1^{z_1/(z_1-1)}y_2)}. \tag{36}$$

The two-particle partition sums are explicitly

$$\begin{aligned}Z_{12} = {} &\frac{x_1^{4S(S+1)}}{1-wy_1y_2^{z_2/(z_2-1)}}\sum_{R=0}^{2S}\frac{x_1^{-2R(R+1)}}{[wy_1y_2^{z_2/(z_2-1)}]^R} \\ &+ \frac{x_1^{4S(S+1)}}{1-[wy_1y_2^{z_2/(z_2-1)}]^{-1}}\sum_{R=0}^{2S}\frac{[wy_1y_2^{z_2/(z_2-1)}]^R}{x_1^{2R(R+1)}}\end{aligned} \tag{37}$$

and

$$\begin{aligned}Z_{13} = {} &\frac{x_2^{4S(S+1)}}{1-wy_1^{z_1/(z_1-1)}y_2}\sum_{R=0}^{2S}\frac{x_2^{-2R(R+1)}}{[wy_1^{z_1/(z_1-1)}y_2]^R} \\ &+ \frac{x_2^{4S(S+1)}}{1-[wy_1^{z_1/(z_1-1)}y_2]^{-1}}\sum_{R=0}^{2S}\frac{[wy_1^{z_1/(z_1-1)}y_2]^R}{x_2^{2R(R+1)}}.\end{aligned} \tag{38}$$
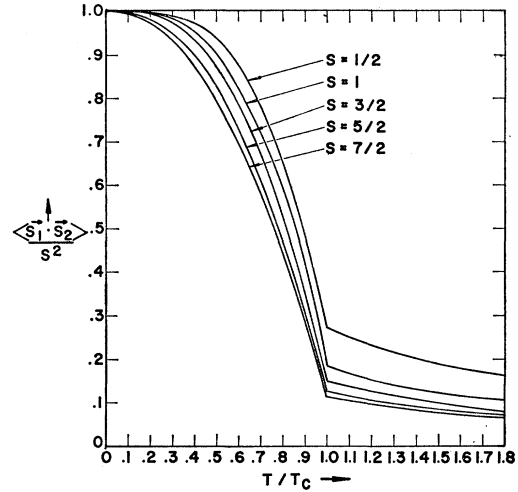

FIG. 2. Nearest-neighbor spin correlation versus T/T_c, for nearest-neighbor exchange (constant coupling), for various spin values.

The magnetization is

$$\langle S^z\rangle = -\frac{1}{\mu N}\frac{\partial F}{\partial H} = -\frac{1}{N}\frac{\partial(-\beta F)}{\partial \ln w}, \tag{39}$$

which becomes

$$\langle S^z\rangle = (z_1 J_1/J_0)\langle S^z\rangle_{12} + (z_2 J_2/J_0)\langle S^z\rangle_{13}. \tag{40}$$

As we have remarked above, it is noteworthy that the magnetization is not given by its one-particle average $\langle S^z\rangle_1$, nor by either of the two-particle averages $\langle S^z\rangle_{12}$ or $\langle S^z\rangle_{13}$, nor is it equal to $\bar{S}$; it is the weighted average of $\langle S^z\rangle_{12}$ and $\langle S^z\rangle_{13}$, with the weight factors $z_1 J_1/(z_1 J_1 + z_2 J_2)$ and $z_2 J_2/(z_1 J_1 + z_2 J_2)$, respectively.

Finally, the correlation functions of nearest-neighbor spins and of next-nearest-neighbor spins are given by

$$\begin{aligned}\langle\mathbf{S}_1\cdot\mathbf{S}_2\rangle &= \frac{1}{Nz_1}\frac{\partial(-\beta F)}{\partial(\beta J_1)} \\ &= \langle\mathbf{S}_1\cdot\mathbf{S}_2\rangle_{12} + 2\bar{S}\{\langle S^z\rangle - \langle S^z\rangle_{12}\},\end{aligned} \tag{41}$$

$$\begin{aligned}\langle\mathbf{S}_1\cdot\mathbf{S}_3\rangle &= \frac{1}{Nz_2}\frac{\partial(-\beta F)}{\partial(\beta J_2)} \\ &= \langle\mathbf{S}_1\cdot\mathbf{S}_3\rangle + 2\bar{S}\{\langle S^z\rangle - \langle S^z\rangle_{13}\},\end{aligned} \tag{42}$$

where

$$\langle\mathbf{S}_1\cdot\mathbf{S}_2\rangle = -\tfrac{1}{4}(\partial \ln Z_{12}/\partial \ln x_1) \tag{43}$$

and

$$\langle\mathbf{S}_1\cdot\mathbf{S}_3\rangle = -\tfrac{1}{4}(\partial \ln Z_{13}/\partial \ln x_2). \tag{44}$$

At the Curie temperature, $\bar{S}$ vanishes. We determine this temperature by expanding the partition sums to third order in the small quantities (y_1-1) and (y_2-1),

whence Eq. (25) becomes

$$2S(S+1)(z_1J_1+z_2J_2)[z_1(z_1-1)J_1+z_2(z_2-1)J_2+z_1z_2(J_1+J_2)]$$

$$=z_1[(z_1-1)J_1+z_2J_2]^2\sum_{R=0}^{2S}x_1^{-2R(R+1)}R(R+1)(2R+1)\Big/\sum_{R=0}^{2S}x_1^{-2R(R+1)}(2R+1)$$

$$+z_2[z_1J_1+(z_2-1)J_2]^2\sum_{R=0}^{2S}x_2^{-2R(R+1)}R(R+1)(2R+1)\Big/\sum_{R=0}^{2S}x_2^{-2R(R+1)}(2R+1). \quad (45)$$

It is reassuring that this condition reduces to the constant coupling condition Eq. (20) if we let $J_2=0$; for this purpose we must also invoke the identity

$$\sum_{R=0}^{2S}R(R+1)(2R+1)\Big/\sum_{R=0}^{2S}(2R+1)=2S(S+1). \quad (46)$$

In Fig. 3 we show $k_BT_c/S(S+1)J_1$ versus J_2/J_1 for $S=\frac{7}{2}$ with $z_1=12$ and $z_2=6$, appropriate to the europium chalcogenides. Curves for some other spin values are also given. For comparison, on the same figure, we show the Curie temperatures predicted by molecular field theory [$k_BT_c=\frac{2}{3}S(S+1)J_1(z_1+z_2J_2/J_1)$] and by the Green function theory.[13] Furthermore, for $J_2=0$ the system is a nearest-neighbor ferromagnet, which has been investigated[15] extensively by Padé extrapolation of the high-temperature series; the resultant predicted Curie temperatures are indicated by isolated points in Fig. 3.

For EuS, Charap and Boyd[10] have found

$$J_1/k_B=0.20°K, \quad J_2/k_B=-0.08°K, \quad (47)$$

by comparison of spin-wave theory with low-temperature magnetization and specific-heat data. With these values we find, from Fig. 3,

$$T_c=16.9°K. \quad (48)$$

The measurements of Argyle[7] give $T_c=16.5°K$, and those of Benedek and Heller[14] give $T_c=16.52°K$, although Moruzzi and Teaney[9] have reported $T_c=16.3°K$ from specific-heat data. For the same values of exchange constants the molecular field theory predicts $T_c=20.2°K$.

In Fig. 4 we show the theoretical reciprocal susceptibility in the paramagnetic region, and the experimental data of McGuire, Argyle, Shafer, and Smart.[5] The theoretical calculations were carried out for $J_2/J_1=0$ and -0.4, but the numerical results superpose so exactly that only a single curve appears in the figure.

The $1/\chi=0$ intercept in Fig. 4 is independent of the assumed g value, and we find a paramagnetic Curie temperature $\theta=17.5°K$. McGuire, Argyle, Shafer, and Smart report $\theta=18°K$, and McGuire and Shafer[16] later report $\theta=19°K$.

The slope of the theoretical $1/\chi$ versus T curve depends on the assumed value of gN_A, the product of the g factor and the number N_A of Eu ions per mole of sample. The g factor has been independently evaluated[17]
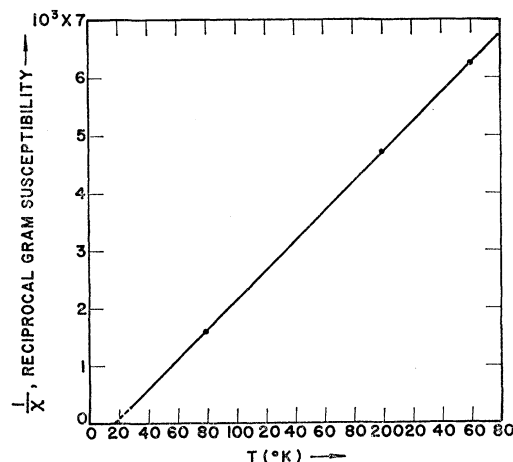

FIG. 3. Curie temperature as a function of exchange constants, for various spin values. The molecular field result, the Green function result (Ref. 13) and the Padé approximant estimates (Ref. 15) at $J_2=0$ are also shown.

[15] G. S. Rushbrooke and P. J. Wood, Mol. Phys. 1, 257 (1958).

FIG. 4. The reciprocal of the susceptibility versus temperature for EuS. The theoretical curve applies both to $J_2/J_1=0$ and to $J_2/J_1=-0.4$. Experimental points from the measurements of McGuire, Argyle, Shafer, and Smart (Ref. 5).

[16] T. R. McQuire and M. W. Shafer, J. Appl. Phys. 35, Suppl. 2, 984 (1964).
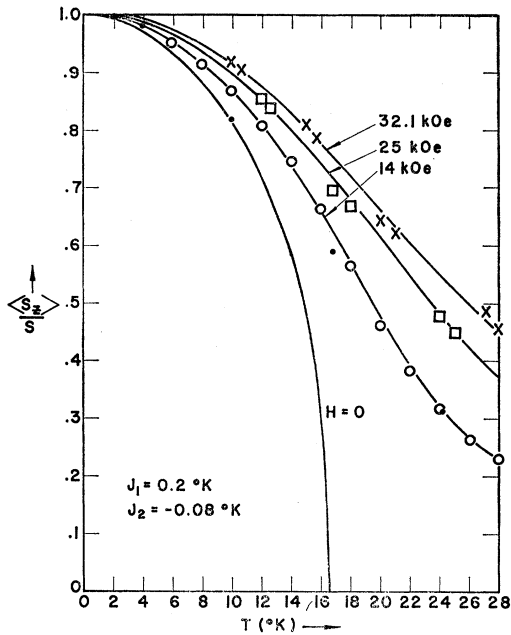[17] W. Low (private communication).

FIG. 5. Magnetization of EuS as a function of temperature, for several values of applied field. Solid curves indicate theoretical results corresponding to the labeled values of field. Open circles are the measurements of Argyle (Ref. 7) for 14 kOe. All other data are by Enz, Fast, van Houten, and Smit (Ref. 6), for 14.3 kOe (solid circles), for 25 kOe (squares), and for 32.1 kOe (crosses).

FIG. 6. Nearest- and next-nearest-neighbor spin correlations as a function of temperature, for EuS.

by paramagnetic resonance as 1.99. However, McGuire informs us that the samples of EuS, on which magnetic measurements have been made, deviate from stoichiometry. Hence N_A is uncertain and the value of gN_A is best treated as an adjustable parameter. To obtain agreement of the slope in Fig. 4 with the experimental data we have chosen a value of gN_A which corresponds to $g=1.99$ and $N_A/(\text{Avogadro's number}) = 0.941$.

In Fig. 5 a comparison is made of experimental and theoretical magnetization curves for EuS, with various values of the applied field.

The open circles indicate the measurements of Argyle[7] modified for demagnetization by use of Fig. 3 of his paper; the effective field (applied field minus demagnetizing field) is 14 kOe. The remaining data points, from Enz, Fast, van Houten, and Smit,[6] for fields of 14.3, 25, and 32.1 kOe, have not been corrected for demagnetization. Such a correction would raise the experimental points slightly, particularly in the range of the Curie temperature.

The theoretical curves are drawn with the spin-wave values of J_1 and J_2 for EuS. For nonzero field the curves also depend upon the assumed value of gN_A, and the curves shown correspond to $g=1.99$ and $N_A/(\text{Avogadro's number}) = 0.873$.

In Fig. 6 we show the temperature dependence of the nearest-neighbor and the next-nearest-neighbor correlation functions $\langle S_1 \cdot S_2 \rangle$ and $\langle S_1 \cdot S_3 \rangle$. Again the spin-wave values of the exchange constants of EuS have

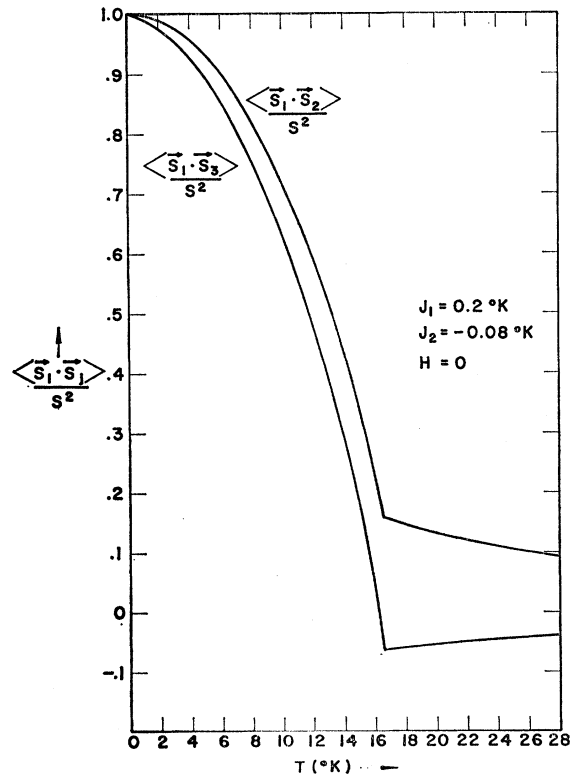been adopted, and the external field has been taken as zero.

Two features of Fig. 6 are of interest. The nearest-neighbor correlation function falls at the Curie temperature to about 16% of its $T=0$ value, abruptly changes slope, and persists far into the paramagnetic region. This behavior is in at least qualitative agreement with the known high-temperature behavior of nearest-neighbor ferromagnets, and it is in marked contrast to the prediction of molecular field theory. According to the latter theory the correlation functions fall abruptly to zero at T_c, being simply proportional to the square of the magnetization. The next-nearest-neighbor correlation function falls to a negative value at T_c, abruptly changes slope, and again persists far into the paramagnetic region. This negative correlation, mediated of course by the negative value of J_2, is a novel and interesting feature which might well be observable experimentally, particularly in EuSe in which J_2/J_1 is more negative.

The magnetic contribution to the specific heat is given by

$$c = -Nz_1 J_1 \frac{d}{dT}\langle S_1 \cdot S_2 \rangle - Nz_2 J_2 \frac{d}{dT}\langle S_1 \cdot S_3 \rangle. \quad (49)$$

This quantity has been measured at low temperatures by McCollum and Callaway,[8] and over a broad tem-
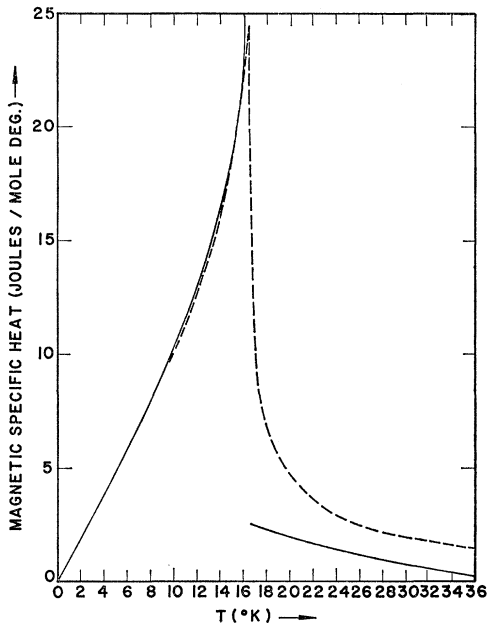
FIG. 7. Magnetic specific heat of EuS as a function of temperature. Dashed curve from the measurements of Moruzzi and Teaney (Ref. 9), solid curve theoretical with $J_1/k_B = 0.2°K$, $J_2/k_B = -0.08°K$.

perature range by Moruzzi and Teaney.[9] In Fig. 7 we show a comparison between theory and experiment. The dashed curve is taken from Moruzzi and Teaney, who have subtracted the lattice contribution to the specific heat by means of the Debye theory. The solid curve is the theoretical specific heat using the spin-wave values of the exchange constants for EuS, and taking the derivatives of the correlation functions from Fig. 6; there are no adjustable constants. While our calculated specific heat is in accurate agreement with experiment
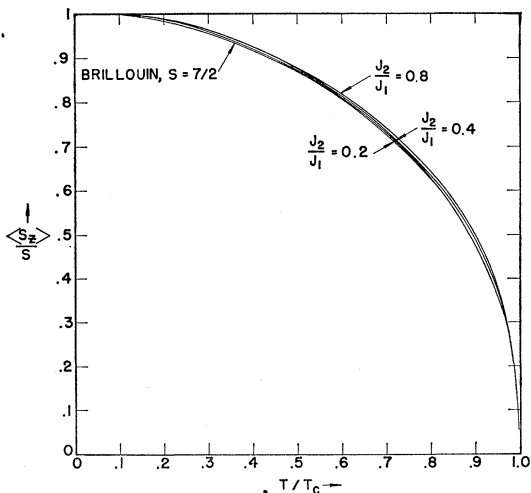

FIG. 8. Magnetization as a function of T/T_c, for various values of J_2/J_1. The molecular field result (the Brillouin function) is also shown for comparison.

in the ferromagnetic region, above the Curie temperature it is only about half of the observed value, or of that calculated by Wojtowicz,[11] who has extended the Rushbrooke and Wood high-temperature power series to include next-neighbor interactions.

5. EFFECT OF VARIATION OF EXCHANGE CONSTANTS

In evaluating the theory above we have calculated magnetization curves and correlation functions for EuS, using the spin-wave values of J_1 and J_2. It is of interest to explore the sensitivity of these curves to changes in the J_2/J_1 ratio.

In Fig. 8 we show magnetization curves for zero field as a function of T/T_c, plotted for several values of J_2/J_1. All the curves are quite close together, the $J_2/J_1 = 0$ curve lying lowest. Although the curves for
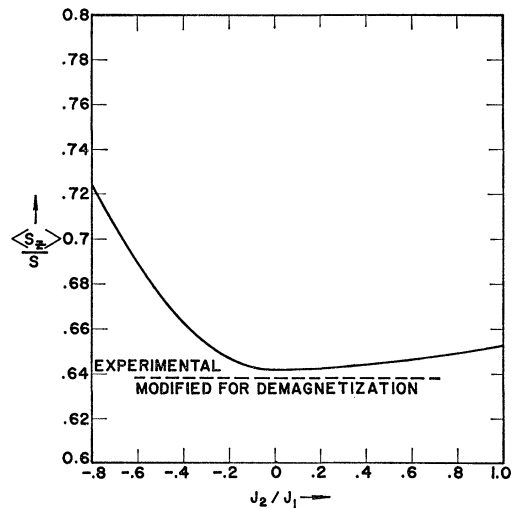

FIG. 9. Magnetization at the Curie temperature as a function of J_2/J_1, for an applied field of 14 kOe.

both negative and positive J_2/J_1 lie slightly above the $J_2/J_1 = 0$ curve, we show only those for $J_2/J_1 = 0$, 0.4 and 0.8, for clarity. The molecular field result (the Brillouin function) is also shown in Fig. 8, and it is seen that the two-spin cluster theory and molecular field theory are in rather close agreement for the magnetization.[18]

The insensitivity of the zero-field magnetization curves to J_2/J_1, as observed in Fig. 8, precludes the determination of J_2/J_1 on the basis of this type of data.

Turning to magnetization data in the presence of applied fields, in Fig. 9 we show the magnetization at the Curie temperature as a function of J_2/J_1, for an

[18] Although the two-spin cluster curves for the magnetization are slightly more "square" than the molecular field curve, this deviation does not appear to be large enough to account for the squareness observed in many ferrimagnets and antiferromagnets [cf. D. S. Rodbell, I. S. Jacobs, J. Owen, and E. A. Harris, Phys. Rev. Letters 11, 10 (1963)].

applied field of 14 kOe. In this curve we have taken $g=2$ and assumed perfect stoichiometry. The field of 14 kOe has been selected for comparison with the data of Argyle, whose value is shown on Fig. 9 (and given in detail in Fig. 5). We find that at this field, as in zero field, the magnetization is lowest if $J_2/J_1=0$; the rise is more rapid for negative J_2/J_1 than for positive J_2/J_1, and the minimum is rather broad. The experimental value lies close to this minimum. Thus magnetization data at 14 kOe merely indicates that J_2/J_1 is in the vicinity of zero, but is again rather insensitive to J_2/J_1 in this region. To illustrate the type of agreement to be obtained we show, in Fig. 10, magnetization curves for $J_1/k_B=0.146°K$, $J_2=0$, $g=2$, and perfect stoichi-
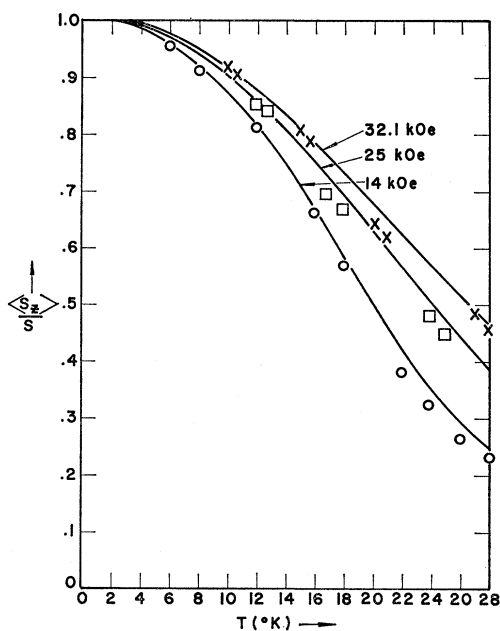

FIG. 10. Magnetization of EuS as a function of temperature. Theoretical curve with $J_1/k_B=0.146°K$, $J_2=0$, $g=2$, and perfect stoichiometry. Experimental points as in Fig. 5.

ometry. These exchange constants would predict a Curie temperature of 16.6°K.

Perhaps the properties most sensitive to the J_2/J_1 ratio are the spin-correlation functions. These are shown in Fig. 11 as functions of T/T_c for various values of J_2/J_1. The negative value of $\langle S_1 \cdot S_3 \rangle$ at T_c, noted previously in Fig. 6, vanishes at $J_2/J_1=0$ and becomes positive for $J_2/J_1>0$. Conversely, the nearest-neighbor correlation function at T_c, fairly large at $J_2/J_1=-0.4$, decreases as J_2/J_1 increases.

The inverse behavior of the first- and second-neighbor correlation function results in a relative insensitivity of the magnetic energy,

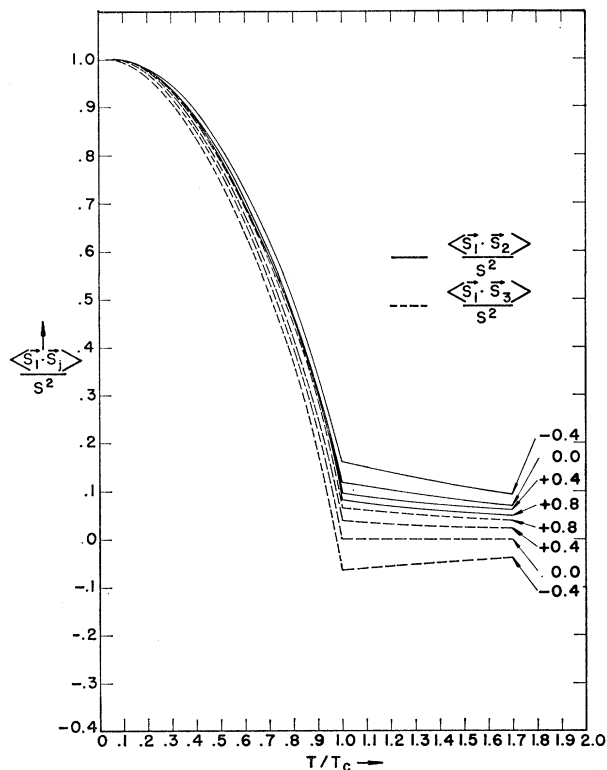$$U_M = -Nz_1J_1\langle S_1 \cdot S_2 \rangle - Nz_2J_2\langle S_1 \cdot S_3 \rangle,$$

FIG. 11. Nearest- and next-nearest-neighbor spin correlations as a function of temperature, for various values of J_2/J_1. For each value of J_2/J_1 the value of J_1 is adjusted to give $T_c=16.6°K$.

to the ratio J_2/J_1. In fact for values of $J_2/J_1=0.8$, 0.4, 0.0, and -0.4 the magnetic energies at the Curie temperatures stand in the ratios 1.04, 1.02, 1.00, and 0.997, respectively. These differences all lie within the experimental error. Similarly the specific heat, being the derivative of the energy, is extremely insensitive to J_2/J_1.

We conclude that the single-spin effects, such as magnetization and susceptibility, are rather insensitive to J_2/J_1 (when J_1 is chosen to give the proper T_c). Similarly the magnetic energy and specific heat are insensitive because of the compensatory variations of the first- and second-neighbor correlations. The correlation functions themselves are quite sensitive, particularly in the neighborhood of the Curie temperature. A direct measurement of the correlation functions would provide the most reliable criterion for the evaluation of the exchange constants.

ACKNOWLEDGMENTS