APPENDIX C: LONG-RANGE INTERACTIONS

In Sec. II.2 it was observed that the term $O((1+t)^{1/2})$ in $g'(t)$ is directly responsible for the discontinuity in the derivative of the specific heat. For an exchange potential of range λ (2.23) we have

$$g'(t)=\frac{l^3}{2(2\pi)^3}\int d^3k\frac{1}{1+t+\lambda^2k^2}. \qquad \text{(C1)}$$

The coefficient of the term in $(1+t)^{1/2}$ will be

$$\lim_{t\to-1}(1+t)^{-1/2}[g'(t)-g'(-1)],$$

which from (C1) reduces to

$$-\lim_{t\to-1}\frac{l^3(1+t)^{1/2}}{2\lambda^2(2\pi)^3}\int d^3k\frac{1}{k^2(1+t+\lambda^2k^2)}. \qquad \text{(C2)}$$

Since the dominant contribution of the integral (C2) is from the region of small k, we are justified in replacing the integration over the basic cell by integration over a sphere in **k** space, which gives

$$\lim_{t\to-1}\frac{-l^3}{2(2\pi)^3\lambda^3}\tan^{-1}\frac{\lambda k_{\max}}{(1+t)^{1/2}},$$

where $k_{\max}$ is the radius of the sphere. Proceeding to the limit one gets

$$g'(t)=\frac{1}{2}\left(\frac{l}{\lambda}\right)^2q-\frac{1}{2}\left(\frac{l}{\lambda}\right)^3\frac{1}{16\pi^2}(1+t)^{1/2}+O(1+t).$$

The term $O((\beta-\beta_c)^3)$ in the free energy is proportional to α^{-2}, and so in the present case this proportionality factor will be $2^{10}3^{-2}\pi^4(\lambda/l)^6$.

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Theory of High-Temperature Susceptibility of Heisenberg Ferromagnets Having Nearest-Neighbor Bilinear and Biquadratic Exchange Interactions

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The high-temperature susceptibility series is derived for the nearest-neighbor Heisenberg ferromagnet when nearest-neighbor biquadratic exchange is included. The general diagrammatic technique developed by Rushbrooke and Wood for the bilinear interaction is extended to include the biquadratic interaction. The complete coefficients of terms through $1/T^2$ are computed, and since it is expected that the value of the ratio of the biquadratic (j) to bilinear exchange (J) constants is quite small, only terms linear in the biquadratic exchange in the coefficients of the terms $1/T^3$ and $1/T^4$ are determined. The coefficients are computed for arbitrary spin and general lattice structure. The series expansion has been applied to the susceptibility of $KMnF_3$ to determine the quality of information which can be obtained from the experimental data. $KMnF_3$ was selected since the biquadratic exchange between Mn^{++} ions has been extensively studied and the second-neighbor bilinear interaction is expected to be negligible. The experimental data, corrected for the temperature-independent diamagnetism, was root-mean-square-analyzed to determine the values of J, j, and C, the Curie constant, which give the best fit to the data. A value of $|j/J|=0.015$ was thus found, in good agreement with the results of previous studies.

I. INTRODUCTION

THERE now seems to be considerable evidence for the existence of intrinsic biquadratic exchange in ordered magnetic systems.[1,2] Except for its direct observation by means of a microwave resonance technique by Harris and Owen,[1] the effect of biquadratic exchange on magnetic properties has thus far only been taken into account by using molecular field theories.[2] Since it is known that such theories do not even treat the bilinear exchange adequately, their ability to treat biquadratic exchange is suspect. It therefore seems appropriate at this stage to make a more exact theory of the effect of biquadratic exchange on a magnetic property, combine this with highly accurate experimental data, determine the exchange constants, and then compare this result with the results of the molecular field theories and with other theoretical estimates of the magnitude of the biquadratic exchange constant.[3,4] In the present paper the exact high temperature susceptibility series is derived for the Heisenberg ferromagnet when both nearest neighbor bilinear and biquadratic exchange interactions are included.

Section IIA contains the results of a formal statistical mechanical derivation of the susceptibility expansion based on a Heisenberg Hamiltonian containing both

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[1] E. A. Harris and J. Owen, Phys. Rev. Letters **11**, 9 (1963).

[2] D. S. Rodbell, I. S. Jacobs, J. Owen, and E. A. Harris, Phys. Rev. Letters **11**, 10 (1963).

[3] P. W. Anderson, Phys. Rev. **115**, 2 (1959); in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 14, p. 99.

[4] N. Huang and R. Orbach, Phys. Rev. Letters, **12**, 275 (1964).

nearest-neighbor bilinear and biquadratic exchange interactions. The Hamiltonian to be used is *formally* identical to one treated by Wojtowicz and Joseph,[5] for a different problem. The formal results of that paper may be taken over directly. Section IIB briefly discusses the calculation of the new coefficients required to describe the effect of the biquadratic exchange interaction on the susceptibility series. This is accomplished by an extension of a diagram technique described by Rushbrooke and Wood.[6] In Sec. III, we consider the application of the enlarged susceptibility series to the determination of the bilinear and biquadratic exchange constants between the Mn^{++} ions in $\mathrm{KMnF_3}$ and compare the results with previous studies.

II. THEORY

A. Formal Statistical Mechanics

We consider a system consisting of a lattice of N sites containing atoms of spin S and gyromagnetic ratio g, each atom having z nearest neighbors. The Hamiltonian for the system in the presence of an external magnetic field H_z is taken to be

$$\begin{aligned} \mathcal{H} &= -2J\mathbf{P}-2j\mathbf{R}-g\mu H_z\mathbf{Q}\,, \\ \mathbf{P} &= \sum_{\langle ij\rangle} (\mathbf{S}_i\cdot\mathbf{S}_j)\,, \\ \mathbf{R} &= \sum_{\langle kl\rangle} (\mathbf{S}_k\cdot\mathbf{S}_l)^2\,, \\ \mathbf{Q} &= \sum_m S_{mz}\,, \end{aligned} \tag{1}$$

where J and j are the magnitudes of the nearest-neighbor bilinear and biquadratic exchange interactions, respectively, and where μ is the Bohr magneton. $\mathbf{P}$ and $\mathbf{R}$ are the sum of bilinear and biquadratic Heisenberg exchange operators for all first-neighbor pairs, respectively, while $-g\mu H_z\mathbf{Q}$ is the Zeeman energy operator for the entire lattice. The operator $\mathbf{Q}$ commutes with both $\mathbf{P}$ and $\mathbf{R}$, but $\mathbf{P}$ does not commute with $\mathbf{R}$. The Hamiltonian as written in the first line of Eq. (1) is identical in form to that considered by WJ [in fact, the only difference in the details of the Hamiltonian are in the second term]. The formal derivation of the susceptibility series is then the same as given there, so that the low-field susceptibility is given as the following double series:

$$\begin{aligned} \chi &\doteq (C/T)\Big[1+\sum_{m,n=0}^{\infty}{}' a_{nm}(\beta J)^n(\beta j)^m\Big]\,, \\ a_{nm} &= \frac{3\times 2^{n+m}}{(n+m)!NS(S+1)}\sum_{\mathrm{perm}}\Gamma_N\langle\mathbf{P}^n\mathbf{R}^m\mathbf{Q}^2\rangle\,, \\ C &= Ng^2\mu^2S(S+1)/3k\,, \\ \beta &= 1/kT\,, \end{aligned} \tag{2}$$

where C is the Curie constant, k the Boltzmann constant, and T the thermodynamic temperature. $\langle\mathbf{O}\rangle$ stands for the normalized trace of the $(2S+1)^N$-dimensional direct product matrix representation of the operator $\mathbf{O}$ and the symbol $\Gamma_N f$ means "that part of f which is proportional to N." $\sum_{\mathrm{perm}}$ denotes the sum over all permutations in the order of appearance of the operators $\mathbf{P}$ and $\mathbf{R}$ and arises from the noncommutability of $\mathbf{P}$ and $\mathbf{R}$. The prime on the summations excludes the term $n=m=0$. The first term of the top line of Eq. (2) is Curie's law for noninteracting spins, while succeeding terms represent increasing orders of the statistical mechanical perturbation of the nearest-neighbor bilinear and biquadratic exchange on the free ion paramagnetism. The reciprocal susceptibility may also be written as a double series:

$$\chi^{-1}=(T/C)\Big[1+\sum_{m,n=0}^{\infty}{}' b_{nm}(\beta J)^n(\beta j)^m\Big]. \tag{3}$$

The coefficients b_{nm} may be computed directly from the coefficients a_{nm} by use of the formula,

$$b_{nm}=-\sum_{r=0}^{n}\sum_{q=0}^{m}{}' a_{rq}b_{n-r,m-q}. \tag{4}$$

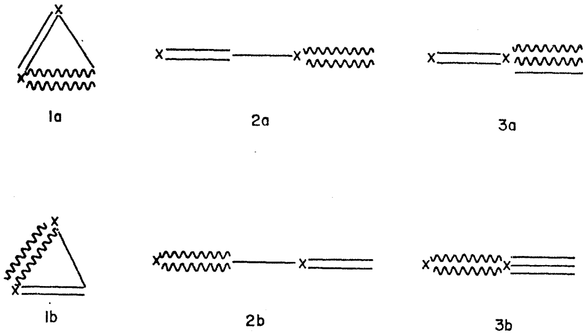

FIG. 1. Several typical diagrams encountered in evaluating the coefficient a_{31}.

B. Evaluation of the Coefficients

The general diagrammatic technique developed by RW for the bilinear interaction may be extended to include the biquadratic interaction. In RW, the classification, enumeration and evaluation of the many different contributions contained in a given $\langle\mathbf{P}^n\mathbf{Q}^2\rangle$ were facilitated by the representation of these contributions in terms of diagrams (localized graphs) on the lattice. The pertinent diagrams consisted of n lines and two crosses. A line connecting nearest-neighbor sites i and j represents the pair exchange operator $(\mathbf{S}_i\cdot\mathbf{S}_j)$, while a cross on site k represents the spin operator S_{kz}. The diagrammatic analysis of the traces $\langle\mathbf{P}^n\mathbf{R}^m\mathbf{Q}^2\rangle$

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[5] P. J. Wojtowicz and R. I. Joseph, Phys. Rev. **135**, A1314 (1964); henceforth referred to as WJ in the text.

[6] G. S. Rushbrooke and P. J. Wood, Mol. Phys. **1**, 257 (1958); henceforth referred to as RW in the text.

requires the introduction of another device with which to construct the necessary diagrams. A double wiggly line connecting nearest-neighbor sites i and j will be taken to represent the nearest-neighbor biquadratic pair-exchange operator $(\mathbf{S}_i\cdot\mathbf{S}_j)^2$. The introduction of the double wiggly line rather than simply a double straight line (i.e., simply a pair of bilinear operators between the same neighboring sites, to which it is formally equivalent) is necessitated by the need to keep track of the origin of the pairs of operators. Thus, the relevant diagrams consist of n straight lines, m double wiggly lines and two crosses. In Fig. 1 several of the diagrams derived from $\sum_{\text{perm}}\langle\mathbf{P}^3\mathbf{R}\mathbf{Q}^2\rangle$ are shown. The corresponding pairs 1 a–b, 2 a–b, and 3 a–b differ only in the interchange of double straight lines and double wiggly lines. The contribution of each member of the pair to the coefficient a_{31} is *not* the same.

The calculation of the coefficients according to the diagrammatic method involves three separate phases: (1) The finding and cataloging of all the diagrams or graphs which can be constructed from n straight lines, m double wiggly lines, and two crosses; (2) counting the number of times that a diagram can occur on a lattice of N sites; (3) evaluation of the traces of the products of spin variables which correspond to the diagrams. The details of these steps are fully discussed in RW and WJ.

The coefficients a_{n0} [corresponding to bilinear exchange only] have already been derived by RW. Because of extensive cancellation [by use of Eq. (4)] the coefficients b_{nm} appear considerably simpler than the corresponding a_{nm}. In the following only the results for the b_{nm} will be presented. The first six b_{n0} are tabulated in RW as functions of S, z and other lattice parameters such as the p_n and, are not repeated here. The p_n are defined such that $Nzp_n/2(n+2)$ gives the number of $n+2$ sided polygons, which can be placed on the lattice so that the sides connect only nearest-neighbor sites. The p_n are tabulated for various lattices by RW. We have calculated the coefficients b_{01}, b_{11}, b_{02}, b_{21}, and b_{31}. Since it is expected that $|j/J|\ll 1$, these coefficients are adequate to describe the effect of the biquadratic exchange on the coefficients of terms through $1/T^4$. The results are presented below:

$$b_{01}=Xz/3\,, \tag{5}$$

$$b_{11}=4Xz(-4X^2+X-6)/45\,, \tag{6}$$

$$b_{02}=-Xz(-2X^2+5X-3)/9\,. \tag{7}$$

Here, X stands for $S(S+1)$. The coefficient b_{21} and b_{31} [Eqs. (8) and (9)] are given in tabular form in Fig. 2. The meaning of the tables is straightforward: The numerical coefficients within the table are multiplied by the power of X above and by the lattice parameters on the left. The sum of all these is then multiplied by the common factor preceding the dot.

$$b_{21}=-\frac{2}{135}Xz\cdot\quad \begin{array}{c|cccc} & X^3 & X^2 & X & 1 \\ \hline 1 & -32 & -12 & 27 & -45 \\ p_1 & 16 & 6 & 24 & \end{array} \tag{8}$$

$$b_{31}=-\frac{4}{14175}Xz\cdot\quad \begin{array}{c|ccccc} & X^4 & X^3 & X^2 & X & 1 \\ \hline z & & -840 & 560 & -1260 & \\ 1 & 720 & 2480 & -515 & -1740 & 2880 \\ p_1 & -3248 & 168 & -63 & -2646 & \\ p_2 & 560 & 560 & 1015 & & \end{array} \tag{9}$$

FIG. 2. Tabular representation of the coefficients, b_{21} and b_{31} [Eqs. (8) and (9)].

The first two terms of the power series given by the right-hand side of Eq. (3) correspond to the results of a molecular field treatment of the susceptibility. Combining Eqs. (3) and (5) with the coefficient b_{10} as obtained from RW, we find that in this approximation

$$\chi^{-1}\approx(T-\theta)/C\,, \tag{10}$$

with

$$\theta=2Xz(J-\tfrac{1}{2}j)/3k\,. \tag{11}$$

Thus, when $|j/J|\ll 1$, the molecular field result implies that the biquadratic interaction has a negligible effect on the susceptibility. That the situation is more complex than this indicates, is seen from examining the higher order terms in the power series. Doing this, we find that the lead term due to the biquadratic interaction in each of the temperature coefficients is multiplied by an additional factor of X, which can be quite sizable, so that the biquadratic interaction can make a sizable correction to these coefficients.

III. APPLICATION TO $KMnF_3$

The series expansion has been applied to the susceptibility of $KMnF_3$ to determine the quality of information which can be obtained from the experimental data. We wish to know if it is possible to extract unambiguous values of the exchange parameters from susceptibility measurements. $KMnF_3$ was selected for study for several reasons: (1) the biquadratic exchange between Mn^{++} ions has been extensively studied, (2) the second-neighbor bilinear interaction is expected to be negligible for the perovskites, and (3) extensive, high-accuracy, high-temperature susceptibility measurements were readily available.

The high-temperature susceptibility data used in the present study were kindly supplied to us by Professor Kinshiro Hirakawa and his colleagues at Kyushu University. These data are qualitatively similar to those previously published by Hirakawa, Hirakawa, and Hashimota.[7] The new measurements have been made on a more pure sample and the results are more precise. In the present experimental study $MnCl_2\cdot 4H_2O$ was used as a standard to determine an absolute value for the susceptibility whereas in the previously reported work[7] MnO was used (an error in the value of the standard susceptibility previously used was discovered, so that

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[7] K. Hirakawa, K. Hirakawa, and T. Hashimoto, J. Phys. Soc. Japan **15**, 2063 (1960).

the previous measurements are about 4% higher than those used in the present study). The temperature range examined fell between 300 and 872°K (32 data points); the Néel point is 88°K. The lowest temperature used was 300°K so as to insure the rapid convergence of the series.

The first step in the analysis was a correction for the temperature-independent susceptibility which arises from the atomic core diamagnetism. The sum of the individual ionic contributions obtained from Selwood[8] was used. This gave a temperature-independent contribution of -0.4×10^{-6} cm^3/g. This amounts to 0.6% and 1.4% of the spin susceptibility at 300 and 872°K, respectively.

The remaining spin susceptibility was analyzed with the aid of Eq. (3). For the simple cubic lattice $[z=6, p_1=0, p_2=4]$ with $S=\frac{5}{2}$ the numerical values of the coefficients used are[9]

$$\begin{aligned} &b_{10}=-35\,, && b_{01}=17.5\,,\\ &b_{20}=221.67\,, && b_{11}=-1\,416.33\,,\\ &b_{30}=-608.22\,, && b_{21}=17\,239.44\,,\\ &b_{40}=26\,049.56\,, && b_{31}=-260\,544.75\,,\\ &b_{50}=-210\,986.52\,, && b_{02}=655.52\,.\\ &b_{60}=8\,014\,980.04\,, \end{aligned} \tag{12}$$

The procedure adopted for the determination of the exchange constants is as follows: Values of J and C were assumed and substituted into Eq. (3). The theory and data were fitted by adjusting j so as to give the least root mean square deviation (rmsd). The resulting rmsd for each set of the quantities J, C were plotted as a function of J and C. The set of quantities J, C which gives the best fit to the data is then determined by seeking the position of the minimum in the surface, rmsd of J and C.

The anticipated sharp and well defined minimum was *indeed* found. The values of the exchange constants corresponding to this minimum are

$$\begin{aligned} J/k&=-4.03\text{°K}\,,\\ j/k&=0.062\text{°K}. \end{aligned} \tag{13}$$

On a molar basis, the Curie constant so obtained has the value

$$C=4.568\,. \tag{14}$$

The rmsd corresponding to these values is about 35 g/cm^3 (this gives deviations of about 0.2%). The value of g corresponding to this C is 2.043. This value of g is higher than one might expect for an S-state ion and may be compared to the value of 2.004 determined by electron paramagnetic resonance[10] on 0.1% atomic Mn^{++} in KMgF$_3$. There are two ways of considering this result. The first is that it is real, that is, the g value is this high; the second is that we are again running into the problem of determining an absolute value for the susceptibility, referred to previously. If the latter is the case, the values of the exchange constants will not be affected by a uniform scaling of the susceptibility data (the diamagnetic correction is, of course, not scaled, but the small change in this already small correction does not have any significant effect). The value of J determined may be compared to the less precise estimates of Smart[11] based on a Bethe-Peierls-Weiss analysis of the Néel point and the susceptibility at the Néel point which gave $J/k=-(3.1\text{–}3.6)$°K. Finally, from the values of J and j given in Eq. (13), we obtain

$$|j/J|=0.015\,. \tag{15}$$

TABLE I. Comparison of the values of $|j/J|$ found in previous studies with the result of the present work.

Source–Material	$\|j/J\|$
Reference 3—Mn^{++}	~0.01
Reference 4—MnO	0.016
Reference 2—MnO	0.01–0.02
Reference 4—Mn^{++} in MgO	0.022
Reference 1—Mn^{++} in MgO	0.05±0.03
Present—KMnF$_3$	0.015

In Table I we compare the present result with those of previous studies. We thus see that the present result is in good agreement with the results of previous studies.[1–4] Although the results of the present analysis by no means "prove" the existence of a biquadratic exchange interaction, since the biquadratic interaction does not drastically alter our ability to fit the high-temperature susceptibility data, it at least shows that the previous studies[1–4] are not making any *drastic* overestimates of the magnitude of the biquadratic exchange interaction.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Professor Kinshiro Hirakawa and his colleagues at Kyushu University for kindly supplying the experimental data on the susceptibility of KMnF$_3$. He also wishes to thank Dr. P. J. Wojtowicz for his encouragement and generous help. Thanks are due to D. Jones for his aid with the numerical analysis.

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[8] P. W. Selwood, *Magnetochemistry* (Interscience Publishing Company, Inc., New York, 1956) 2nd ed., p. 78.

[9] Note that the values of the coefficients b_{50} and b_{60} are included here even though the corresponding coefficients b_{41} and b_{51} required for consistancy are not known. The reason for including these terms was to investigate what effect truncation of the series would have. The data were analyzed both with and without these two terms; the results of the analysis were essentially the same for both cases.

[10] J. S. Van Wieringen, Discussions Faraday Soc. **19**, 118 and 173 (1955).

[11] J. S. Smart, in *Magnetism*, edited by H. Suhl and G. Rado (Academic Press Inc., New York, 1963) Vol. 3, p. 63.