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A Note on Biquadratic Exchange

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Calculations of the Curie temperatures of e Heisenberg ferromagnet with biquadratic exchange are presented as a function of the strength of the biquadratic term for several spins and lattices. The possible measurement of this strength is briefly discussed.

Apresentamos cálculos de temperaturas de Curie, de um ferromagneto de Bekenberg com termos de troca biquadráticos, em função da intensidade do termo biquadrático para vários spins e Iátices. Discute-se brevemente a possível medida dessa intensidade.

The usual Heisenberg Hamiltonian' includes a bilinear exchange term

$$-2J\mathbf{S}_i \cdot \mathbf{S}_j$$

and the Zeeman term

$$-\mu H(S_{iz} + S_{jz})$$

for neighboring atoms i and j with spin angular momenta $\mu S_{i,j}$· J is the Heisenberg exchange integral and H the magnetic field. It is thought that this Hamiltonian should be extended in some cases by the inclusion of a term proportional to $(\mathbf{S}_i \cdot \mathbf{S}_j)^2$. Some reasons for this are the following: It was suggested by Anderson[2] that the superexchange calculation of Kramers[3], when extended from third to fifth-order perturbation theory, would yield such a term. Another possible origin, suggested by Birgeneau, Hutchings, Baker, and Riley[4], is the fact that in many rare-earth compounds the orbital angular momentum is not completely quenched. That is to say that the spherical symmetry seen by the electrons of the unfilled inner shell is not completely destroyed in the solid. As a result, the Hamiltonian can include a biquadratic term. Harris and Owen[5] and Rodbell *et al.*[6] found it necessary to use a small negative biquadratic term to explain their paramagnetic resonance data on Mn pairs in MgO. Joseph[7] used a similar Hamiltonian in calculating the high-temperature susceptibility series applicable to $KMnF_3$. In this paper we will consider the effect

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of biquadratic exchange that is positive and not necessarily small on the Curie temperatures of ferromagnets.

For the first part of the calculation, we use the Hamiltonian

$$\mathscr{H} = -2J \sum_{ij} [\mathbf{S}_i \cdot \mathbf{S}_j + \alpha(\mathbf{S}_i \cdot \mathbf{S}_j)^2] - \mu m \sum_i S_{iz} . \tag{1}$$

The first summation is taken over all nearest-neighbor pairs of spins and the second over all spins. The numerical parameter α indicates the strength of the biquadratic term.

The partition function for N particles ($\beta = 1/kT$),

$$Z_N = \text{trace } \exp(-\beta\mathscr{H}),$$

is expanded in a power series in $1/T$, the coefficients in the series being traces of powers of $\mathscr{H}$. This procedure is due to Kramers[8] and was first carried through by Opechowski[9]. It has been used many times since.

From the partition function, we obtain the susceptibility from

$$\chi = \frac{\mu^2}{NkT} \frac{\partial^2}{\partial\lambda^2} (\ln Z_N),$$

where $\lambda = \mu H/kT$ is set equal to zero after the differentiation. Since the exchange and Zeeman parts of the Hamiltonian commute, we can write the partition. function as

$$Z_N = \text{trace}\,(\exp(-\beta\mathscr{H}_{ex}) \exp(-\beta\mathscr{H}_z)).$$

Then, if the symbol $\langle\rangle$ is defined to mean, for any operator, Q,

$$\langle Q \rangle = \frac{\text{trace}\,[Q \exp(-\beta\mathscr{H}_z)]}{\text{trace}\,[\exp(-\beta\mathscr{H}_z)]},$$

we see that

$$\begin{aligned} Z_N &= \langle \exp(-\beta\mathscr{H}_{ex}) \rangle \text{ trace}\,[\exp(-\beta\mathscr{H}_z)] \\ &= (1 - \beta\langle\mathscr{H}_{ex}\rangle + \tfrac{1}{2}\beta^2 \langle \mathscr{H}_{ex}{}^2 \rangle \ldots) \text{ trace}\,[\exp(-\beta\mathscr{H}_z)]. \end{aligned}$$

Taking the second λ-derivative of $\ln Z_N$, we find

$$\chi = (1/3)\beta\mu^2 S(S+1)[1 + a_1/t + a_2/t^2 + \ldots], \tag{2}$$

where

$$t = kT/J, \quad \mathbf{a}, = 2f\sigma(2 - a),$$
$$a_2 = 2f\sigma\{[4(2f - 1)\mathbf{o} - 1] + 20[(24\mathbf{p}^2 - 2\sigma + 4)/5 - 4f\sigma]$$
$$+ \mathbf{a}^2[- 12\mathbf{a}^2 + 5\sigma - 1 + 2f\sigma]\},$$
$$a = S(S + 1)/3, \quad \mathbf{2f} = \mathbf{n} = \text{lattice coordination number.}$$

The first coefficient, **a, ,** is porportional to $\frac{\partial^2}{\partial\lambda^2}\langle\mathscr{H}_{ex}\rangle$ and the second to $\frac{\partial^2}{\partial\lambda^2}\{\langle\mathscr{H}_{ex}{}^2\rangle - \langle\mathscr{H}_{ex}\rangle^2\}$. Since all the neighbor pairs are equívalent,

$$\langle\mathscr{H}_{ex}\rangle = Nf\langle\mathbf{S}_1 \cdot \mathbf{S}_2\rangle.$$

For the other term, we see that there are three topologically different terms and

$$\langle\mathscr{H}_{ex}{}^2\rangle = Nf\langle(\mathbf{S}_1 . \mathbf{S}_2)^2\rangle + 2Nf(2f - 1)\langle(\mathbf{S}_1 . \mathbf{S}_2)(\mathbf{S}_2 . \mathbf{S}_3)\rangle$$
$$+ Nf(Nf - 4f + 1)\langle(\mathbf{S}_1 \cdot \mathbf{S}_2)(\mathbf{S}_3 \cdot \mathbf{S}_4)\rangle.$$

All of these involve relatively simple traces'and lead to the results shown above.

To find the Curie temperatures, we look for a singularity in χ. This can be done by setting $\chi^{-1} = 0$ (roots) or from the radius of convergence of the series, $\lim_{n\to\infty}(a_n/a_{n-1})$, which in this case we take as a_2/a_1 (ratios). For face-centered cubic **(FCC),** body-centered cubic (BCC), and simple cubic (SC) lattices with spins S = 1, 2, 3 the results are shown in Figs. **1, 2,** and **3,** the solid lines indicating the ratios, the dashed lines the roots. Also shown in Figure 1 by two black rectangles at $\alpha = 0$ and **1** are the results of two much more ambitious calculations[7,10] in which the series for χ were carried to 8 terms for the FCC with spin **1.** These serve to verify that our three-term series is qualitatively correct. **A** more complete discussion of the figures will be given below.

In the second part of the calculation, we use the Hamiltonian for a pair of spins:

$$\mathscr{H}_{12} = -2J\,[\mathbf{S}_1 . \mathbf{S}_2 + \alpha(\mathbf{S}_1 \cdot \mathbf{S}_2)^2] - \mu HM.$$

Here **H** includes, as well as any applied field, the interna1 field introduced to account for the interactions of **S,** and $\mathbf{S}_2$ with the rest of the lattice,

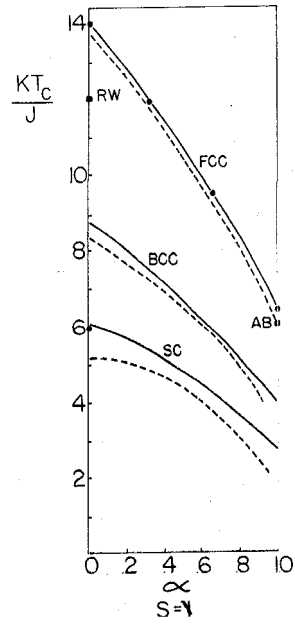

Fig. 1 - The behavior of the Curie temperature, T_C, with the strength of the biquadratic exchange, α, for three lattices of spin-1 atoms. The solid lines refer to ratios, the broken lines to roots from Eq. 2. The circles are from the constant-coupling approximation for the FCC lattice (ref 1). Where the dashed lines end, the roots become complex. The constant coupling approximation also has complex roots for $S = 2$ and 3 when the value of a exceeds that of the last circle shown. The points marked RW and AB are from refs. 9 and 3.

and $M = S_{1z} + S_{2z}$. Using $S = \mathbf{S}_1 + \mathbf{S}_2$ and $S_0 = |\mathbf{S}_1| = |\mathbf{S}_2|$, the eigenvalues of this Hamiltonian can be written down immediately:

$$E_{SM} = -(1/2)JS(S+1)[\alpha S(S+1) + 2 - 4\alpha S_0(S_0+1)] + \hat{A}M + \text{a constant.}$$

The partition function then follows by summing $\exp(-\beta E_{SM})$ over M from $-S$ to S and over S from 0 to $2S_0$.

To evaluate the unknown interna1 field, we proceed as follows: Consider the one-spin Hamiltonian (molecular field theory)

$$\mathscr{H}_1 = -\mu H' S_z \cdot$$

Here H' also includes the interactions of S with its neighbors. The partition function requires only a sum over S_z from $-S_0$ to S_0 of $\exp(-\beta\mathscr{H}_1)$. Let us now form the two density matrices

$$\rho_{12} = [\exp(-\beta\mathscr{H}_{12})]/Z_{12} \quad \text{and} \quad \rho_1 = [\exp(-\beta\mathscr{H}_1)]/Z_1 .$$

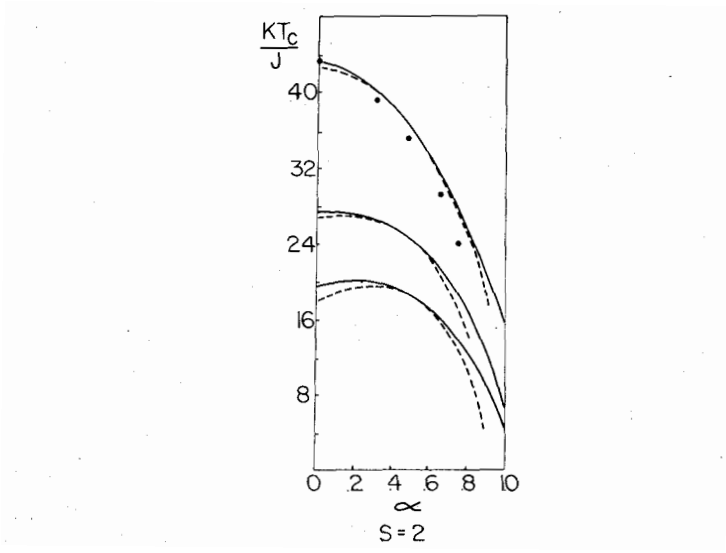

Fig. 2 - Same as 1 but for spin 2. The last circle shown ($a \simeq .75$) indicates where the roots for T_c from the constant-coupling approximation become complex.

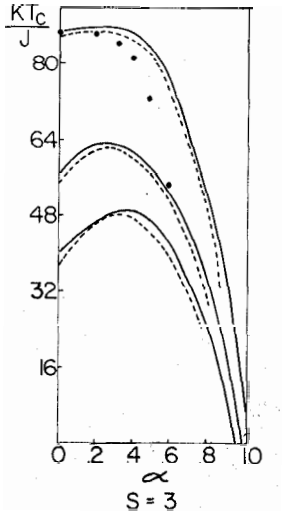

Fig. 3 - Same as 1 and 2 but for spin 3.

By a theorem due to Peierls[11], the molecular field theory is known to be the best one-particle approximation. Hence we take the trace over the spin'of one particle in ρ_{12} and require that the resulting density matrix equals ρ_1 with the additional condition that, when there is no applied field, the two interna1 fields are related by

$$H' = nh \quad \text{and} \quad H = (n-1)h$$

for the same h. This procedure, it turns out, is equivalent to a method known as constant coupling[12] but is formally simpler. It is also equivalent to calculating the average magnetization from the two partition functions and requiring that they be equal, with the same conditions imposed on H and H'. The last is the simplest for purposes of calculation and is the method actually employed, namely, we calculate the average magnetization from both Z, and Z_{12} and set their difference equal to zero. The resulting function is then expanded in a power series in h. (It must be an odd function.) The vanishing of the coefficient of the linear term in h gives T_C, the Curie temperature.

Returning to the figures, the results are:

1. There is generally close agreement between the values of T_C found as roots or ratios.
2. The constant-coupling approximation shows excellent agreement with the roots and ratios for spin 1, good agreement for spin 2, and only fair agreement for spin 3.
3. For all spins and lattices, as a increases, T_C (eventually) decreases, more rapidly for larger spin.
4. In all cases shown, except for the FCC for spin 1, the roots of $\chi^{-1} = 0$ and from the constant-coupling approximation eventually become complex for large enough a.

The decrease of T_C between a = 0 and 1 can be explained on the basis of the degeneracy of the ground state of the operator $(S_1 \cdot S_2) + (S_1 \cdot S_2)^2$ for spin 1. This explanation is modified for spin 2 and 3 when the decrease is even more drastic, the roots becoming complex and the ratios negative. Here one finds that degeneracy occurs for a < 1, and the ground state changes from that of maximum total spin $2S$ for a = 0 to the state of zero spin at a = 1. For example, for spin 2, one finds that the following eigenvalues (e.v.) (See Fig. 4.):

Total spin $(S_1 + S_2)$	4	3	2	1	0
e. v. of $(S_1 . S_2)$	4	0	−3	−5	−6
e. v. of $(S_1 . S_2) + (S_1 . S_2)^2$	20	0	6	20	30.

There is the interesting possibility that another type of transition occurs in the region of complex roots. There could be a first-order transition[6], or quadrupolar ordering[13] could take over for large a. Our calculations would not detect such transitions but the abrupt fall-off of T_C with a and the occurrence of complex roots suggests the possibility of their existence.

Finally, let us brieflyconsider an experiment to ascertain the presence of biquadratic exchange. Thermodynamic properties such as the specific heat capacity or the spontaneous magnetization show a strong α-dependence[14], but a is not an experimentally adjustable parameter. (Actually, if one could form solid solutions of two materials with different a's, the effective a would depend on the composition in a predicatable way.) A more direct test might come from electron spin resonance experiments" Here one measures indirectly the separations of the energy levels, i.e., the intervals $W_{s,s-1}$. Electrori spin resonance determines the multiplicity of the levels $(2S + 13$, and relative intensity of the transitions belonging to different levels' as a function of temperature fixes their separations. Consider the intervals between the S-levels of the operator

$$-2J[(\mathbf{S}_1 \cdot \mathbf{S}_2) + \alpha(\mathbf{S}_1 \cdot \mathbf{S}_2)^2].$$

For spin 2, they are

$$W_{S,S-1} = E_S - E_{S-1} = -2JS[1 + \alpha(S^2 - 12)],$$

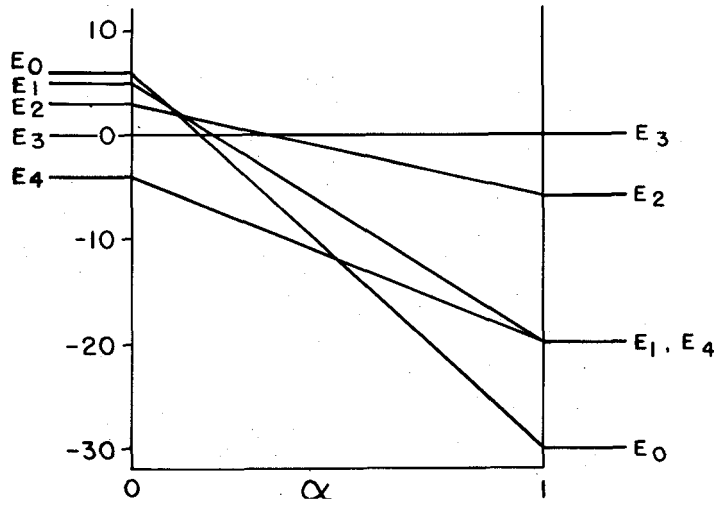

Fig. 4a - The energy levels, E,, of the operator (3), for spin-2 atoms

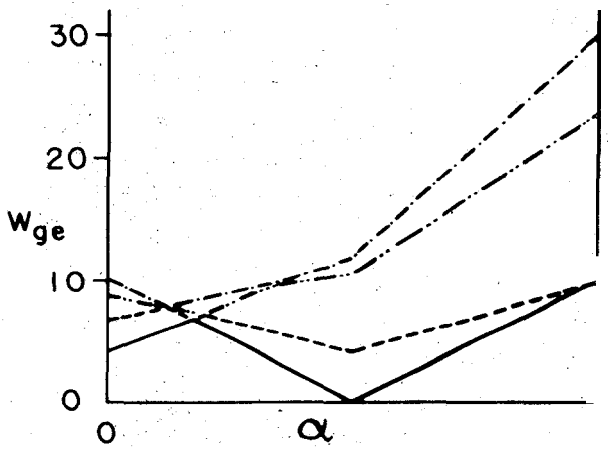

Fig 4b - The intervals, W_{ge}, between the ground state and the excited states, both in units of $2J$;

— — — , - to 1st excited state,

– – – – – – – – – – – – to 2nd excited state,

– – – – – – – – – – – – – to 3rd excited state,

to 4th excited state.

Note the region near $\alpha = 0.1$ where the levels for $S = 0$, 1, and 2 are approximately degenerate, leaving only two intervals (in the ratio of 3:4) to be fixed. (If we apply the same analysis to an antiferromagnet, the ground state would be the degenerate levels.) Slightly away from this region, the experimental situation might be very confusing with the levels too far apart to be considered degenerate and yet close enough to produce overlapping signals. For large $\alpha (> 1/2)$, the situation would be much improved with large intervals which means very different Boltzmann factors for different levels. In addition, this is the region where T_c is decreasing rapidly thus enlarging the paramagnetic region toward lower T allowing the values of W/kT to be increased further.

where S is the total spin with eigenvalues $0 \rightarrow 4$. The energy levels and the resulting intervals are shown in Figs. 4. The experimental problem is to attempt to find a unique value of a that fits the measured level multiplicities and intervals. The large number of possibilities for various a's is an embarrassment of riches. However, if the value of J is fairly well known and the actual energy level spectrum is close to the ideal shown in Fig. 4(in which various possible perturbing effects are ignored), it does seem possible to make an unambiguous determination of a by this method.

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