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Ground State of Interacting Spins

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The question is posed of how the ground state of the Heisenberg Hamiltonian $H=-\Sigma F_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$ depends on the magnitude s of N interacting spins, particularly in the case of long-ranged oscillatory interactions F_{ij}. It is discussed whether fixing the geometry and the bond strengths F_{ij} suffices to determine the nature of the spin correlations in the ground state, and a review is given of known instances when this is the case; those are special situations in ferromagnetism and antiferromagnetism when qualitative ground-state properties such as "lack of nodes" can be proved to be independent of s. These are valuable examples for the application of semiclassical methods, which are strictly valid only for $s\rightarrow\infty$ and depend on the convergence of a series in powers of s^{-1}. But these examples are, after all, only special cases, and it is argued that, in general, the nature of the ground state can depend sensitively on s. The following situation is considered in some detail: An oscillatory interaction which leads to a ferromagnetic ground state in the correspondence limit $s\gg 1$, but for which the ferromagnetic state of saturation magnetization may be unstable for small quantum mechanical spins, e.g., $s=\frac{1}{2}$ or 1. Two distinct types of interaction are considered which lead to this result, and it is seen that the ferromagnetic instability is a consequence, not so much of the long range of the interaction as of the presence of some relatively strong antiferromagnetic (negative) bonds. However, the variational approach which is used casts no light on the nature of the true ground state or of the thermal properties, problems which are increasingly interesting in these instances when semiclassical procedures are seen to fail.

INTRODUCTION

THE direct overlap of wave functions belonging to neighboring spins leads to a magnetic interaction which can be of either sign—ferromagnetic or antiferromagnetic.[1] Lately, interest has been focused on theories of "indirect exchange interactions" via conduction electrons, which result in oscillatory magnetic coupling as a consequence of the sharp Fermi surface.[2] The "indirect exchange" coupling may or may not be more important than the "direct coupling" in a given material, and the two mechanisms doubtless can coexist in the same substance. In the indirect exchange theory originally ascribable to Ruderman and Kittel,[3] the interaction was long ranged and decreased only as the inverse cube of the distance at large separation. A subsequent modification by Yosida[4] even further increased the range. Bloembergen and Rowland[5] adapted the concept to nonmetals, and found qualitatively the same oscillatory behavior but a range reduced by "tunneling." On the experimental side, recent investigations on rare earth solutes in palladium by Peter *et al.*[6] have uncovered an interaction between magnetic atoms which is even longer ranged than predicted by any of these theories.

On the other hand, in the case of the Heisenberg spin Hamiltonian,

$$H=-\sum F_{ij}\mathbf{S}_i\cdot\mathbf{S}_j, \tag{1}$$

by far the greatest theoretical effort has been expended in understanding the properties of the nearest-neighbor interaction ($F_{ij}=0$ unless i and j are nearest neighbors). Obviously, in order to tie in with modern theory and experiment, as briefly outlined above, one should also wish to understand the properties of H when both ferromagnetic ($F_{ij}>0$) and antiferromagnetic ($F_{ij}<0$) bonds are present, and when the interaction is not necessarily short ranged.

We shall find, in this event, the interesting possibility for some such interactions that even if we maintain the positions of the spins and the magnitudes and signs of the bonds fixed, but vary only the magnitude of the N interacting spins ($s=\frac{1}{2}$, 1, $\frac{3}{2}$, $\cdots$in units where $\hbar=1$), that the ground state can be nonferromagnetic for small spins even if it be proved to be ferromagnetic for large $s\gg 1$.

This implies that classical or semiclassical methods[7] valid for $s\rightarrow\infty$, although well known and applied in problems of interacting spins, must be cautiously used when spins as small as $s=\frac{1}{2}$ or 1 interact via an oscillatory interaction F_{ij}, and that quantum fluctuations may be of essential importance in the ground state.

But before exploring this possibility, we first review some instances of magnetic interactions when the structure of the ground state is definitely not a sensitive function of s, and semiclassical methods can be expected to work best.

We shall follow this by a necessary condition for ferromagnetism, which will also turn out to be a sufficient condition in the correspondence limit $s\gg 1$. However, we shall then emphasize that this does not ensure ferromagnetism for the ground state of quantum mechanical, finite spins, by displaying a trial state of variationally lower energy than the state of saturation magnetization for a sufficiently fluctuating interaction.

[1] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955).
[2] W. Kohn, Phys. Rev. Letters **2**, 393 (1959).
[3] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).
[4] K. Yosida, Phys. Rev. **106**, 893 (1957).
[5] N. Bloembergen and T. J. Rowland, Phys. Rev. **97**, 1679 (1955).
[6] M. Peter, D. Shaltiel, J. H. Wernick, H. J. Williams, J. B. Mock, and R. C. Sherwood, Phys. Rev. Letters **9**, 50 (1962).

CASE OF NODELESS GROUND STATE

In some special cases it can be proved that some important ground-state property persists for all values of s, and it is then plausible that the ground-state energy and other properties may be developed as a series in powers of s^{-1}. It is, of course, difficult to justify such an expansion, but the motivation is clearly that one wishes to tie into the known properties of the solution in the correspondence limit.[7]

Let us distinguish the possibility (a) of proving antiferromagnetism for all s, and (b) proving ferromagnetism for all s, under the following circumstances:

(a) *Antiferromagnetism*. We shall follow, with only slight changes of notation, a recent paper by Elliott Lieb and the author,[8] to which the reader is referred for a complete proof. For present purposes, a simplified theorem may be proved as follows.

Consider those arrays for which an A and a B sublattice can be defined, such that if A spins interact with other A spins, they do so ferromagnetically and similarly for interactions among B spins,

$$F_{A,A'}\geq 0, \quad F_{B,B'}\geq 0, \quad F_{A,B}\leq 0; \qquad (2)$$

but B spins and A spins are coupled antiferromagnetically if they are coupled at all. There is no restriction made as to the range of the interaction.

We may define a "natural representation" as follows. Let the ferromagnetic state of all spins "down" be denoted the "vacuum state,"

$$\phi(0,\cdots 0,\cdots)\equiv|0\rangle \qquad (3)$$

and all other states are of the form

$$\phi(n_1\cdots n_j\cdots)\equiv\prod_{j=i}^{M}(S_j^{\dagger})^{n_j}|0\rangle \qquad (4)$$

for given positive integers n_j. The jth spin raising operator is, as usual,

$$S_j^{\dagger}\equiv S_j^x+iS_j^y. \qquad (5)$$

The Hamiltonian is not yet in a convenient form, so we make the transformation on the A spins,

$$S_i^x\to -S_i^x, \quad S_i^y\to -S_i^y, \quad S_i^Z\to +S_i^Z, \qquad (6)$$

(which corresponds to a classical rotation of A spins about the Z axis) but leave the B spins invariant. In this representation, we have

$$H=-\{\tfrac{1}{2}\sum|F_{ij}|S_i^{\dagger}S_j^{-}+\text{H.c.}\}-\sum F_{ij}S_i^ZS_j^Z, \qquad (7)$$

making use of (2). The off-diagonal matrix elements are all negative, and it can be proved that the ground state of H is nodeless in this representation, i.e., if the ground state ψ is expanded in our complete set (4),

$$\psi=\sum f(n_1,n_2,\cdots,n_j,\cdots)\phi(n_1,n_2,\cdots,n_j,\cdots), \qquad (8)$$

all the amplitudes f are of the same sign. Even though the states change with s, this property does not, and is as valid for $s=\frac{1}{2}$ as in the correspondence limit. For N even (but for all s), ψ is always a singlet, and moreover, it can be proved that the energy of the lowest state of spin $S-1$ is lower than the energy of the lowest state of spin S up until the maximum $S=Ns$.

It seems plausible that semiclassical methods for the ground state and thermal properties will be successful in this instance, given the independence of these important properties on s. However, we have no explicit proof of this.

In the following example, the ground-state correlations are exactly, and trivially the same both classically and quantum mechanically.

(b) *Ferromagnetism*. The case we consider is,

$$\text{all } F_{ij}\geq 0, \qquad (9)$$

in which case it is easy enough to verify that the ground state is nodeless in the "natural" representation, and is, therefore, either the ferromagnetic state of all spins "down,"

$$|0\rangle, \qquad (3)$$

or any of its rotations,

$$(\textstyle\sum_j S_j^{\dagger})^n|0\rangle. \qquad (10)$$

The ground-state energy is equal to the classical ferromagnetic energy

$$E_{Ns}=-\sum_{\{i,j\}}F_{ij}s^2 \qquad (11)$$

and all spins are parallel in the ground state, quantum mechanically or classically.

In the special but very important case of this, i.e., *nearest-neighbor ferromagnetic coupling*, an investigation by Dyson[9] of the thermal properties of this ferromagnet revealed that the quantum-mechanical effects of spins as small as $s=\frac{1}{2}$ were unimportant at very low temperatures just as in the ground state, and that the semiclassical picture of noninteracting spin waves was accurate in this range. It can also be assumed that so long as all $F_{ij}\geq 0$, the greater the range of the interaction the better is the accuracy of some semiclassical procedures.

But let us recall, in view of some of the remarks in the introduction, that ferromagnets are not likely to satisfy the condition for case (b) in general, and, therefore, let us seek a less stringent condition for ferromagnetism in cases when the interaction can be oscillatory.

[7] For example, the formal expansion of operators in powers of s^{-1}, of T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940). For present purposes any approximation which is accurate in the limit $s\to\infty$ will be considered semiclassical, without prejudice, although some methods may be far more accurate than others for finite s.

[8] E. Lieb and D. Mattis, J. Math. Phys. **3**, 749 (1962).

[9] F. J. Dyson, Phys. Rev. **102**, 1230 (1956).

NECESSARY CONDITION FOR FERROMAGNETISM

For the sake of definiteness, we shall, henceforth, assume that the spins form a Bravais lattice, and that

$$F_{ij}=F(\mathbf{R}_i-\mathbf{R}_j), \tag{12}$$

which establishes translational invariance. This also insures that (regardless of the signs and magnitudes of F) we know an entire set of eigenstates consisting of one spin wave,

$$|k\rangle\equiv\sum_j e^{i\mathbf{k}\cdot\mathbf{R}_j}S_j^\dagger|0\rangle, \tag{13}$$

(unnormalized). The energy of these states, relative to the ferromagnetic energy, is readily calculated to be

$$\epsilon(\mathbf{k})=s[f(\mathbf{k})-f(0)], \tag{14}$$

where

$$f(\mathbf{k})=-\sum_{j\neq 0} e^{i\mathbf{k}\cdot\mathbf{R}_j}F(\mathbf{R}_j). \tag{15}$$

The case of dilute random magnetic alloys[10] will not be considered in this work.

Evidently, a necessary condition that the ground state be the ferromagnetic state (3) or (10) is

$$\epsilon(\mathbf{k})>0, \quad \mathbf{k}\neq 0, \tag{16}$$

and it is easy enough to verify that the positive semidefinite interaction of case (b) always satisfies (16). We shall call any system which obeys (16), "spin-wave stable."

IS THIS CONDITION SUFFICIENT?

Remarkably, (16) is both the necessary and the sufficient condition for saturation ferromagnetism of classical spins ($s\gg 1$). According to the method of Luttinger and Tisza,[11] the configuration of lowest energy [subject to Eq. (12) and *supra*] can be chosen classically as

$$S_i^Z=0, \quad S_i^x=s\cos\mathbf{k}\cdot\mathbf{R}_i, \quad S_i^y=s\sin\mathbf{k}\cdot\mathbf{R}_i, \tag{17}$$

and it is a simple matter to substitute in (1), and find the energy proportional to $f(\mathbf{k})$. Thus, an interaction which is spin-wave stable is ferromagnetic in the correspondence limit.

However, because spin-wave stability is not a sufficient condition quantum mechanically, we shall find it possible to prove that the ground state is not ferromagnetic in some instances of small s even when (16) is obeyed.

The basic reason is that the antiferromagnetic bond

$$+\mathbf{S}_i\cdot\mathbf{S}_j \tag{18}$$

benefits from a ground-state energy of

$$-s(s+1), \tag{19}$$

whereas the ferromagnetic bond

$$-\mathbf{S}_i\cdot\mathbf{S}_j \tag{20}$$

has precisely the classical energy

$$-s^2 \tag{21}$$

as we have already mentioned. Crudely, the effect is of order

$$s(s+1)/s^2=1+1/s \tag{22}$$

which is most significant for $s=\frac{1}{2}$ or 1.

TWO EXAMPLES OF THE EFFECT

I. *Classically* and in the *simple cubic lattice*, the Ruderman-Kittel interaction,

$$-F(R)\approx\left[\frac{(2k_FR\cos 2k_FR-\sin 2k_FR)}{R^4}\right], \tag{23}$$

leads to ferromagnetism over the range, $2k_F$ greater than zero but less than half a reciprocal lattice vector.[12] At the upper end of this range F is strongly oscillatory and the ferromagnetic state, even classically, is only slightly more stable than some antiferromagnetic configurations. There is reason, therefore, to believe that some quantum-mechanical effects may be important. Unfortunately, (23) must be analyzed numerically,[12] therefore we shall investigate a reasonable imitation of this interaction in one dimension, for which lattice sums can be trivially performed. Let this be

$$F(R)=e^{\lambda}(-1)^{n-1}e^{-\lambda|n|}, \quad \text{where } R=na \text{ and } \lambda\geq 0. \tag{24}$$

Only the nearest-neighbor ferromagnetic bonds survive in the limit $\lambda\to\infty$, and in this limit, therefore, the interaction is of class (b) with a ferromagnetic ground state, regardless of spin magnitudes. But the situation is different for finite λ.

First, we must calculate the negative Fourier sum as n Eq. (15),

$$f(k)=-\sum_{n\neq 0} e^{ikn}F(R)=-\frac{1+e^{\lambda}\cos k}{\cosh\lambda+\cos k}, \tag{25}$$

and it follows that the spin-wave energy

$$\epsilon(k)=s[f(k)-f(0)]=s\frac{(e^{\lambda}\sinh\lambda)(1-\cos k)}{(1+\cosh\lambda)(\cosh\lambda+\cos k)} \tag{26}$$

is positive for all allowed (positive) values of λ, and this interaction is always spin wave stable.

The energy of the ferromagnetic state is

$$E_{Ns}=\tfrac{1}{2}Nf(0)s^2=-Ns^2/(1+e^{-\lambda}). \tag{27}$$

It shall be compared to the variational energy of a trial singlet ($S=0$) state. When the singlet energy E_0 lies lower,

$$E_0<E_{Ns}, \tag{28}$$

[10] An Ising theory for this situation was given by W. Marshall, Phys. Rev. **118**, 1519 (1960). It is not known whether the properties of a Heisenberg Hamiltonian for random spins and long-range oscillatory interaction have been investigated.

[11] The method devised by J. M. Luttinger and L. Tisza, Phys. Rev. **70**, 954 (1946), has recently been discussed by A. Yoshimori, J. Phys. Soc. (Japan) **14**, 807 (1959); M. J. Freiser, Phys. Rev. **123**, 2003 (1961); and D. Lyons and T. Kaplan, *ibid.* **120**, 1580 (1960).

[12] D. Mattis and W. Donath, Phys. Rev. **128**, 1618 (1962).

this will be sufficient indication of the instability of the state of saturation ferromagnetism in the absence of external fields. (But the ferromagnetic state might be even less stable than we find variationally, particularly in one dimension.)

The trial function is constructed as follows. We pair off spins at

$$R=4na, \quad R'=(4n+2)a$$

and (29)

$$R=(4n+1)a, \quad R'=(4n+3)a$$

and letting

$$\theta_0(R,R') \tag{30}$$

be the singlet pair wave function, we take the uncorrelated product over all such pairs,

$$\psi_0 \equiv \prod \theta_0(R,R'). \tag{31}$$

The pairs have been chosen to take advantage of the largest existing antiferromagnetic bond, to the neglect of all others. The energy is readily calculated, noting that

$$\begin{aligned} \langle\psi_0|\mathbf{S}_i\cdot\mathbf{S}_j|\psi_0\rangle &= -s(s+1) \quad \text{if } R_i, R_j \text{ are paired,} \\ &= \quad 0 \qquad\quad \text{otherwise,} \end{aligned} \tag{32}$$

so that the variational energy is

$$E_0=\langle\psi_0|H|\psi_0\rangle/\langle\psi_0|\psi_0\rangle=-\tfrac{1}{2}Ne^{-\lambda}s(s+1). \tag{33}$$

For sufficiently small λ and s we find instability of the type (28), i.e., when

$$s\leqslant\frac{1+e^{\lambda}}{2e^{2\lambda}-(1+e^{\lambda})}. \tag{34}$$

We have not found a simple three-dimensional extension of this example of a spin-wave stable system which can be unstable against such a highly uncorrelated and crude product of pair functions. This suggests that "spin-wave stability" is a better criterion for the occurrence of ferromagnetism in three dimensions than in one, but it is not foolproof as we shall now see.

II. The second example is a model[13] of a direct antiferromagnetic interaction superposed on a long-ranged indirect ferromagnetic interaction. [An instance of the latter is (23) in the limit $k_F\rightarrow 0$, in which case bonds between spins less than $\pi/4k_F$ apart are ferromagnetic, with a negligible antiferromagnetic "tail" beyond.] We can simulate this effect quite well by the model,

$$F(R)=F_a(R)+F_f(R), \tag{35}$$

where we define the interactions in the simple cubic structure,

$$\begin{aligned} F_a(\mathbf{R}) &= -A \quad \text{for } R=(\pm a,0,0) \text{ or } (0,\pm a,0) \\ &\qquad\qquad\qquad\qquad \text{or } (0,0,\pm a), \\ &= 0 \qquad \text{otherwise.} \end{aligned} \tag{36}$$

[13] This magnetic model was suggested to the author by R. K. Nesbet. Also, cf., R. K. Nesbet, Phys. Rev. **122**, 1497 (1961), where the antiferromagnetic "direct" interaction is discussed.

The value of the constant A will be discussed shortly. The ferromagnetic part decays exponentially with distance, but in a separable way:

$$F_f(\mathbf{R})=V(n_1)V(n_2)V(n_3), \tag{37}$$

where

$$V(n)=e^{-|n|\lambda}, \tag{38}$$

and the distance vector is the triad,

$$\mathbf{R}=a(n_1,n_2,n_3).$$

The negative Fourier sum of this interaction is readily calculable,

$$f(\mathbf{k})=2A[\cos k_1+\cos k_2+\cos k_3] \\ +[1-G(k_1)G(k_2)G(k_3)], \tag{39}$$

where

$$G(k_j)=\sinh\lambda/(\cosh\lambda-\cos k_j), \tag{40}$$

and from this it can be deduced that the interaction is spin-wave stable for A in the range,

$$0<A<A_0\equiv(4+3\sinh^2\lambda)/6\sinh^3\lambda. \tag{41}$$

When A excels the value A_0 defined just above, then $f(\mathbf{k})$ has its minimum value at $\mathbf{k}=\mathbf{Q}$, where $\mathbf{Q}$ is the reciprocal lattice vector

$$\mathbf{Q}=\frac{1}{a}(\pi,\pi,\pi), \quad f(\mathbf{Q})=-6A+1-\left(\frac{\sinh\lambda}{\cosh\lambda+1}\right)^3. \tag{42}$$

The classical ground state is the Néel state in that case, which consists of each "up" spin being surrounded by "down" nearest-neighbor spins. Let us discuss this antiferromagnetism in somewhat more detail.

Anderson[14] has given a method for calculating the lowest order quantum-mechanical corrections to the Néel state energy, and Oguchi[15] has shown that this procedure is satisfactory and that further corrections are probably negligible. If one applies the Anderson procedure for an arbitrary interaction, he finds for the energy

$$E_0=+\tfrac{1}{2}Nf(\mathbf{Q})s^2-\tfrac{1}{2}\Delta s, \tag{43}$$

where

$$\Delta=\textstyle\sum_{\text{B.Z.}}\omega_k-(\omega_k^2-\tau_k^2)^{1/2}, \tag{44}$$

and

$$\omega_k=\tfrac{1}{2}[f(\mathbf{k})+f(\mathbf{k}+\mathbf{Q})]-f(\mathbf{Q}), \tag{45}$$

$$\tau_k=\tfrac{1}{2}[f(\mathbf{k}+\mathbf{Q})-f(\mathbf{k})]. \tag{46}$$

The quantities have been so defined that the sum (44) is over all N states in the first Brillouin zone. Now, this can be further simplified by using the definition of $f(\mathbf{k})$, Eq. (15), to prove that

$$\textstyle\sum_{\text{B.Z.}} f(\mathbf{k})=\sum_{\text{B.Z.}} f(\mathbf{k}+\mathbf{Q})=0. \tag{47}$$

Therefore,

$$\Delta=-Nf(\mathbf{Q})-N\Phi, \tag{48}$$

[14] P. W. Anderson, Phys. Rev. **86**, 694 (1952).
[15] T. Oguchi, Phys. Rev. **117**, 117 (1960).

where (converting sums to integrals in the usual way)

$$\Phi\equiv\left(\frac{1}{2\pi}\right)^3\int_{-\pi}^{\pi}dk_1dk_2dk_3 \times\{[f(\mathbf{Q})-f(\mathbf{k})][f(\mathbf{Q})-f(\mathbf{k}+\mathbf{Q})]\}^{1/2}. \quad (49)$$

These formulas (43)–(49) are valid for arbitrary interaction in a simple cubic antiferromagnet. Returning now to the model defined above, which is classically an antiferromagnet for $A>A_0$, we recall that in this range of the parameter A, $f(\mathbf{Q})$ is the minimum value of $f(\mathbf{k})$ and; therefore, the integral Φ is real and Δ is positive. Let us now set down the ferromagnetic energy, which is

$$E_{Ns}=\tfrac{1}{2}Nf(\mathbf{0})s^2=-\tfrac{1}{2}N\left[-6A+\frac{3e^{\frac{1}{2}\lambda}+e^{-\frac{1}{2}\lambda}}{4\sinh^3\frac{1}{2}\lambda}\right]s^2. \quad (50)$$

When $A=A_0$, it occurs that $f(\mathbf{0})=f(\mathbf{Q})$, and the classical ferromagnetic and antiferromagnetic (Néel) states become degenerate. The quantum corrections, however, always favor the antiferromagnetic state, so that

$$E_0-E_{Ns}=-\tfrac{1}{2}\Delta s<0 \quad \text{when} \quad A=A_0, \text{ for all } s. \quad (51)$$

As A is lowered still further, an interesting phenomenon occurs in the neighborhood $A\lesssim A_0$. In addition to its minimum at $k=0$, the function $f(\mathbf{k})$ retains a local minimum at $k=Q$; and one notices that the integrand of Eq. (49) for Φ becomes imaginary near the origin and near $\mathbf{Q}$. Thus, the energy of the Anderson-Néel state becomes complex and the antiferromagnetic state is unstable. Note that the breakdown for small $\mathbf{k}$ indicates a radical change in long-range order, and at $\mathbf{k}\approx\mathbf{Q}$ in short-range order.

Nor does the ferromagnetic state succeed as the ground-state configuration until A is somewhat less than the critical value A_0, so there exists a range of A depending on s, over which both ferromagnetic and antiferromagnetic states are unstable.

Let us analyze this for spin $s=\frac{1}{2}$. We use a simple trial function

$$\psi=\prod_{\substack{\mathbf{R}=\text{such that}\\ n_1+n_2+n_3=\text{even}}}(\alpha S_{\mathbf{R}}^\dagger-\beta S^\dagger_{\mathbf{R}+a(1,0,0)})|0\rangle, \quad (52)$$

where $\alpha^2+\beta^2=1$. This reduces to the Néel state when $\alpha=1, \beta=0$ or $\alpha=0, \beta=1$.

We shall show that this function leads to an energy lower than $E_{\frac{1}{2}N}$ over some of the spin-wave stable region, $A<A_0$. The variational energy [after eliminating $\alpha=(1-\beta^2)^{1/2}$] is

$$E_0(\beta)=\tfrac{1}{2}Nf(\mathbf{Q})(\tfrac{1}{4})(1-2\beta^2)^2-\tfrac{1}{2}N[A-e^{-\lambda}](\tfrac{1}{4}) \times\{1-(1-2\beta^2)^2+4[\beta^2(1-\beta^2)]^{1/2}\}, \quad (53)$$

where it must not be forgotten that $f(\mathbf{Q})$ depends on A by Eq. (42). This energy is minimized by the choice

$$\beta^2=\frac{1}{2}\left\{1-\left[1-\left(1+\frac{f(Q)}{A-e^{-\lambda}}\right)^{-2}\right]^{1/2}\right\}. \quad (54)$$

It may be verified that β, as defined in this manner, is appropriately real provided $A_0>A>e^{-\lambda}$, which includes the requirement for antiferromagnetic bonds to exist in this model. With the value of β, the variational energy is

$$E_0=\tfrac{1}{8}Nf(\mathbf{Q})-\tfrac{1}{8}N\frac{(A-e^{-\lambda})^2}{-f(\mathbf{Q})-A+e^{-\lambda}} \quad (55)$$

and is to be compared to the ferromagnetic energy

$$E_{\frac{1}{2}N}=\tfrac{1}{8}Nf(0)=\tfrac{1}{8}Nf(\mathbf{Q})-\tfrac{3}{2}N(A_0-A). \quad (56)$$

The latter is not the ground state until A is less than is required to satisfy the equality

$$\tfrac{3}{2}(A_0-A)=\frac{1}{8}\frac{(A-e^{-\lambda})^2}{-f(\mathbf{Q})-A+e^{-\lambda}}. \quad (57)$$

(Note that $f(\mathbf{Q})$ is negative in this range.) However, one should be cautioned against attaching any importance to this precise value, considering the crude nature of the trial function.

MOTIVATION AND CONCLUSION

Recently, Donath and the author investigated the nature of the ground state of classical spins disposed on a single cubic lattice and interacting via the Ruderman-Kittel interaction[3] (23), by evaluating $\epsilon(\mathbf{k})$ numerically on an IBM 7090 computer. It was found that over a relatively important range of values of the parameter $2k_F$ the ferromagnetic state lay lowest. But the fact that some antiferromagnetic bonds were clearly not negligible led the author to wonder whether, in the physically important case of small spins, new and interesting quantum-mechanical ground-state correlations might not be present. However, it was possible to show in special cases (a) and (b) that the antiferromagnetic or ferromagnetic behavior was insensitive to the magnitude s of the interacting spins. In such cases, the classical or semiclassical analyses would be sufficient for many purposes. But, in general, new quantum-mechanical correlations could be expected to exist and to manifest themselves in such important properties as the long-range order.

We have not found what these correlations might be, but in this work we have shown that the classical criterion for ferromagnetism, which we have called "spin-wave stability" is, in any event, not sufficient to insure ferromagnetism of quantum-mechanical spins. This is because of what might be termed, quantum fluctuations associated with the antiferromagnetic bonds. (The converse—a classical antiferromagnetic interaction which leads to ferromagnetism for small spins—is clearly impossible.) It appears that just as long-range ferromagnetic interactions are good for classical methods, long-range oscillatory interactions lead to these fluctuations and are bad for classical or semiclassical methods applied for small spins.

We have examined the Anderson spin-wave theory of antiferromagnetism[14,15] which is patently correct in case (a) (although it is not mathematically exact). However, in spin-wave stable systems the approximate antiferromagnetic eigenstate has in general a complex energy and is, therefore, unstable, even in such a favorable model as we have considered, where nearest neighbor bonds are antiferromagnetic, and the lattice is three-dimensional simple cubic.

This suggests that in those spin-wave stable systems which are not actually ferromagnetic because small spins ($\frac{1}{2}$ or 1) and antiferromagnetic bonds favor quantum fluctuations, the long-range ground-state correlations might either vanish, or exhibit a more complicated structure than has heretofore been thought likely on theoretical grounds without introducing anisotropy.

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Carrier Mobility and Shallow Impurity States in ZnSe and ZnTe†

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Electrical transport measurements have been made on p-type ZnTe and n-type ZnSe. In ZnTe crystals, doping with Cu, Ag, and Au produces acceptor levels at 0.15, 0.11, and 0.22 eV, respectively. An acceptor with an ionization energy of 0.048 eV was found in the undoped crystals and is identified as the first charge state of the Zn vacancy. A shallow donor state, at approximately 0.01 eV below the conduction band, was found in n-type ZnSe. It also proved possible to prepare degenerate ZnSe. The scattering mechanisms limiting the lattice mobilities of both materials were considered. It was found that the polar interaction with the longitudinal optical phonons dominates the scattering of electrons in ZnSe. This mechanism probably also predominates in the scattering of the holes in ZnTe. However, the nonpolar interaction with the optical modes could also contribute significantly if the appropriate coupling parameter is larger than we presently believe.

I. INTRODUCTION

SEVERAL of the II–VI compounds have been under investigation by luminescence and photoconductive techniques for a great many years. Much of this work was directed toward the goal of understanding the role of the impurities and of identifying the states associated with them. Despite this work, however, the identification of the specific impurity states is still a matter of considerable debate and uncertainty. At present there is still little conclusive evidence about the identity of any shallow impurity states, which, for example, play an important role in the optical properties of these crystals.

The primary aim of the present work was to obtain additional information about the shallow donor and acceptor levels in some of the II–VI compounds by means of electrical transport studies. In the past, extensive electrical measurements have not generally been possible due to the unavailability of suitable material. However, considerable advances have recently been made in the preparation of some of these materials, including the compounds that are the subject of the present study, ZnSe and ZnTe.[1–3] It is, of course, well known that in addition to yielding information about the energy levels of the defects, the electrical transport measurements provide a valuable means for studying the mechanism by which the carriers are scattered. This question was considered in some detail for the two compounds studied.

In an earlier work, the results of optical and preliminary electrical measurements on ZnSe were reported.[4,5] The electrical measurements of the n-type

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