Heisenberg magnetic substances with competing interactions

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(Submitted 27 February 1984; resubmitted 10 May 1984)
Zh. Eksp. Teor. Fiz. **87**, 960–970 (September 1984)

The properties of Heisenberg magnetic substances with nearest- and next-nearest-neighbor interactions competing with each other in the determination of the type of magnetic order are investigated. For magnetic substances with classical spins the Curie temperature T_C is equal to zero at the ferromagnetic-antiferromagnetic phase boundary, and its pressure derivative diverges at the ferromagnetic-helicoidal phase boundary. The optical-absorption edge depends nonmonotonically on the temperature in the vicinity of a phase boundary. In a magnetic substance with quantum spins there should occur a temperature phase transition of the order-order or order-improper disorder type in the vicinity of a phase boundary. Such a magnetic substance should also possess specific metamagnetic properties.

1. INTRODUCTION

In this paper we investigate the properties of Heisenberg magnetic substances with competing nearest- and next-nearest-neighbor exchange interactions. Each of these interactions strives to establish its own type of magnetic order, and, as a result of the competition between them, the order with the lowest energy gets established. A change in the relation between the competing interactions leads to a change in the type of magnetic order that obtains at $T = 0$. Such magnetic substances can naturally be expected to possess nontypical properties in the vicinity of a phase boundary. A similar problem has already been solved for the Ising magnetic substances in the ANNNI model, and it has been shown that there occur a cascade of order-order phase transitions as the temperature rises.[1–3] There is no reason to suppose that a similar phenomenon occurs in the Heisenberg magnetic substances: it is peculiar to single-component spins.

Below we shall prove the following properties of Heisenberg magnetic substances:

1) the vanishing of the Curie temperature T_C at a phase boundary in a magnetic substance with classical spins if the change in the type of order occurs abruptly at this boundary (e.g., when an antiferromagnetic state goes over discontinuously into a ferromagnetic state upon the variation of the exchange parameters);

2) the infinite pressure derivative of the T_C at a phase boundary in a magnetic substance with classical spins if the change in the type of order occurs gradually (e.g., when a ferromagnetic order goes over into a helicoidal order);

3) the discontinuous nature of the temperature phase transitions induced in magnetic substances with small spins in the vicinity of a phase boundary by the quantum fluctuations of these spins;

4) the metamagnetic properties of the isotropic Heisenberg magnetic substances with quantum spins;

5) the nonmonotonic temperature dependence of the optical-absorption edge for magnetic semiconductors and insulators in the vicinity of a phase boundary.

The results obtained in this paper disagree with the hitherto prevalent opinion that the T_C of magnetic substances with classical spins not only remains finite at a phase boundary, but does not change its value at all in an abrupt change of the type of order.[4] From the physical standpoint such a situation seems improbable, whereas the absence of long-range order at finite temperatures at a phase boundary seems entirely natural. As to the singularities of T_C as a function of pressure in the vicinity of the ferromagnetic-helicoidal phase boundary, this question has, as far as the present author knows, not been investigated at all before.

Further, the above results include new mechanisms of first-order phase transitions and the appearance of metamagnetic properties, underlying which are the quantum fluctuations of the spins. Thus far, the discontinuous nature of magnetic phase transitions has been attributed to either critical fluctuations,[5,6] or a non-Heisenberg exchange, to which the magnetostriction effects amount.[7] As to such a nonstandard phenomenon as the metamagnetism of isotropic antiferromagnets, it was previously related only to either a non-Heisenberg exchange,[7] or the Jahn-Teller character of the magnetic atoms.[8] Finally, the results according to which the temperature dependence of the optical absorption edge in a Heisenberg magnetic substance can be nonmonotonic are new. They allow us to explain the anomalous magneto-optical properties of a number of magnetic semiconductors.

2. THE SPHERICAL MODEL AS THE ZEROTH APPROXIMATION FOR THE HEISENBERG MODEL

We cannot, when investigating the properties of magnetic substances in the vicinity of a phase boundary, use the standard methods of finding the T_C and the correlation functions. The self-consistent-field approximation leads here not only to quantitatively but also to the qualitatively erroneous results described in Ref. 4. And it is extremely difficult to use the high-temperature expansions when there are two exchange parameters of arbitrary signs. Moreover, with the aid of the high-temperature expansions we cannot obtain the correlators in the entire Brillouin zone, which are necessary for the computation of the position of the optical-absorption edge.

As the basic model for the solution of the problem in question we can use the spherical model,[9] since Stanley[10] has demonstrated its equivalence to the generalized Heisenberg

0038-5646/84/090547-07$04.00

model, in which the spins have an infinitely large number n of components. Stanley[10] has also remarked that the spherical model should reproduce the properties of the ordinary Heisenberg model with $n = 3$ much better than the XY model with $n = 2$ or the Ising model with $n = 1$. A procedure has now been developed for finding the critical exponents through a power series expansion of them in $1/n$ (Ref. 11). But a similar procedure for finding the T_C and the correlators has not yet been developed. And what is more, as far as the present author knows, not even estimates have been made of how accurate the spherical-model results for the Heisenberg model in the zeroth approximation in $1/n$ are. Meanwhile, as will be shown below, this accuracy turns out to be surprisingly high, especially for the T_C. The results obtained below compel us to assume that the true expansion parameter for the computation of the T_C and the correlators in the paramagnetic region is $1/n$ raised to a power higher than one.

The Hamiltonian of the system under consideration has the usual form:

$$H=-\frac{1}{2}\sum \mathcal{J}_{\mathbf{q}}\mathbf{S}_{\mathbf{q}}\mathbf{S}_{-\mathbf{q}}, \qquad \mathbf{S}_{\mathbf{q}}=\frac{1}{\sqrt{N}}\sum \mathbf{S}_{\mathbf{g}}e^{i\mathbf{q}\mathbf{g}}, \tag{1}$$

where $\mathbf{S}_{\mathbf{g}}$ is the spin of the atom $\mathbf{g}$. For the binary correlators the following sum rule should be obeyed:

$$\frac{1}{N}\sum \langle \mathbf{S}_{\mathbf{q}}\mathbf{S}_{-\mathbf{q}}\rangle = S(S+1), \tag{2}$$

where S is the magnitude of the spin. This sum rule is obtained through the thermodynamic averaging with the Hamiltonian H of the equality

$$\mathbf{S}_{\mathbf{g}}^{2}=S(S+1). \tag{3}$$

We shall assume that the spins are classical. In the spirit of the spherical model, the exact relation (2) is replaced in the zeroth approximation by

$$\frac{1}{N}\sum \mathbf{S}_{\mathbf{q}}\mathbf{S}_{-\mathbf{q}}=S^{2}. \tag{4}$$

Such a replacement is equivalent to the assumption that both the spin of any atom and all its three components can assume entirely arbitrary values consistent with (4), i.e., that the equality (3) is satisfied only in the mean. It is natural to expect that, everywhere, except in the immediate neighborhood of T_C, the spin-magnitude fluctuations introduced into (4) have little effect on the properties of the magnetic substance, i.e., that in actual fact (4) is equivalent to (2) outside this neighborhood.

An elementary generalization of Berlin and Kac's calculations[9] to the case of a three-component spin yields for the T_C of a structure with wave vector Q the expression

$$T_C=\frac{S^{2}}{3}\left\{\frac{1}{N}\sum_{\mathbf{q}}\frac{1}{\mathcal{J}_{Q}-\mathcal{J}_{\mathbf{q}}}\right\}^{-1}, \tag{5}$$

and for the correlator in the paramagnetic region the expression

$$\langle \mathbf{S}_{\mathbf{q}}\mathbf{S}_{-\mathbf{q}}\rangle = 3T/(\Lambda^{2}+\mathcal{J}_{Q}-\mathcal{J}_{\mathbf{q}}), \tag{6}$$

where the parameter Λ should be determined from (2). It is worth noting that the expression (5) can also be derived by entirely different methods without the use of the idea of spin-magnitude fluctuations. Specifically, the quantum analog of (5) has been obtained with the aid of the Bogolyubov-Tyablikov decoupling procedure in the equal-time Green-functions method,[12] as well as through the introduction into the self-consistent field equations of a chemical-potential analog determined from (2).[13] From this it is clear that the spin fluctuations artificially introduced through (4) have little effect on the T_C value obtained.

Let us now find out how accurate the results (5) and (6) are for Heisenberg magnetic substances. First of all it is easy to verify that, at high temperatures, the formulas (2) and (6) are in accord with the thermodynamic perturbation theory results for the Heisenberg magnetic substances, i.e., in this limit the fluctuations of the magnitudes of the spins are indeed totally unimportant. Further, from (5) we immediately obtain the correct result for the one- and two-dimensional Heisenberg magnetic substances: the absence in them of long-range order at finite temperatures.

A more detailed analysis shows that, in the low-dimensional cases, the formulas (2) and (6) duplicate well the true behavior of the correlation functions not only at high, but also at low, temperatures. As is well known, the solution of the problem of the one-dimensional chain of classical spins is elementary. A comparison of the formulas (2) and (6) with this exact solution shows that they lead to the correct dependence of the binary correlators $\langle \mathbf{S}_0\mathbf{S}_{\mathbf{g}}\rangle$ on the distance g and to the correct temperature dependence of the correlation length. The latter differs from the true function by only a factor of 2/3 for $T\to 0$, and coincides with it in the case when $T\to\infty$.

In the two-dimensional case we also obtain from (2) and (6) results that are in good agreement with the known results. These formulas correctly reproduce the asymptotic exponential law of decrease of the binary correlator with increasing $|\mathbf{g}|$ at all temperatures. At low temperatures the correlation length increases exponentially with $1/T$ as $T\to 0$, in accord with Ref. 14. At smaller distances, the correlations decrease with increasing $|\mathbf{g}|$ according to the Berezinskiĭ law $|\mathbf{g}|^{-\varkappa T}$, with $\varkappa$ differing from Berezinskiĭ's value[15] by only a factor of 2/3. At high temperatures, as has already been indicated, these formulas fully reproduce the thermodynamic perturbation theory results.

It can clearly be seen in the particular case of two-dimensional systems that the use of the spherical model as the zeroth approximation in $1/n$ is justified for the Heisenberg model, but does not work for the XY model and, especially, the Ising model. For the XY model, even though such an approximation correctly predicts the absence of long-range order at $T\neq 0$, it does not reproduce the Berezinskiĭ phase transition from a power to an exponential law of decrease of the correlations with distance. And in the case of the Ising model, in general, it incorrectly predicts the absence of long-range order at finite temperatures.

Let us now proceed to the three-dimensional case. In the limit of infinite sign-constant-interaction range the result (5) goes over into the self-consistent field theory result, which is exact in this limit. As the exchange-interaction range decreases, the degree of accuracy of (5) decreases, but only slightly, remaining very high. It has its lowest value in the nearest-neighbor approximation, in which we find that, for the simple cubic lattice, $T_C = 0.22556 \mathscr{I}_0 S^2$ (ferromagnetic order). But this result differs by only 5% from the most accurate result

$$T_C = 0{,}021666[11S(S+1)-1]\mathscr{I}_0, \qquad (7)$$

obtained in Ref. 16 through the use of high-temperature expansions accurate to within 1%. Thus, even in this limit the accuracy of (5) is comparable to the highest accuracy that has thus far been obtained. We should, for the purpose of comparison, point out that, in this limit, the self-consistent-field approximation (SFA) leads to an error higher than 50%. Below we shall show that the formula (5) guarantees a high degree of accuracy in the case of sign-variable exchange interactions as well. Thus, in contrast to the high-temperature expansions, which yield a high degree of accuracy only in the nearest-neighbor approximation, the formula (5) gives such an accuracy in the case of an arbitrary dependence of the exchange integral on distance.

As to the correlators, it is clear that the results (2) and (6) can be valid for a Heisenberg magnetic substance only at temperatures that are further away from the true Curie point T_C^{ex} than the T_C given by (5). The critical exponents obtained from (2) and (6) for $T \to T_C$ can differ greatly from the exponents for the Heisenberg model. For the purpose of verifying that the formulas (2) and (6) are indeed valid for a Heisenberg magnetic substance, starting from $T - T_C \gtrsim |T_C - T_C^{\text{ex}}|$, we find it expedient to carry out in the nearest-neighbor approximation a numerical computation for the temperature-dependent exponent $\nu(\tau)$ defined in terms of the reciprocal correlation length $\Lambda(\tau)$ by the relation

$$\Lambda(\tau) = C\tau^{\nu(\tau)}, \qquad \tau = T/T_C - 1.$$

It is, in accord with the indicated accuracy of the expression (5), to be expected that in this case the formulas (2) and (6) will reproduce well the properties of the Heisenberg magnetic substances if $\tau \gtrsim 0.05$–0.1. The calculation confirms this: as τ is varied from 0 to 0.1, the exponent $\nu(\tau)$ decreases rapidly from 1 to 0.7. As τ is increased further, this exponent varies very slowly, remaining close to the critical exponent for a Heisenberg magnetic substance. (It should be recalled that, for a Heisenberg magnetic substance with nearest-neighbor interactions, the fluctuation region extends to $\tau \gtrsim 5$. Inside this region $\nu(\tau)$ varies from 0.7 to 0.5.)

3. MAGNETIC SUBSTANCES WITH CLASSICAL SPINS

In this section the general results presented above will be applied to the Heisenberg magnetic substances in which the exchange interactions among the unequally spaced neighbors compete with each other in the determination of the type of magnetic order. For definiteness, we shall consider a simple cubic lattice of magnetic atoms with nearest- and next-nearest-neighbor exchange interactions (the corresponding exchange integrals are denoted by I_1 and I_2). The standard procedure for finding the stable magnetic configurations consists in the replacement of the spin operators by the corresponding classical vectors in the system's Hamiltonian. At $T = 0$ the stable structure should be that structure for which the Fourier transform

$$\mathscr{I}_{\mathbf{q}} = I_1 \sum_{\alpha} \cos q_\alpha + I_2 \sum_{\alpha \neq \beta} \cos q_\alpha \cos q_\beta \qquad (8)$$

of the exchange integral has its maximum value.

Let us first consider the case in which $I_1 > 0$ and $I_2 < 0$. For small values of the ratio $r = |I_2|/I_1$ the ferromagnetic (FM) order is stable in such a system. But for $r > r_b = 0.25$ the antiferromagnetic (AFM) ordering of the layered type, with the FM layers alternating along the cube axis (the structure vector $\mathbf{Q}_L = (\pi, 0, 0)$), is energetically more advantageous. Since the exchange integrals $\mathscr{I}_0$ and $\mathscr{I}_{\mathbf{Q}_L}$ are equal to each other when $r = r_b$, and they differ from the T_C in the SFA by only a constant factor, an abrupt change in the type of order—from a state with FM order into a state with AFM order—is not accompanied by a change in the critical temperature. It remains different from zero at the phase boundary, and does not possess any singularities as a function of r. Such a result is, on the basis of physical arguments, not plausible.

The formula (5) leads to a diametrically opposite result: the Curie temperature is equal to zero at the phase boundary $r_b = 0.25$. This is due to the fact that, for each r, the quantity $\mathscr{I}_{\mathbf{q}}$, (8), attains its maximum at only one inequivalent point in the Brillouin zone. When $r = r_b$ the $\mathscr{I}_{\mathbf{q}}$ maximum at $q = 0$ is transformed into a minimum if r is increasing, and the $\mathscr{I}_{\mathbf{q}}$ maximum at the points defined by the complex conjugate of the vector $\mathbf{Q}_L$ is transformed into a saddle point if r is decreasing. Accordingly, as $q \to 0$ in the denominator of the integrand in (5), all the terms quadratic in $\mathbf{q}$ vanish at the phase boundary, and the integrand becomes $\sim q^{-4}$. Moreover, this expression diverges again as a result of the vanishing of one of the coefficients of $(q^\alpha - Q_L^\alpha)$ in the expansion of $\mathscr{I}_{\mathbf{q}}$ around $\mathbf{Q}_L$.

From the physical standpoint, T_C becomes equal to zero because the structure, which is stable on one side of the phase boundary, is absolutely unstable on the other side. Therefore, both structures are unstable at the phase boundary.

The validity of the result, obtained from (5), that $T_C = 0$ at the phase boundary is corroborated by the following arguments. Firstly, the same result qualitatively follows from the spin-wave theory of ferromagnetism, extended to r_b. Indeed, according to (8), the magnon frequency $\omega_q = (\mathscr{I}_0 - \mathscr{I}_{\mathbf{q}})S$ for $q \to 0$ is proportional to $r_b - r$. Therefore, as $r \to r_b$, the mean number of magnons per atom diverges at any finite temperature, indicating that magnetic ordering cannot occur at this temperature. Secondly, it is not difficult to verify that at the phase boundary the crystal breaks up into FM planes effectively not coupled to each other by exchange interaction. Indeed, in the adopted geometry the energy characterizing the exchange interaction between an atom and the atoms of a neighboring FM plane is equal to $(I_1 + 4I_2)S^2 \cos \varphi$, where φ is the angle between the moments of the planes. It vanishes at $r = r_b$, and therefore there should be no long-range order in the orientation of the moments of the FM planes at any finite temperature. The arguments adduced above confirm the validity of the formula (5) as a whole.

The vanishing of T_C at phase boundaries where an abrupt change in the magnetic order occurs has a general character. This is attested by another example of the change that can occur in the type of order: If I_2 is negative as before, but I_1 changes its sign from positive to negative, then when $I_1 = 0$ the layered AFM ordering is replaced by a chain AFM ordering with a structure vector $\mathbf{Q}_T = (\pi, \pi, 0)$. Such a structure consists of FM chains oriented along one of the cube edges, the moment of each chain being opposite to the moments of the neighboring chains closest to it. Here the $\mathscr{I}_{\mathbf{q}}$ maxima are converted into saddle points on crossing the phase boundary in any direction. Consequently, according to (5), the T_C is equal to zero at the phase boundary.

Some ambiguity arises in the determination of the T_C when at the phase boundary the crystal splits up into two uncoupled three-dimensional structures in which magnetic ordering is possible. Such is the case when I_2 is positive. Then when $I_1 = 0$ the type of order in the crystal as a whole changes: the FM order is replaced by a staggered AFM order. In the absence of exchange interaction between the nearest neighbors, the crystal splits up into two FM sublattices consisting of the next-nearest neighbors. Since there is no correlation whatsoever between the directions of the moments of the sublattices, we can assert that, when $I_1 = 0$, the T_C of the crystal as a whole is also equal to zero. But we can introduce in place of the T_C of the whole crystal a T_C for each sublattice. Such a Curie temperature should not be equal to zero when $I_1 = 0$, since the type of magnetic order for each of these sublattices does not change at this value of I_1. Therefore, the fact that the T_C given by (5) does not vanish in this case does not at all contradict the assertion made above. Mathematically, in this case $\mathscr{I}_{\mathbf{q}}$ as a function of $\mathbf{q}$ formally has not one, but two maxima at inequivalent points of the Brillouin zone. At the transition point these maxima do not disappear; they simply undergo inversion. Therefore, the integrand in (5) does not have singularities at the phase boundary, and the T_C is not equal to zero there.

Besides the abrupt changes in the type of order that occur as the ratio of the exchange integrals is varied, there can occur a continuous change of the FM-helicoidal transition type. It is not difficult to verify that in this case the T_C is not equal to zero at the phase boundary, but then its derivative with respect to the exchange integrals (i.e., essentially its pressure derivative) exhibits a singularity. To do this, let us consider a layered magnetic substance with FM exchange inside the layers and alternating exchange in the direction perpendicular to them. We shall assume that in this direction the exchange integral I_1 between the nearest neighbors is positive, while the exchange integral I_2 between the next-nearest neighbors is negative. In this case the T_C, (5), remains different from zero at the FM-helicoidal phase boundary, but its derivatives with respect to the exchange integrals $r = I_1/|I_2|$ become infinite as the phase boundary is approached from either side:

$$dT_C/dr \sim |r - r_b|^{-1/2}, \qquad r_b = 4.$$

4. TEMPERATURE DEPENDENCE OF THE OPTICAL-ABSORPTION EDGE IN ANTIFERROMAGNETS

The procedure developed above allows us to find the correlators in a broad range of temperatures in the entire Brillouin zone. This enables us to solve a number of problems connected with the interaction of the magnetic subsystem of a crystal with the other subsystems (the lattice, current carriers, etc.). In the present section we shall solve one of such problems: We shall determine the temperature dependence of the optical-absorption edge of AFM semiconductors in the paramagnetic region. This dependence in the magnetic semiconductors is anomalously strong, as compared to what obtains in the nonmagnetic semiconductors, and its character can give us some idea about the type of correlation that exists between the spins. In FM semiconductors there occurs a giant red shift of the absorption edge when the temperature is lowered, whereas in the AFM ones the shift is, as a rule, a blue one, and is much weaker.[17] The question arises: What should this shift be under conditions when we have AFM and FM interactions competing with each other, and leading to the establishment of a layered AF structure (Sec. 3).

In the absence of long-range FM correlation between the *f* spins, if the *s*-band conduction width is large compared to the AS, the conduction-band shift due to the *s-f* exchange is given by the expression[17]

$$\delta = \frac{A^2}{4N} \sum_{\mathbf{q}} \frac{\langle \mathbf{S}_{\mathbf{q}} \mathbf{S}_{-\mathbf{q}} \rangle}{\varepsilon(\mathbf{q}_0) - \varepsilon(\mathbf{q}_0 + \mathbf{q})}, \tag{9}$$

where A is the *s-f* exchange integral, $\varepsilon(\mathbf{q})$ is the bare conduction-electron energy, and $\mathbf{q}_0$ is the quasimomentum corresponding to the bottom of the conduction band. If, as is often the case in magnetic semiconductors, the valence band is quite insensitive to the state of the magnetic subsystem, then (9) furnishes the temperature dependence of the crystal's optical absorption edge. From (9) it can be seen at once why in FM semiconductors the thermal shift of the absorption edge is red, while in normal AFM semiconductors it is blue. In fact, the more developed the long-wave components of the fluctuations are, the lower is the bottom of the band. But in ferromagnets, as the temperature is lowered, these components intensify, while in antiferromagnets they weaken.

All the numerical estimates will be made below using the following simple cosine dispersion law for the conduction electrons:

$$\varepsilon(\mathbf{q}) = -2B(\cos q_x + \cos q_y + \cos q_z), \quad B > 0. \tag{10}$$

Using (9) and (10), we immediately obtain in the case of classically large spins the following expression for the *s–f*-exchange-induced band shift at $T = 0$:

$$\delta_0 = -A^2S^2/8B. \tag{11}$$

A characteristic of the model (8)–(10) consists in the fact that the asymptotic value of the *s–f*-exchange-induced shift δ_∞ for $T \to \infty$ is very close to the value of the shift at $T = 0$:

$$\delta(T) = 0.98\delta_0 - \frac{A^2S^4I_1}{12BT}(0.49 - 0.56r). \tag{12}$$

In the general case the position of the bottom of the band in the paramagnetic region can be represented as a function of the correlation length Λ regarded as an implicit function of the temperature. Replacing the correlator in (9) by the expression (6), and expressing the temperature with the aid of (2) in terms of the susceptibility averaged over the Brillouin zone, we rewrite (9) with allowance for (10) in the form

$$\delta(\Lambda)=C(\Lambda)\delta_0,$$
$$C(\Lambda)=4B\left\{\sum[\mathcal{J}_{\mathbf{Q}_L}-\mathcal{J}_{\mathbf{q}}+\Lambda^2]^{-1}[\varepsilon_0-\varepsilon_{\mathbf{q}}]^{-1}\right\}$$
$$\times\left\{\sum[\mathcal{J}_{\mathbf{Q}_L}-\mathcal{J}_{\mathbf{q}}+\Lambda^2]^{-1}\right\}^{-1}. \tag{13}$$

The results of the numerical computations performed with the use of the formulas (13) can be summarized as follows: If I_1 and I_2 in (8) are comparable with each other, then the temperature dependence of the absorption edge is nonmonotonic, but is very weak. It is much stronger in the vicinity of a boundary between the layered AFM phase and another phase. We can illustrate the behavior of the absorption edge in the vicinity of the boundary with the FM phase if we choose the value $2r = 0.55$. As the temperature is lowered right down to the Néel point T_N (here we use this designation in place of the T_C used in Sec. 3), a monotonic red shift of the absorption edge occurs, attaining at T_N the value $0.75\ \delta_0$. According to (11), this shift is of the order of 0.1 eV for typical values of the crystal parameters ($AS/2 \sim B \sim 0.3$ eV).

Physically, the red shift that occurs in an antiferromagnet is explained by the fact that, as the temperature is lowered, there occurs a buildup of secondary fluctuations with $\mathbf{q} \approx 0$ along with the principal fluctuations with $\mathbf{q} \approx \mathbf{Q}_L$. But, as has already been indicated, the growth of the long-wave fluctuations shifts the bottom of the band downwards. That this growth occurs can easily be seen from (2) and (6). In particular, in the high-temperature limit, where the thermodynamic perturbation theory is applicable, the temperature-dependent part of the correlator $\langle \mathbf{S}_\mathbf{q} \mathbf{S}_{-\mathbf{q}} \rangle$ is equal to $\mathcal{J}_\mathbf{q} S^2/3T$, and, according to (8), $\mathcal{J}_0 > 0$ for $r < 0.5$. Below T_N the long-wave fluctuations, on the contrary, freeze out, and the bottom of the band shifts upwards, reaching its high-temperature position at $T = 0$. Thus, in the considered case the forbidden-band width of an AFM semiconductor goes through a minimum in the vicinity of T_N.

In the vicinity of the boundary of the layered AFM phase with the filamentary AFM phase ($I_1 = 0$) the absorption-edge shift has the opposite character: as the temperature is lowered, the forbidden-band width goes through a maximum, and not through a minimum. We can see why the absorption-edge shift is blue at high temperatures from the following arguments. Here, as the temperature is lowered, the long-wave fluctuations die out, while the short-wave fluctuations—and not just the principal ones, with wave vectors $\mathbf{q}$ close to $\mathbf{Q}_L$, but also the secondary ones with $\mathbf{q} \approx \mathbf{Q}_T$, for which the $\mathcal{J}_\mathbf{q}$ are also positive—intensify. Thus, the peak of the integrand in (9) shifts into the short-wave region, which corresponds to a blue shift of the absorption edge. As the temperature is lowered further, the secondary fluctuations, having passed through their peak, should begin to die out, since they do not occur at $T = 0$. Consequently, the peak of the integrand in (9) will shift into the long-wave region, since $\mathbf{Q}_L < \mathbf{Q}_T$, i.e., the shift will be red. Since the integrand in (9) is small in the region of the momenta $\mathbf{Q}_L$ and $\mathbf{Q}_T$, the magnitude of the shift in the case under consideration should be significantly smaller than the magnitude of the shift that occurs in the vicinity of the boundary with the FM phase. The numerical calculation for $|I_2| = 5I_1$ shows that the highest position of the bottom of the conduction band is attained back in the paramagnetic region at $\Lambda^2 = 0.8I_1$. There $|\delta|$ is 20% higher than $|\delta_0|$. In filamentary antiferromagnets the absorption-edge shift should be monotone blue.

The nonmonotonic temperature dependence of the absorption edge has been experimentally observed in a number of magnetic semiconductors. For example, in MnO and $ZnCr_2Se_4$, as the temperature T is lowered, the absorption edge shifts into the red region when $T > T_N$ and into the blue region when $T < T_N$.[17] But in order to establish whether this effect can be attributed to the existence of short-range ferromagnetic order in these crystals, we must investigate small-angle neutron scattering.

5. MAGNETIC SUBSTANCES WITH QUANTUM SPINS IN THE VICINITY OF A PHASE BOUNDARY

The analysis above cannot be automatically carried over to the case of quantum spins. Furthermore, the quantum nature of the spins leads to qualitatively new effects, i.e., effects which cannot occur in magnetic substances with classical spins. If the spins in a Heisenberg magnetic substance are classical, then the type of long-range order that appears at the Curie point on lowering the temperature does not change down to $T = 0$. Indeed, according to (6), which is the leading term in T_C, the correlator with the greatest Fourier transform $\mathcal{J}_\mathbf{q}$ diverges, and it is precisely such a wave vector that should be associated with the long-range order that is established below T_C. But on the other hand, the fact that $\mathcal{J}_\mathbf{q}$ is a maximum quarantees at the same time that the energy (1) is a minimum at $T = 0$, i.e., the stability of such a state as the ground state. In the quantum case, however, the criteria for the types of long-range order for $T = 0$ and $T = T_C$ do not, generally speaking, coincide with each other: the fluctuations that grow at the fastest rate as the T_C is approached may have a wave vector entirely different from that of the long-range order that secures a minimum energy at $T = 0$.

This is precisely the situation that obtains in the vicinity of the ferromagnetic-layered antiferromagnetic phase boundary investigated in the classical limit in Sec. 3. If we take account of the zero-point vibrations of the spins in the AF state, vibrations which lower the energy of this state in comparison with the classical energy, we find that the equality $\mathcal{J}_0 = \mathcal{J}_{\mathbf{Q}_L}$ no longer guarantees the equality of the energies E_{FM} and E_{AFM} of the FM and AFM states. The second turns out to be lower than the first by the amount $(0.14/S)E_{\mathrm{FM}}$ (this estimate is obtained by the standard methods of spin-wave theory for antiferromagnets). Thus, the FM phase should be stable at $T = 0$ not up to $r_b = 0.25$, but up to a lower value r_g, although in the interval $[r_g, r_b]$ the integral

$\mathscr{I}_{\mathbf{q}}$ remains greatest for $q = 0$. For small spins the interval $[r_g, r_b]$, within which the quantum fluctuations destroy the FM order, is comparable to the interval $[0, r_b]$, within which this order is stable.

If, on the other hand, we proceed from the high-temperature region, then the criterion for the type of long-range order should be much closer to the classical criterion, i.e., to the $\mathscr{I}_{\mathbf{q}}$ maximality criterion. Indeed, the effect of the quantum spin oscillations on the thermodynamics of the magnetic material should be much weaker in the paramagnetic region than at $T = 0$, since the degree of short-range order in that region is not high and the spins are, on the average, randomly oriented with respect to each other. As for the quantum fluctuations, they are important when the spins are, in the main, antiparallel to each other. Corroborating the assertion that the thermodynamics of a magnetic material at $T \sim T_C$ weakly depends on the zero-point vibrations of the spins is the fact that both in the self-consistent field approximation and according to Refs. 12 and 13 (the quantum analog of (5)) the T_C's for all the types of order depend on the spins in an identical fashion: they are proportional to $S(S+1)$. Essentially the same spin dependence is exhibited by the expression (7), which is the most accurate expression for T_C in the nearest-neighbor approximation. Therefore, the phase boundary r_c determined from the critical properties should be closer to the classical boundary r_b than r_g.

In order to elucidate the physical picture in the interval $[r_g, r_b]$, we should first demonstrate the stability of the AFM state in this interval, which is classically forbidden to it. To do this, we must compute the magnon frequencies $\omega_{\mathbf{k}}$ not in the usual leading approximation in $1/S$, but in the next approximation, since in the leading approximation the frequencies in this interval are imaginary. The real character, proved below, of the $\omega_{\mathbf{k}}$ in the higher-order approximations in $1/S$ indicates that the quantum effects can stabilize the AF structure in the region classically forbidden to it.

The magnon Hamiltonian in the approximation under consideration is obtained from the Hamiltonian (1) by carrying out the Holstein-Primakoff transformation in each of the sublattices with allowance made for the ternary terms in the magnon operators. These terms can be uncoupled according to the scheme

$$A_1A_2A_3A_4 = \sum \langle A_iA_j\rangle_0 A_kA_l, \tag{14}$$

where A_i is an arbitrary magnon operator, the symbol $\langle \ldots \rangle_0$ denotes averaging over the ground state, and the summation in (14) is over all possible pairings. The thus obtained pair Hamiltonian can be diagonalized with the aid of the Bogolyubov *u-v* transformation. As a result, we obtain the following formally closed expression for the frequency:

$$\begin{aligned}
\omega_{\mathbf{k}} &= (B_{\mathbf{k}}^2 - C_{\mathbf{k}}^2)^{1/2}, \qquad (15)\\
B_{\mathbf{k}} &= 2I_1S\Big[1-\cos k_x-\cos k_y+2r(1+\cos k_x\cos k_y)\\
&\quad+\frac{1}{S}(\nu_{100}-\nu_{000})(2-\cos k_x-\cos k_y)\\
&\quad-\frac{2r}{S}(\nu_{110}-\nu_{000})(1-\cos k_x\cos k_y)\\
&\quad+\frac{1}{S}(\nu_{000}-\mu_{001})-\frac{4r}{S}(\nu_{000}-\mu_{110})\Big],\\
C_{\mathbf{k}} &= 2I_1S\cos k_z\Big\{2r(\cos k_x+\cos k_y)\Big[1-\frac{1}{S}(\nu_{000}-\mu_{110})\Big]\\
&\quad-1+\frac{1}{S}(\nu_{000}-\mu_{001})\Big\},\\
\nu_{pqr} &= \frac{1}{2N}\sum\Big(\frac{B_{\mathbf{k}}}{\omega_{\mathbf{k}}}-1\Big)\cos^p k_x\cos^q k_y\cos^r k_z,\\
\mu_{pqr} &= \frac{1}{2N}\sum\frac{C_{\mathbf{k}}}{\omega_{\mathbf{k}}}\cos^p k_x\cos^q k_y\cos^r k_z.
\end{aligned}$$

In essence, the expression (15) is a functional equation for the frequency, since the quantities ν_{pqr} and μ_{pqr} are functionals of it. For $r < r_b$ the frequencies are nonanalytic in $1/S$, which is manifested in the fact that we cannot compute them through direct expansion in powers of this parameter. But for small $r_b - r$ the frequencies can be computed by the method of successive approximations in this difference. As the initial values of ν_{pqr} and μ_{pqr} we take the values for $r_b = 0.25$, at which value these quantities can be computed through power series expansions in $1/S$.

From (15) it follows that the condition for the magnon frequencies to be real is equivalent to the condition for the quantity B_0 to be positive. From this we immediately obtain the following estimate for the value r_m up to which the magnon frequencies remain real:

$$r_b - r_m \approx \frac{1}{2S}[\mu_{001}(r_b) - \mu_{110}(r_b)] = \frac{0{,}07}{S}. \tag{16}$$

Consequently, (16) yields an estimate for r_g as well.

On the basis of the above results, we can assert that a short-range order inversion should occur in the interval $[r_c, r_b]$ as the temperature is lowered. At the highest temperatures we find, in complete agreement with thermodynamic perturbation theory, that those fluctuations to which correspond the greatest $\mathscr{I}_{\mathbf{q}}$ i.e., the ferromagnetic fluctuations, should grow at the fastest rate. But as we approach the T_C, and the quantum effects begin to manifest themselves, a short-range AFM order, which is transformed into a long-range order below T_C, should begin to predominate.

Another situation obtains in the interval $[r_g, r_c]$. The fact that in this interval the short-range order that occurs in the region $T \to T_C$ is of a type different from the long-range order occurring at $T = 0$ (the first is a ferromagnetic order, while the second is an antiferromagnetic order) necessitates the occurrence of a first-order phase transition. There are two possibilities. 1) As the temperature is lowered, a second-order paramagnetic-ferromagnetic phase transition first occurs, which is then followed by a first-order order-order phase transition from the FM into the AFM state. 2) There occurs a first-order phase transition directly from the paramagnetic state with short-range ferromagnetic order into the AFM state, i.e., in the terminology of Ref. 7, there occurs an order-improper disorder phase transition. At the present stage it is not possible to determine which of these two variants is actually realized. In any case the first-order phase transition mechanism considered above, in which the transition is due to the quantum fluctuations, is new for the order-order and order-improper disorder phase transitions.

In principle, the establishment of a long-range AFM order could occur not through a single phase transition, but through a whole series of them, as occurs in the ANNNI model.[1–3] But here we cannot see any reason for the occurrence of a series of phase transitions, since in the vicinities of the AFM and FM phase boundaries the free energies for the other types of long-range order are much higher.

The quantum fluctuations induce first-order phase transitions not only when the temperature is varied, but also when the magnetic field is varied, i.e., an isotropic Heisenberg magnetic substance should possess metamagnetic properties in the interval $[r_g, r_b]$. This is due to the fact that, in zero magnetic field, to the AFM state corresponds the absolute minimum of the energy, while to the FM state corresponds a relative minimum. A magnetic field causes the inversion of these minima, making the FM state the ground state. The fact that to the FM state corresponds an energy minimum follows directly from the positiveness of the magnon frequencies in the FM state inside this interval:

$$\omega_k{}^{\mathrm{FM}} = (\mathcal{J}_0 - \mathcal{J}_k) S,$$

$\mathcal{J}_0$ being the greatest in the interval. Such a state differs from the usual metamagnetic state by the presence of magnetic memory: if the field is removed, the crystal can, in the case when $T \to 0$, remain indefinitely in the metastable FM state. Evidently, the closer r is to r_g, the weaker is the field necessary for the transformation of the crystal from the AFM into the FM state.

It should be noted that the possibility of an isotropic magnetic substance's being in the metamagnetic state is in itself nontrivial: the overwhelming majority of metamagnetic substances are crystals with very large anisotropy. It has been pointed out before that metamagnetism is possible in isotropic magnetic substances with non-Heisenberg exchange[7] and Jahn-Teller ions.[8] But metamagnetic memory does not occur in those cases.

It is natural to expect all the effects described in this section to occur in antiferromagnets with small atomic spin and a paramagnetic Curie temperature that is either positive or negative, but that is small in magnitude (this indicates strong FM exchange). There are quite a large number of such antiferromagnets (DyAs, FeSi, etc.).

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Translated by A. K. Agyei