Exact inequalities and their consequences in the theory of amorphous magnets

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It is proved by means of a theorem of Bogolyubov that the magnetic ("phonon", electron, ...) part of the free energy F of an amorphous system is always less than or equal to the free energy F_0 of the corresponding "crystal" described by a Hamiltonian averaged over the structure, i.e., $\Delta F = F - F_0 \leq 0$. Estimates are given for $|\Delta F|$ and the qualitative behavior of the variations of the thermodynamic quantities as a result of fluctuations of the structure is elucidated.

1. INTRODUCTION

The physical properties of amorphous systems have been studied more and more intensively in the last 10—15 15 years. Attention has been given primarily to the electrical properties, while the magnetic properties have not been the subject of particular interest. But there is no doubt that the magnetic properties of amorphous systems deserve more attention, since in many cases they are closely connected with the electrical properties and with the concrete geometrical and chemical structures of the amorphous systems.

The following questions are of fundamental significance: 1) Can long-range magnetic order exist in amorphous systems, i.e., without long-range structural order? 2) If yes, then under what conditions? 3) How are the magnetic properties in amorphous systems changed in comparison with crystals?

The first question was first formulated theoretically by Gubanov as long ago as 1960[1]. He determined the Curie temperature within the framework of a quasi-chemical approximation for the Ising model with spin $S = 1/2$ with the exchange integral depending on distance, and arrived at the conclusion that amorphous Ising systems can have a finite Curie temperature. The author of the present article pointed out the importance of fluctuations of the structure for the magnetic properties of amorphous ferromagnets[2].

From 1964 onwards, a number of amorphous ferromagnets have been found and investigated experimentally. They were prepared in the form of films of thickness 400—1000 Å by means of deposition on to a very cold substrate, films of thickness 50 μm − 0.2 mm by rapid cooling of the melt, and films of thickness up to 0.2 mm by electrolytic methods. Measurements have been made of, e.g., the temperature dependence of the spontaneous magnetization[3-6], the coercive force[7,8], the ferromagnetic resonance (FMR) spectra[9,10], the internal magnetic fields by means of the Mössbauer effect[3,11,12], and the magnetic domain structure by means of Lorentz microscopy[13] (see also the subsequent experimental papers[14-19]). The existence of a ferromagnetic or ferromagnet-like phase in amorphous systems follows unambiguously from these experiments.

The absence of crystalline structure in the samples investigated was proved by means of X-ray and electron diffraction. Highly diffuse diffraction patterns, which are also characteristic of liquids, were obtained. For example, from the diffraction patterns for the amorphous ferromagnetic alloy with composition $Fe_{80}P_{12.5}C_{7.5}$ the mean distance between nearest neighbors is found to be 2.6 Å, and the standard deviation of this distance is 0.5 Å[3]. It can be concluded from this that, in the amorphous ferromagnets investigated, we can exclude with certainty the existence of long-range crystalline order and, in the majority of cases, we can also exclude short-range crystalline order with high probability.

An interesting review of experiments on amorphous ferromagnets with compositions Fe—Pd—Si, Fe—Pd—P, Fe—P—C, Co—Au, Co—P, Co—Pd—Si and Ni has been given by Hasegawa[20] (cf. also[12] and[31]). Numerous measurements have also been performed of the susceptibility χ in liquid transition metals and their alloys (cf., e.g.,[21-24]); the curves of $\chi(T)$ behave like those for typical ferro-or antiferromagnets in the paramagnetic regime. Busch and Guentherodt[25] have reported that they have observed ferromagnetism in the liquid alloy Co—Au close to the eutectic composition. However, discussion on this question still continues (cf. e.g.,[26,27]).

Amorphous antiferromagnets have recently been found experimentally[28,29] (cf. also[30]). For these amorphous antiferromagnets, of course, we cannot introduce geometrically completely defined magnetic sublattices in the customary way. However, in these also, an antiparallel arrangement of the spins of "nearest neighbors" is thermodynamically stable. The "mixed" magnets or "amorphous ferrimagnets"[5,6,31], in which ferro- or antiferromagnetic coupling or (Pauli) paramagnetism is locally stable, depending on the structure, are a more general case. In many respects, the physical situation in mixed magnets is reminiscent of the "spin glasses" (cf., e.g.,[43]).

If we also take into account the magnetic anisotropy, which changes in direction and magnitude depending on the local structure, the diversity of the possible magnetic structures is further increased. The magnetic structure of such systems can be described consistently by determining not only the total magnetization but also the spatial correlations of the latter, e.g., $\langle \mathbf{m}_i \rangle$, $\langle \mathbf{m}_i \mathbf{m}_j \rangle$, ..., where $\mathbf{m}_i$ is the "spontaneous magnetization" of the atom at site $\mathbf{r}_i$, and the angular brackets denote averaging over the structure.

Up to now, theoretical studies of amorphous ferro- and antiferromagnets have been based on the Heisenberg and Ising models[1,2,31-39]. The structural model most often applied is the so-called stochastic "lattice" model, in which the spins are situated at lattice sites but the exchange integrals fluctuate stochastically[32-38]. The quantities primarily determined are the Curie temperature T_C, the magnetization σ and susceptibility χ in

different approximations. In the molecular field approximation[2], it was found that fluctuations of the exchange integrals lead to a reduction of the magnetization for $0 < T < T_c$, whereas T_c and χ do not change[1]. The reduction of σ has been confirmed experimentally[3,5,12], and also in other approximations. By means of a Green function method, Montgomery et al.[32] obtained a reduction of σ and T_c as a result of fluctuations of the exchange integrals in the Tyablikov approximation. The author[35], starting from simple thermodynamic perturbation theory for the Ising model with spin $S = 1/2$, obtained a decrease of σ and χ. By means of a high-temperature expansion, Schreiber and the author[36], obtained a decrease of T_c and χ for the Heisenberg model with atomic spin $S = 1/2, 1, 5/2, \infty$. For the Ising model, for $S = 1/2$ a decrease of χ resulted at all temperatures T, and for $S \geq 1$ a somewhat unexpected increase of χ resulted at high temperatures T[37]. It was proposed previously[34,37] that, when sufficient account is taken of the short-range magnetic order, fluctuations of the exchange integrals always lead to a lowering of the Curie temperature. All the results existing at present confirm this hypothesis.

At the present time, only the first attempts to determine the Néel temperature and the susceptibility of amorphous antiferromagnets have been made[28,38,39].

In the present paper, an account is given of the thermodynamics of amorphous magnets assuming the geometrical and chemical structures to be fixed. Attention is paid principally to the role of fluctuations of the structure. It is found that Bogolubov's theorem for the free energy makes it possible to determine qualitatively, in a simple way, the effect of these fluctuations on the free energy. By means of the same theorem, we have obtained inequalities for the free energies in the molecular field approximation for the Ising and Heisenberg models. These inequalities are valid for both crystalline and amorphous magnets. We then give the boundary conditions for the free energy at temperatures $T \to \infty$ and $T = 0$. It is found that structure fluctuations do not change the magnetic part of the free energy at sufficiently high temperatures.

If all the exchange integrals are positive, then structure fluctuations do not change the free energy at $T = 0$ either. If a proportion of the exchange integrals is negative (mixed ferromagnet), the structure fluctuations lead to a lowering of the free energy at $T = 0$ and to a reduction of the energy of the ground state of the magnetic system.

Below we give a qualitative description of the behavior of the free energy change ΔF resulting from structure fluctuations, and of the corresponding entropy change ΔS, internal energy change ΔU, and specific heat change ΔC, as functions of the temperature. Knowing these quantities, we can predict qualitatively the changes of the spontaneous magnetization (ΔM), of the effective exchange integral (ΔI_{eff}), of the density of states of the magnetic system and of the effective rigidity constant, arising as a result of the structure fluctuations. Investigating the change of the thermodynamic quantities on going from the effective field approximation to the Ising model and from the Ising model to the Heisenberg model, we find a relatively close analog with the transitions from the corresponding "crystal" to the amorphous magnet. An explanation of this analogy is given, and on the basis of this analogy a simple physical picture for amorphous magnets is derived.

2. STATISTICS AND THERMODYNAMICS OF AMORPHOUS MAGNETIC SYSTEMS

To be specific, we start from the Heisenberg model with the Hamiltonian

$$\mathcal{H} = -\sum_{i,j} I_{ij}\hat{S}_i\hat{S}_j - \mu_B g H \sum_i \hat{S}_i^z, \tag{1}$$

or from the Ising model, in which the spin operators $\hat{S}_i$ must be replaced by the z-components $\hat{S}_i z$. Here I_{ij} are the exchange integrals, depending only on the distance between neighboring spins, g is the Landé factor, μ_B is the Bohr magneton and H is the external magnetic field, directed along the z-axis. The Hamiltonian (1), unlike that of the crystal, is no longer invariant under translations. Even when the spins are well localized, the Hamiltonian (1) for amorphous systems is an approximation, since the exchange integrals I_{ij} depend in the general case not only on the positions of the two spins i and j but also on their specific environment[31].

In the following we shall assume a rigid spatial arrangement of all the atoms or ions (a fixed structure). With an arbitrary fixed structure, we obtain for the magnetic part of the free energy

$$F(T, H, \mathbf{R}) = -\frac{1}{\beta}\ln \mathrm{Sp}\exp[-\beta\mathcal{H}(\mathbf{R})], \tag{2}$$

where $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N)$ defines the positions of all N localized spins. The trace in (2) is taken only over the spin variables.

Amorphous systems are not found in thermodynamic equilibrium in the true sense, but only in a metastable state. We apply equilibrium statistics to the magnetic subsystem with the structure fixed, regarding the latter as a supplementary external condition. True, these external conditions differ from the usual ones, such as fixed volume of pressure, because they cannot be altered reversibly by means of a macroscopic perturbation. Nevertheless, this does not prevent the application of equilibrium statistics and thermodynamics to the magnetic system, if we regard all the exchange integrals I_{ij} and the atomic spins S_i, which can also fluctuate, as "external" parameters. In particular, we can use all three laws of thermodynamics.

In order to obtain the macroscopic thermodynamic properties of an amorphous system, it is necessary to average Eq. (2) over the structure

$$F(T, H) = \langle F(T, H, \mathbf{R})\rangle = -\frac{1}{\beta}\langle \ln \mathrm{Sp}\exp[-\beta\mathcal{H}(\mathbf{R})]\rangle. \tag{3}$$

This averaging can be performed, e.g., by means of the distribution function $F_N(\mathbf{R})$ of the atoms, which is assumed to be independent of the temperature and of other parameters (fixed structure).

3. BOGOLYUBOV'S THEOREM FOR AMORPHOUS SYSTEMS

We begin with the case of the so-called "lattice" model for an amorphous magnet[32-37], in which all the spins are identical and positioned at the sites of a regular lattice while the exchange integrals fluctuate arbitrarily. For simplicity, we shall consider only cubic lattices, and take into account the exchange interaction between nearest neighbors only. Under these conditions, the Hamiltonian can be written in the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1; \tag{4}$$

$$\mathcal{H}_0 = -\langle I\rangle \sum_{i,j} \hat{\mathbf{S}}_i\hat{\mathbf{S}}_j - \mu_B g H \sum_i \hat{S}_i^z, \tag{5}$$

$$\mathcal{H}_1 = -\sum_{i,j} \Delta I_{ij}\hat{\mathbf{S}}_i\hat{\mathbf{S}}_j. \tag{6}$$

where $\mathcal{H}_0$ describes the corresponding crystal (pseudo-crystal), $\mathcal{H}_1$ contains all the fluctuations of the exchange integrals—the structure fluctuations characteristic of amorphous systems, and the summation over i and j in (5) runs over nearest neighbors. One of the central problems, therefore, is to establish the influence of the fluctuations on the physical properties.

For arbitrary self-adjoint operators $\mathcal{H}_0$ and $\mathcal{H}_1$, Bogolyubov's theorem for the free energy states[40]:

$$F(\mathcal{H}) \leqslant F(\mathcal{H}_0) + \operatorname{Sp}\mathcal{H}_1 e^{-\beta\mathcal{H}_0}/\operatorname{Sp} e^{-\beta\mathcal{H}_0} \equiv F(\mathcal{H}_0) + \overline{\mathcal{H}}_1, \tag{7}$$

where the line denotes averaging over the state with $\mathcal{H}_0$—over the regular crystal with the average exchange integral $\langle I\rangle$. Substituting the operator (4) into this inequality and taking the definitions (5) and (6) into account, we find

$$F_{st}(\mathcal{H}) \leqslant F(\mathcal{H}_0) + \overline{\mathcal{H}}_{1,\,st}.$$

The index st indicates the dependence on the structure.

Since the inequality (7) is fulfilled for any structure (any $I_{ij} = \langle I\rangle + \Delta I_{ij}$), it is also conserved after averaging over the structure:

$$F(\mathcal{H}) \equiv \langle F_{st}(\mathcal{H})\rangle \leqslant F(\mathcal{H}_0) + \langle\overline{\mathcal{H}}_{1,st}\rangle.$$

For the operator (6), we have

$$\langle\overline{\mathcal{H}}_{1,\,st}\rangle = -\Big\langle\sum_{i,j}\Delta I_{ij}\overline{\hat{S}_i\hat{S}_j}\Big\rangle = -\sum_{ij}\langle\Delta I_{ij}\rangle\,\overline{\hat{S}_i\hat{S}_j} = 0, \tag{8}$$

since the correlation function $\overline{\hat{S}_i\cdot\hat{S}_j}$ does not depend on the structure and is determined entirely by $\mathcal{H}_0$

Thus, Bogolyubov's theorem takes the simple form[41]:

$$F \equiv F(\mathcal{H}) \leqslant F(\mathcal{H}_0) \equiv F_0, \quad \Delta F \equiv F - F_0 \leqslant 0. \tag{9}$$

If we write the Hamiltonian in the form

$$\mathcal{H} = \langle\mathcal{H}\rangle + \Delta\mathcal{H} \tag{10}$$

and choose $\mathcal{H}_0 = \langle\mathcal{H}\rangle$ and $\mathcal{H}_1 = \Delta\mathcal{H}$, we again obtain the inequality (9), since

$$\langle\overline{\Delta\mathcal{H}}\rangle = \overline{\langle\Delta\mathcal{H}\rangle} = 0.$$

The latter assumption is true, since the operations of averaging over the structure and over $\mathcal{H}_0$ (the line!) commute. The inequality (9), together with the definitions (10) and (3), is the most general form of Bogolyubov's theorem for amorphous systems, or structurally disordered systems in general, when a fixed structure is assumed.

Bogolyubov's theorem can be formulated in the following way: structure fluctuations that are completely contained in the Hamiltonian (10) or (6) always lead to a decrease of the free energy of the magnetic system or at least do not change it. We emphasize that Bogolyubov's theorem in the form (9) is fulfilled for any structure fluctuations, including fluctuations of the atomic spin, for the Heisenberg, Ising and X—Y models for any dimensionality. Another important point is that the exchange integrals can change sign, so that (9) is also fulfilled for ferro-, antiferro- and mixed magnets. Clearly, it is also applicable for disordered and amorphous alloys.

4. COMPARISON OF THE FREE ENERGIES FOR THE ISING AND HEISENBERG MODELS AND IN THE MOLECULAR FIELD APPROXIMATION

Bogolyubov's theorem (7) makes it possible to compare the free energies for the Ising model and in the molecular field approximation, and also to compare those for the Heisenberg and Ising models. If we write the Hamiltonian in the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1; \tag{11}$$

$$\mathcal{H}_0 = -\sum_{i,j} I_{ij}\overline{\hat{S}_j^z}\hat{S}_i^z - \mu_B g H\sum_i \hat{S}_i^z,$$

$$\mathcal{H}_1 = -\sum_{i,j} I_{ij}(\hat{S}_j^z - \overline{\hat{S}_j^z})\,\hat{S}_i^z,$$

where $\overline{\hat{S}_j^z}$ denotes the time-averaged value of spin j, it can be easily seen that $\mathcal{H}_1 = 0$. Therefore, it follows from Bogolyubov's theorem that

$$F_I \leqslant F_M, \quad \Delta F_{I,M} \equiv F_I - F_M \leqslant 0, \tag{12}$$

i.e., the free energy for the Ising model is always less than or equal to the free energy for the molecular field approximation.

Analogously, we obtain

$$F_H \leqslant F_I, \quad \Delta F_{H,I} \equiv F_H - F_I \leqslant 0, \tag{13}$$

where F_H denotes the free energy for the Heisenberg model. The inequalities (12) and (13) are fulfilled for any dimensionality and any atomic spin, for both crystalline and any amorphous magnets.

5. ESTIMATE FOR $|\Delta F|$

For any self-adjoint operators A and B, we can easily prove the inequality (cf., e.g.,[42])

$$|\ln\operatorname{Sp} e^A - \ln\operatorname{Sp} e^B| \leqslant \|A - B\|, \tag{14}$$

where $\|A-B\|$ denotes limsup(A—B). If we choose $A = -\beta\mathcal{H}$ and $B = -\beta\mathcal{H}_0$, and multiply the inequality (14) by $1/\beta$, we obtain

$$|F_{st}(\mathcal{H}) - F(\mathcal{H}_0)| \leqslant \|\mathcal{H} - \mathcal{H}_0\|.$$

Taking into account that

$$|\langle F_{st}(\mathcal{H})\rangle - F(\mathcal{H}_0)| \leqslant \langle|F_{st}(\mathcal{H}) - F(\mathcal{H}_0)|\rangle,$$

and using also the definitions (10) and (3), we obtain

$$|\Delta F| \leqslant \langle\|\Delta\mathcal{H}\|\rangle. \tag{15}$$

This inequality is again fulfilled for amorphous ferro-, antiferro-, para- and mixed magnets of arbitrary dimensionality. For example, in the framework of the "lattice" model with exchange interaction between nearest neighbors, we obtain

$$|\Delta F| \leqslant NzS^2\langle|\Delta I_{ij}|\rangle,$$

where z is the number of nearest neighbors.

We note further that, for

$$-\Delta S = \Big(\frac{\partial\Delta F}{\partial T}\Big)_H, \qquad -\frac{\Delta C}{T} = \Big(\frac{\partial^2\Delta F}{\partial T^2}\Big)_H$$

also, we can obtain estimates which follow from the positivity of the entropy $S = S_0 + \Delta S \geq 0$ and of the specific heat $C = C_0 + \Delta C \geq 0$, and also from the fact that the entropy per spin is finite.

6. FREE ENERGY FOR T → ∞ AND T = 0

It can be proved easily by means of the high-temperature expansion that

$$\Delta F(T, \mathbf{H}) = 0, \quad F_{II} = F_I = F_{st} \quad \text{при } T \to \infty. \tag{16}$$

The asymptotic relations (16) are fulfilled for both crystalline and amorphous magnets. The first of them shows that, at sufficiently high T, all the thermodynamic quantities of an amorphous system approach those of the corresponding "crystal." This justifies, formally and practically, the introduction of the corresponding "crystal" described by the Hamiltonian $\langle\mathscr{H}\rangle$.

We now consider the case T = 0.

Since at T = 0 the changes ΔF and ΔU of the free and internal energies coincide, it follows from Bogolyubov's theorem (9) that

$$\langle\Lambda\mathscr{H}\rangle_{gr} = \Lambda U = \Lambda F \leqslant 0 \quad \text{for } T = 0, \tag{17}$$

$$\langle\mathscr{H}_{gr}\rangle \leqslant \langle\mathscr{H}\rangle_{gr}, \tag{18}$$

where the index gr denotes the ground state. The inequality (18) shows that the ground-state energy of an amorphous system is always less than or equal to that of the corresponding "crystal." It is valid in the same broad region as Bogolyubov's theorem itself.

If all the exchange integrals I_{ij} are positive, then at T = 0 all the spins are fully parallel and the relations (17) and (18) become equalities. This is also valid when the atomic spin fluctuates[2)]. If negative exchange integrals are also present, as in "mixed" magnets, we must write the inequality sign in (17) and (18), as is completely understandable physically.

7. CONSEQUENCES OF BOGOLYUBOV'S THEOREM

In this section, we shall use Bogolyubov's theorem to establish the qualitative effect of the structure fluctuations on the thermodynamic characteristics of the magnet.

We first assume that all the exchange integrals I_{ij} are positive. Then the simplest dependence of ΔF on T that satisfies the Bogolyubov equality, the limiting value (16) for T → ∞ and the relation

$$\Delta U = \Delta F = 0 \quad \text{for } T = 0 \tag{19}$$

corresponds to a curve with one minimum (Fig. 1)[3)]

The corresponding curves for the entropy ΔS and the specific heat are also depicted in Fig. 1. Thus, structure fluctuations lead at low temperatures to an increase of the entropy, internal energy and specific heat, and at high temperatures to a decrease of the entropy and internal energy and to an increase of the specific heat.

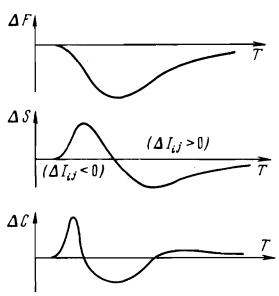

FIG. 1. Qualitative form of the curves of the temperature dependences of the changes of free energy (ΔF) entropy (ΔS) and specific heat (ΔC) of a magnetic system as a result of structure fluctuations (with the limit condition (19)).

The qualitative behavior of ΔF, ΔS, ΔU and ΔC at sufficiently low and high temperatures follows uniquely from Bogolyubov's theorem alone. The behavior of these quantities at intermediate temperatures cannot be derived rigorously. However, the simple form proposed can be confirmed by simple physical considerations.

For this we consider in more detail the behavior of the entropy change ΔS(T). For simplicity, we assume that only the exchange integrals $I_{ij} = \langle I\rangle + \Delta I_{ij}$ fluctuate. Then there is a large number of spins which are more weakly coupled with each other than exchange with $\langle I\rangle$ would have given. These spins can be thermally excited more easily than in the corresponding "crystal," in which all the exchange integrals are replaced by $\langle I\rangle$. Therefore, the entropy, being a measure of the order of the magnetic system, should increase at low T as a result of fluctuations. On the other hand, there is a large number of neighbors with $\Delta I_{ij} > 0$. Spins which are more strongly coupled are more difficult to excite thermally. This leads to a decrease of the entropy at high temperatures. It may be said that fluctuations with $\Delta I_{ij} > 0$ induce, at high T, additional short-range magnetic order, due to the structure fluctuations. The behavior of the entropy is thus fully understandable and substantiates, in turn, the proposed simple form for ΔF. In particular, additional oscillations of ΔS would be physically incomprehensible.

It is easy to interpret the behavior of ΔC on the basis of this physical picture. Because of the exchange with $\Delta I_{ij} < 0$, the magnetic system accepts thermal energy more easily at low T, and this implies an increase of the internal energy and specific heat as a result of the structure fluctuations. At high temperatures, certain degrees of freedom are more difficult to excite; this gives rise to an additional positive specific heat and, in addition, the system increases its internal energy more slowly. Since ΔC is positive at low and high T, it follows from the equation

$$\int_0^\infty \Delta C(T)\, dT = \lim_{T\to\infty} \Delta U(T) = 0$$

that ΔC should be negative at intermediate temperatures (cf. Fig. 1).

If a second-order phase transition occurs in the corresponding "crystal," a peak should appear in the specific heat at the transition temperature $T_c^{(0)}$. In the general case, structure fluctuations change the phase-transition temperature or eliminate it altogether. This means that ΔC should cancel the specific-heat peak at $T_c^{(0)}$. This explains the appearance of a negative peak in ΔC when there exists a phase transition in the corresponding crystal.

The form of the curves of ΔS and ΔC shows that additional degrees of freedom or states appear at low and high energies. This means that the structure fluctuations lead to an increase of the density of states of the magnetic system at low and high energies. However, since the total number of states cannot change, it must be reduced at intermediate energies (Fig. 2). From the increase $\Delta N = N - N_0$ of the density of states at low energies and from the behavior of ΔS and ΔC at low temperatures, it follows that the correction to the magnetization is negative, $\Delta M \leq 0$, i.e., structure fluctuations reduce the spontaneous magnetization at sufficiently low T. In the language of spin waves, this means that the effective stiffness is reduced at low T, i.e., spin waves

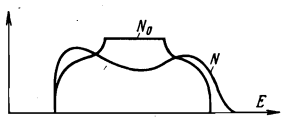

FIG. 2

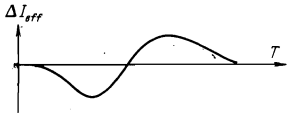

FIG. 3

FIG. 2. Qualitative behavior of the density of states of a magnetic ("phonon") system in the case when the simple limit condition (19) is fulfilled. N—the amorphous sytem, N_0—the corresponding "crystal".

FIG. 3. Qualitative behavior of the change ΔI_{eff} of the effective exchange integral as a function of temperature.

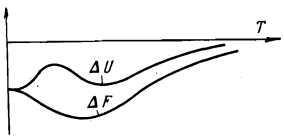

FIG. 4

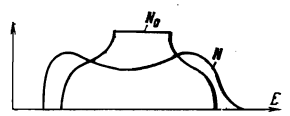

FIG. 5

FIG. 4. Qualitative behavior of the change of free energy (ΔF) and internal energy (ΔU) as functions of the temperature when the ground states of the amorphous system and of the corresponding "crystal" differ, i.e., when the boundary condition (17) with the inequality sign is fulfilled.

FIG. 5. Qualitative behavior of the density of states of a magnetic system when the ground states of the amorphous system and of the corresponding "crystal" differ, i.e., when the boundary condition (17) is fulfilled.

are more easily excited thermally because of the structure fluctuations.

Since the concept of spin waves does not apply to the Ising model and, moreover, is not fully applicable in strongly structurally-disordered systems, it is better to introduce an effective exchange integral. It follows from the behavior of ΔS, ΔC and ΔN that the effective exchange integral $I_{eff}(T) = \langle I\rangle + \Delta I_{eff}(T)$ decreases at low T and increases at high T as a result of structure fluctuations (cf. Fig. 3). It is not clear whether it is possible to describe all the thermodynamic quantities and the density of states by the same effective exchange integral. However, its qualitative temperature dependence should be the same in all cases.

We note that Montgomery et al.[32] calculated the density of states for a weakly amorphous Heisenberg model by the Green function method in the Tyablikov approximation. Their results are in complete agreement with our general conclusions concerning $\Delta N(E)$. For "phonons" in structurally disordered systems, all our conclusions concerning ΔF, ΔS, ΔU, ΔC and ΔN remain valid. Instead of a decrease of the effective stiffness, at low T a decrease of the "phonon" velocity is obtained, and this is of particular interest for amorphous superconductors.

If both negative and positive exchange integrals appear together ("mixed" magnets), the limit condition (19) at T = 0 must be replaced by the inequality (17). Excluding relatively singular distributions of the exchange integrals, e.g., $\langle \mathcal{H}\rangle = 0$, or a large gap in the distribution of exchange integrals close to $\langle I\rangle$, for ΔF and ΔU we obtain the qualitative behavior depicted in Fig. 4. In this more general case also, the qualitative behavior of ΔS and ΔC remains the same as that depicted in Fig. 1. For ΔS and ΔC, we can repeat the arguments given above concerning the role of ΔI_{ij}. Allowance for the decrease of the ground-state energy as a result of the structure fluctuations leads to the behavior shown in Fig. 5 for the density of states of the magnetic system.

8. SIMPLE EXAMPLES

To illustrate the results, we shall consider a few simple examples. For an amorphous one-dimensional Ising system with $S_i^z = \pm 1$, it is possible to calculate exactly all the thermodynamic quantities in the case H = 0 in a simple manner. Its free energy can be determined by introducing the new variable $\xi_i = S_i^z S_{i+1}^z = \pm 1$.

$$F(T) = -\frac{1}{\beta}\left\langle \ln \mathrm{Sp} \times \exp\left[\beta \sum_i I_{i,i+1}\hat{S}_i^z \hat{S}_{i+1}^z\right]\right\rangle$$

Denoting $I_i = I_{i,i+1}$ for brevity, we obtain

$$F(T) = -\frac{1}{\beta}\left\langle \ln \prod_i 4 \operatorname{ch} \beta I_i \right\rangle = -\frac{1}{\beta} N \langle \ln 4 \operatorname{ch} \beta I\rangle.$$

Specifying the distribution function of the exchange integral I, we obtain the free energy by integration.

For a simple distribution of exchange integrals, the internal-energy change ΔU resulting from structure fluctuations, following from Eq. (20), is depicted in Fig. 6. Here, the mean exchange integral is conserved, $\langle I\rangle$ = const, and only its mean-square fluctuations

$$\Delta^2 = \langle (\Delta I)^2\rangle / \langle I\rangle^2.$$

are changed.

It follows from the given distribution of exchange integrals that only positive exchange integrals appear for $\Delta^2 < 1/3$, while negative ones also appear when $\Delta^2 > 1/3$. It can be seen from Fig. 6 that, for $\Delta^2 \leq 0.3$, the internal energy at T = 0, or the ground-state energy, does not change as a result of fluctuations of the exchange integrals. On the other hand, for $\Delta^2 \geq 0.4$, it follows that $\Delta U <$ at T = 0. This result is in complete agreement with the general conclusions about the ground-state energy reached in the preceding section. The general form of the function $\Delta U(T)$ also agrees with the general qualitative predictions (cf. Figs. 1 and 4).

For small fluctuations of the exchange integrals in

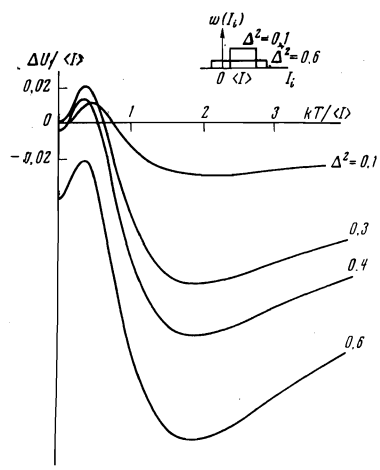

FIG. 6. Change $\Delta U(T)$ of the internal energy for an amorphous one-dimensional Ising model compared with the corresponding "crystal" for different fluctuations $\Delta^2 = \langle (\Delta I_i)^2\rangle / \langle I\rangle^2$ of the exchange integrals, for a rectangular distribution function of the exchange integrals with $\langle I\rangle$ = const.

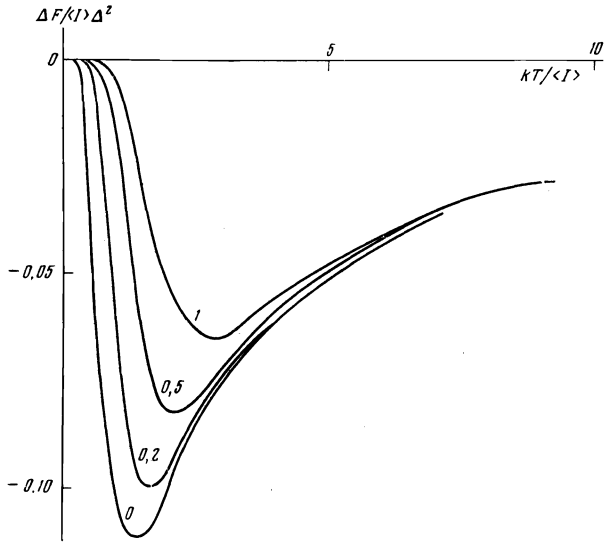

FIG. 7. Change ΔF(T, H) of the free energy as a result of small fluctuations of the exchange integrals for the one-dimensional Ising model with different values of $\mu H/\langle I\rangle$.

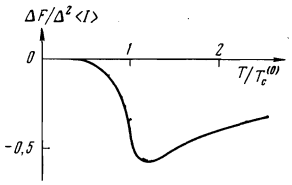

FIG. 8. Change ΔF of the free energy as a result of small fluctuations of the exchange integrals for the two-dimensional Ising model with a square lattice.

the framework of the stochastic "lattice" model, it is possible by means of thermodynamic perturbation theory[35] to obtain, for the one-dimensional Ising model, $\Delta F(T, H)$ (Fig. 7) and all the other thermodynamic quantities (cf. also[44]), and, for the two-dimensional Ising model, $\Delta F(T)$ (Fig. 8) and other thermodynamic quantities for $H = 0$ far from the region $T \approx T_c$. It can be seen that these results too are in complete agreement with the general conclusions of the preceding section.

9. THE ROLE OF STRUCTURE FLUCTUATIONS

The inequalities (12) and (13) and the asymptotic relations (16) are evidence of the close analogy between, on the one hand, the behavior of ΔF_{IM} and ΔF_{HI} and, on the other, the change ΔF of the free energy as a result of the structure fluctuations. Taking into account the well known temperature dependence of the specific heats C_H, C_I and C_M for the Heisenberg and Ising models and the molecular-field approximation respectively, we see that the qualitative behavior of the functions $\Delta C_{IM} = C_I - C_M$ and $\Delta C_{HI} = C_H - C_I$ coincides with the behavior of the function ΔC (cf. Fig. 1). The qualitative agreement between ΔU_{IM}, ΔU_{HI} and ΔU and between ΔS_{IM}, ΔS_{HI} and ΔS also becomes understandable. In addition, as is well known, the inequalities $\Delta M_{IM} \equiv M_I - M_M \leq 0$ and $\Delta M_{HI} \equiv M_H - M_I \leq 0$ for the spontaneous magnetization are fulfilled.

Thus, the transition from the molecular-field approximation to the Ising model or from the Ising model to the Heisenberg model leads to the same qualitative changes of the thermodynamic quantities as in the transition to an amorphous system from the corresponding "crystal" described by the averaged Hamiltonian (5) or (10). This analogy can be understood in the following way. If for the crystal we write the Hamiltonian in the molecular-field approximation in the form

$$\mathcal{H}_M = -\sum_i \hat{S}_i^z \sum_j I_{ij} \overline{\hat{S}^z}^M, \tag{21}$$

then, on going over to the Ising model

$$\mathcal{H}_I = -\sum_i \hat{S}_i^z \sum_j I_{ij} \hat{S}_j^z, \tag{22}$$

additional fluctuations of the "internal field" in which spin i is situated appear as a result of the replacement $\hat{S}^{zM} \to \hat{S}^z_j$. In this transition, the equation $\overline{H}_i^M = 0$ is fulfilled, or

$$\overline{\Delta \hat{S}_j^z}^M \equiv \overline{(\hat{S}_j^z - \overline{\hat{S}^{zM}})}^M = 0. \tag{23}$$

Therefore, the change in the thermodynamic properties of the chosen spin on going over from the molecular-field approximation to the Ising model arise because of the additional fluctuations (additional degrees of freedom) of its "individual internal field." The situation on going over from the Ising model to the Heisenberg model can be represented completely analogously.

It can be seen directly that the transition $\langle I\rangle \to \langle I\rangle + \Delta I_{ij}$, i.e., the transition to the amorphous system from the corresponding "crystal," entails, e.g., additional fluctuations of the "individual internal field" of the spin i in the Hamiltonians (21) and (22); the condition $\langle \Delta I_{ij}\rangle = 0$, which is analogous to the condition (23), is satisfied.

This treatment shows that, in all cases, the additional fluctuations of the "internal field" of the chosen spin are the reason for the change in the thermodynamic quantities; this also explains the analogy described. On the basis of this analogy, we conclude that a sharp phase transition can exist in amorphous ferromagnets too, if the exchange integrals fluctuate stochastically.

Taking into account the well known inequalities for the Curie temperatures, $T_c^{(H)} \leq T_c^{(I)} \leq T_c^{(M)}$, we may conclude that structure fluctuations lead to a decrease of the Curie temperature, i.e., $T_c \leq T_c^{(0)}$. All known consistent calculations confirm this conclusion[2,31,32,34-36].

Taking into account the temperature dependence of the effective exchange integral (cf. Sec. 7), one can also understand the flattening, found in a number of papers[2,5,12], of the curve of the reduced magnetization. The analogy also suggests a tendency of the critical coefficients to change as a result of the fluctuations.

The analogy disappears if the exchange integrals vary more or less systematically over large distances, e.g., as a result of mechanical stresses. In this case, so-called "smeared" phase transitions can arise.

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[1)] An increase was obtained for T_c and χ in a "more exact" molecular field approximation [33].

[2)] True, fluctuations of the atomic spin S_i should strictly be treated in the framework of the band model, but they can be included formally in local models of magnetism, if only in the case $S_i \to \infty$.

[3)] The magnetic field H is constant throughout this section and is therefore omitted.

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