Theory of phase transitions in solid solutions

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A generalization of the cluster approximation to the case of solid solutions is discussed. The method is applied to describe Ising and Heisenberg models consisting of particles of different types; both mobile and fixed impurities are considered. Expressions are given for the thermodynamic functions at all temperatures T, fields H, and concentrations c_i, with the structure of the unit cell taken into account. The results are directly applicable to magnetic insulators; this is illustrated with the impurity-free ferrite yttrium iron garnet as an example. The problems of phase separation in alloys and ordering of magnetic alloys are also considered. In a number of cases the results are a substantial improvement on the accuracy of the molecular-field approximation.

1. INTRODUCTION

Features of phase transitions in solid solutions, their magnetic, ferroelectric and other cooperative properties are widely discussed in the literature. Exact results in this field are not numerous [1–4], but there are a number of indications that these properties can differ appreciably from those in the case of pure systems [4–6].

The simplest method for describing these phenomena theoretically is the molecular-field approximation (MFA) (see, e.g., [7–9]). But in the present case, unlike in pure systems, this approximation can lead to qualitatively incorrect results. Thus, the MFA does not give the differences in the magnetic properties of alloys with mobile and fixed atoms that appear in more exact treatments. In the case of fixed nonmagnetic impurities in a magnet the MFA predicts a phase transition for any impurity concentration c, although it is physically clear that in a system with short-range interaction at small 1 – c the magnetic atoms are isolated and ferromagnetism is impossible. Apart from this, the MFA is also often unsatisfactory in the description of pure systems, if in the latter there are strong short-range correlations, as in the ferroelectrics KH_2PO_4, $NaH_3(SeO_3)_2$ and many other others[10,11].

In view of this, it seems desirable to seek other sufficiently simple but more exact methods for describing the phase transitions in solid solutions. Thus, in[12] a certain generalization of the coherent-potential approximation (CPA) used in the description of the excitation spectra in alloys was proposed to describe the magnetic properties of an alloy of two Heisenberg ferromagnets. For fixed nonmagnetic impurities this approximation already leads to the disappearance of magnetism at a certain concentration, but for the pure substance the approximation in[12] coincides with the MFA, so that its accuracy is, in any case, scarcely higher. Low-temperature approximations related to the CPA have been discussed in[13,14], but, as shown below, their accuracy is also clearly not too high.

In this paper we shall discuss in detail another variant for improving the MFA—the cluster approximation, which for pure Ising and Heisenberg models turns out to be appreciably more exact than the MFA[10,15]. It also has high accuracy in the description of the above-mentioned systems with short-range correlations[10,11]. In alloys this approximation picks up the difference in the properties of mobile and fixed impurities, and for fixed nonmagnetic impurities describes the dissappearance of the magnetism at concentrations above a certain value. At the same time, this approximation is technically only a little more complicated than the MFA.

The above properties of the cluster approximation were noted a fairly long time ago, and it has been applied in a number of papers[16–19] to the study of Ising and Heisenberg models with nonmagnetic impurities. However, the authors gave their main attention to discussing the concentration dependence of the Curie temperature $T_c(c)$. Other properties, the case of an alloy of several magnets, phase-separation effects and ordering in alloys with mobile atoms, etc., were not considered in these papers. Taking into account the growing interest in these questions, it is clear that it will be useful to discuss the complete results of the cluster approximation in solid solutions for the two principal models used in the theory of phase transitions – the Ising and Heisenberg models.

For brevity we shall confine ourselves to alloys of the substitutional type; the generalization to interstitial alloys is sufficiently obvious. The principal features of the approximation will be described in detail in Sec. 2, using the simpler example of the Ising model. For comparison, the results of the MFA are also given. In Sec. 3 the relations obtained are generalized to the case of the Heisenberg model and a complex unit cell. In Sec. 4 phase separation and ordering of alloys are considered. The application to the Slater model and to crystals of the type $K(H_xD_{1-x})_2PO_4$ will be made in another paper.

To avoid misunderstanding, we remark here that, although we shall often use the term "alloy" for brevity, the models used actually imply application primarily to dielectric solid solutions. The application to metallic alloys, as mentioned in Sec. 4, requires a more careful treatment in each specific case.

2. ISING MODEL

The Ising model is used principally to describe structural and ferroelectric phase transitions[10], but for brevity and uniformity of the expressions we shall use "magnetic" terminology. We shall consider an Ising lattice consisting of atoms of several types, positioned only at lattice sites, and let the interaction potential for atoms of type i and type k situated at the sites $\mathbf{r}$ and $\mathbf{r}'$ be made up of an "exchange" potential $J_{ik}(\mathbf{r}-\mathbf{r}')$, depending on the spins, and a nonexchange part $V_{ik}(\mathbf{r}-\mathbf{r}')$. Then the Hamiltonian can be written in the form

$$\mathscr{H}=-\frac{1}{2}\sum_{\mathbf{r}\mathbf{r}'ik}\eta_{\mathbf{r}}^{i}\eta_{\mathbf{r}'}^{k}[J_{ik}(\mathbf{r}-\mathbf{r}')\sigma_{\mathbf{r}}^{z}\sigma_{\mathbf{r}'}^{z}+V_{ik}(\mathbf{r}-\mathbf{r}')]-H\sum_{\mathbf{r}i}\eta_{\mathbf{r}}^{i}g_{i}\sigma_{\mathbf{r}}^{z}. \quad (1)$$

Here H is the external field and g_i is the magnetic moment of an atom of type i. The quantities $\eta_{\mathbf{r}}^{i}$ describe the distribution of the atoms over the sites[8]: if the site $\mathbf{r}$ is occupied by an atom of type k, then $\eta_{\mathbf{r}}^{i} = \delta_{ik}$. The average over the lattice, $\langle\eta_{\mathbf{r}}^{i}\rangle$, is, by definition, the atomic concentration c_i. For fixed atoms the distribution $\{\eta_{\mathbf{r}}^{i}\}$ over the sites is specified. For mobile atoms (i.e., if the time of relaxation of the distribution over the sites is shorter than the time of thermodynamic experiments), the results must be averaged over all distributions $\{\eta_{\mathbf{r}}^{i}\}$.

a) The MF approximation. Several forms of the MFA for alloys are described in the literature[7-9]; we shall use that which seems to us the most consistent for the models being investigated[8,9]. We begin with the case of fixed atoms; then the term with V_{ik} in 1 is an inessential constant which for brevity will be omitted below, in expressions (2) and (3).

We shall separate in (1) the lattice averages $\langle\eta_{\mathbf{r}}^{i}\sigma_{\mathbf{r}}^{z}\rangle = c_i\sigma_i$, where σ_i is the average value $\langle\sigma_{\mathbf{r}}^{z}\rangle$ for atoms of type i, and the fluctuations, or deviations, from these values:

$$\begin{aligned}\mathscr{H} = \frac{1}{2}N\sum_{ik} c_i\sigma_i c_k\sigma_k J_{ik}{}^0 - \sum_{\mathbf{r}i}\eta_{\mathbf{r}}{}^i\sigma_{\mathbf{r}}{}^z\Big(g_iH + \sum_k J_{ik}{}^0 c_k\sigma_k\Big)\\ -\frac{1}{2}\sum_{\mathbf{r}\mathbf{r}'ik} J_{ik}(\mathbf{r}-\mathbf{r}')\,(\eta_{\mathbf{r}}{}^i\sigma_{\mathbf{r}}{}^z - c_i\sigma_i)\,(\eta_{\mathbf{r}}{}^k\sigma_{\mathbf{r}}{}^z - c_k\sigma_k).\end{aligned} \tag{2}$$

Here N is the total number of sites (atoms); $J_{ik}^{0} = \sum_{\mathbf{r}} J_{ik}(\mathbf{r})$. For the MFA to be applicable, it is necessary that the number of particles of each type in the sphere of influence of the potential $J_{ik}(\mathbf{r})$ be large. Then the term with interaction fluctuations in (2) is small and can be discarded, and the consistency equation for σ_i and the free energy per atom (F) take the form

$$\sigma_i = \operatorname{th}\alpha_i,\quad \alpha_i = \beta\Big(g_iH + \sum_k J_{ik}{}^0 c_k\sigma_k\Big),\quad \beta = 1/T; \tag{3a}$$

$$F = \frac{1}{2}\sum_{ik} c_i\sigma_i c_k\sigma_k J_{ik}{}^0 - T\sum_i c_i \ln 2\operatorname{ch}\alpha_i. \tag{3b}$$

The relations (3) determine the thermodynamics of the system. Thus, in a two-component alloy we obtain for the transition point T_c and the para-phase susceptibility $\chi_p(T)$:

$$D(T_c) = 0,\quad D(T) = 1 - \beta(c_1J_{11}{}^0 + c_2J_{22}{}^0) + \beta^2c_1c_2[J_{11}{}^0J_{22}{}^0 - (J_{12}{}^0)^2]; \tag{4a}$$

$$\begin{aligned}\chi_p(T) &= \frac{\partial}{\partial H}\Big(\sum_i g_ic_i\sigma_i\Big)\Big|_{H\to 0}\\ &= \frac{1}{TD(T)}[g_1{}^2c_1 + g_2{}^2c_2 - \beta c_1c_2(g_1{}^2J_{22}{}^0 - 2g_1g_2J_{12}{}^0 + g_2{}^2J_{11}{}^0)].\end{aligned} \tag{4b}$$

From (4a) it can be seen, in particular, that for nonmagnetic impurities ($J_{12}^{0} = J_{22}^{0} = 0$) a phase transition exists in this approximation for arbitrarily small $c_1 = c$, and $T_c = cJ_{11}^{0}$ falls linearly with c.

In the approximation described, the effect of the impurity distribution $\{\eta_{\mathbf{r}}^{i}\}$ is described only by the average values $\langle\eta_{\mathbf{r}}^{i}\rangle = c_i$. It is clear, therefore, that for mobile atoms too the equation for σ_i will have the same form (3a), and the expression for F will differ from (3b) only by the term with V_{ik} that was not written out and by a term corresponding to the configurational entropy, i.e., to allowance for the different possible permutations of the atoms over the lattice. For the following, however, it is convenient to treat the problem of mobile atoms by another method, calculating not F but the thermodynamic potential Ω with variable $N_i = Nc_i$:

$$\Omega = F - \sum_i \mu_ic_i = -\frac{T}{N}\ln\operatorname{Sp}e^{-\beta\mathscr{H}'},\quad \mathscr{H}' = \mathscr{H} - \sum_{\mathbf{r}i}\mu_i\eta_{\mathbf{r}}{}^i, \tag{5a}$$

$$c_i = -\partial\Omega/\partial\mu_i. \tag{5b}$$

The symbol Sp in (5a) denotes summation over all sets $\{\sigma_{\mathbf{r}}^{z}\}$ and $\{\eta_{\mathbf{r}}^{i}\}$, and the Hamiltonian $\mathscr{H}$ in the MFA differs from the first two terms of (2) only by the terms with V_{ik}. The equations for μ_i in terms of c_i and for σ_i are given by the consistency conditions for $\langle\eta_{\mathbf{r}}^{i}\rangle$ and $\langle\eta_{\mathbf{r}}^{i}\sigma_{\mathbf{r}}^{z}\rangle$ (which are equivalent to (5b) and to the condition for minimizing with respect to the σ_i: $\partial\Omega/\partial\sigma_i = 0$):

$$c_i = \frac{e^{\beta\mu_i'}\operatorname{ch}\alpha_i}{\sum_k e^{\beta\mu_k'}\operatorname{ch}\alpha_k},\quad c_i\sigma_i = \frac{e^{\beta\mu_i'}\operatorname{sh}\alpha_i}{\sum_k e^{\beta\mu_k'}\operatorname{ch}\alpha_k}, \tag{6}$$

where $\mu_i' = \mu_i + \Sigma V_{ik}^{0}c_k$, and V_{ik}^{0} is defined analogously to J_{ik}^{0} in (2).

Dividing the second equation by the first we arrive at (3a), and expressing μ_i in terms of c_i by the first equation (6) and transforming back to $F = \Omega + \Sigma c_i\mu_i$, we obtain

$$F = F_{\text{fix}} + T\sum_i c_i\ln c_i - \frac{1}{2}\sum_{ik} c_ic_kV_{ik}{}^0, \tag{7}$$

where F_{fix} is the free energy (3b) of the fixed atoms. The second term is clearly the above-mentioned entropy term, and the third corresponds to the term with V_{ik}, calculated in the MFA.

(b) The cluster approximation. Fixed atoms. We shall use the cluster approximation in the form described in[10,15,18]. For the Ising model it is equivalent to the so-called quasi-chemical approximation, by means of which certain problems in the theory of alloys have been treated[16,20]. However, we shall present a derivation of the basic thermodynamic relations, since different generalizations of the previous results will then be obtained in a highly compact form. In addition, the results will permit a direct generalization to quantum systems too—in particular, to the Heisenberg model, for which the quasi-chemical method is not directly applicable.

Suppose that each atom in (1) interacts only with n nearest neighbors in the lattice and that the potentials J_{ik}, V_{ik} are the same for all neighboring atoms of types i and k, as, e.g., in the simple cubic (sc), bcc or fcc lattices. If, for convenience of notation, we select a certain direction for each bond in the lattice (e.g., in the positive direction along certain crystal axes), the average value E of the energy per atom can be written, according to (1), in the form

$$E = \frac{1}{N}\langle\mathscr{H}\rangle = -\frac{n}{2}\sum_{ik} w_{ik}(J_{ik}\langle\sigma_i{}^z\sigma_k{}^z\rangle + V_{ik}) - H\sum_i g_ic_i\langle\sigma_i{}^z\rangle. \tag{8}$$

Here $\langle\sigma_i^{z}\sigma_k^{z}\rangle$ is the lattice average of the product of the spins of neighboring atoms of types i and k, and w_{ik} is the frequency of appearance of bonds going from an atom i to an atom k, i.e., the ratio of the number N_{ik} of such bonds to the total number of bonds ($N_{\text{bonds}} = 1/2nN$). The quantities w_{ik} are connected with the concentrations by the relation

$$\sum_k w_{ik} = c_i. \tag{9}$$

For a completely disordered alloy ("quenching from high temperatures"), $w_{ik} = c_ic_k$. For quenching from a finite temperature the difference $w_{ik} - c_ic_k \neq 0$ and its magnitude can serve as a measure of the correlation of the positions of the atoms in the alloy. For mobile atoms this quantity varies also with variation of T or H.

To calculate the averages in (8) in the cluster approximation we shall introduce, as usual[10], one-particle and two-particle clusters and shall assume that the effect of the external particles on a particle of a cluster can be described by a field $n\varphi_i$ depending only on the type i of the particle and proportional to the number n of its neighbors. Then the cluster Hamiltonians H_1 and H_2 can be written in the form

$$H_1{}^i=-\sigma_i{}^z(g_iH+n\varphi_i), \tag{10a}$$

$$H_2{}^{ik}=-(J_{ik}\sigma_i{}^z\sigma_k{}^z+V_{ik})-\sigma_i{}^z[g_iH+(n-1)\varphi_i] -\sigma_k{}^z[g_kH+(n-1)\varphi_k]. \tag{10b}$$

In (10b) it has been taken into account that in a binary cluster one of the neighbors is already included in the cluster, so that only n − 1, and not n, neighbors are external for a given atom.

Assuming that the density matrices of each of the clusters can be written in the form

$$\rho_{1,2}=\text{const}\cdot\exp(-\beta H_{1,2}), \tag{11}$$

we shall require that averaging the matrix ρ_2^{ik} over the variables of the atom k give the matrix ρ_2^{i}, or, which is the same thing[10], that the average values $\langle\eta_{\mathbf{r}}^{i}\sigma_{\mathbf{r}}^{z}\rangle_1$ and $\langle\eta_{\mathbf{r}}^{i}\sigma_{\mathbf{r}}^{z}\rangle_2$ calculated from the one-particle and binary clusters coincide:

$$\langle\eta_r{}^i\sigma_r{}^z\rangle=c_i\sigma_i=c_i\frac{\operatorname{Sp}\sigma_i{}^z\exp(-\beta H_1{}^i)}{\operatorname{Sp}\exp(-\beta H_1{}^i)}=\sum_k w_{ik}\frac{\operatorname{Sp}\sigma_i{}^z\exp(-\beta H_2{}^{ik})}{\operatorname{Sp}\exp(-\beta H_2{}^{ik})}. \tag{12}$$

Using the relation (10b), we supplement the average $J_{ik}\langle\sigma_i^z\sigma_k^z\rangle$ in (8) to give the total Hamiltonian $\langle H_2^{ik}\rangle$, collecting the remaining terms into the one-particle Hamiltonians $\langle H_1^i\rangle$. Integrating next the thermodynamic identity $E = \partial(\beta F)/\partial\beta$ over β using (12), we obtain[10]

$$F=\frac{n}{2}\sum_{ik}w_{ik}F_{ik}-(n-1)\sum_i c_iF_i; \tag{13a}$$

$$F_{ik}=-T\ln Z_{ik}=-T\ln\operatorname{Sp}e^{-\beta H_2{}^{ik}},\qquad F_i=-T\ln Z_1{}^{(i)}=-T\ln\operatorname{Sp}e^{-\beta H_1{}^i}. \tag{13b}$$

Eqs. (12) can also be obtained by minimizing F. If we regard the expression (13) with unknown φ_1 as given, the conditions $\partial F/\partial\varphi_1 = 0$ give (12).

Calculating the partition functions Z in (13), we find

$$Z_{ik}=2e^{\beta(V_{ik}+J_{ik})}(\operatorname{ch}2\beta h_{ik}{}^++e^{-2\beta J_{ik}}\operatorname{ch}2\beta h_{ik}{}^-),\quad Z_1{}^{(i)}=2\operatorname{ch}\beta h_i. \tag{14}$$

here $h_i = g_iH + n\varphi_i$, $2h_{ik}^{\pm} = (g_i \pm g_k)H + (n-1)(\varphi_i \pm \varphi_k)$, and the φ_i are determined by Eq. (12):

$$c_i\operatorname{th}\beta h_i=\sum_k w_{ik}\frac{\operatorname{sh}2\beta h_{ik}{}^++e^{-2\beta J_{ik}}\operatorname{sh}2\beta h_{ik}{}^-}{\operatorname{ch}2\beta h_{ik}{}^++e^{-2\beta J_{ik}}\operatorname{ch}2\beta h_{ik}{}^-}. \tag{15}$$

We shall discuss the case of a two-component alloy in more detail. In this case, for T_c and $\chi_p(T)$ we obtain, in place of (4)

$$D(T_c)=0,\qquad D(T)=1-(b_{11}+b_{22})+b_{11}b_{22}-b_{12}{}^2, \tag{16a}$$

$$\chi_p(T)=\frac{n}{(n-1)TD(T)}[g_1{}^2c_1(1-b_{22})+2g_1g_2\sqrt{c_1c_2}\,b_{12} +g_2{}^2c_2(1-b_{11})]-\frac{1}{(n-1)T}(g_1{}^2c_1+g_2{}^2c_2), \tag{16b}$$

where $b_{ik} = (c_ic_k)^{-1/2}w_{ik}(n-1)\tanh\beta J_{ik}$.

Comparing (16a) and (4a), we see that if there is no correlation in the positions ($w_{ik} = c_ic_k$) Eq. (16a) for T_c differs from the MFA result by replacement of the quantities $\beta_c\overset{0}{J}_{ik} = \beta_c nJ_{ik}$ by $(n-1)\tanh\beta J_{ik}$. These quantities are close to each other when n is large, and the constants J_{ik} are of the same order, so that the values $\beta_cJ_{ik} \sim 1/n \ll 1$. If these conditions are not fulfilled or if the correlation of the positions of the atoms is strong, the cluster approximation not only increases the accuracy but also corrects qualitatively incorrect MFA results.

Thus, in the one-dimensional case (n = 2) the MFA predicts a phase transition, which is absent according to (16a). In this case, in the absence of a field H, the expression (13) for F, as in the no-impurity case[10], turns out to be exact[3]. Another well-known example is the case of nonmagnetic impurities ($J_{12} = J_{22} = g_2 = 0$) (for a disordered alloy ($w_{ik} = c_ic_k$) the relations (13)–(16) then go over into the results of the paper[16]). Eq. (16a) takes the form $b_{11} = 1$, and for $(n-1)\,w_{11} < c_1$ (for $c_1 \le c_0 = 1/(n-1)$ in the case of a disordered alloy) there is no phase transition, in contrast to the MFA result.

For the case of nonmagnetic impurities we shall also indicate the behavior of T_c, $\chi_p(T)$ and the saturation polarization per magnetic atom (σ_s) near the critical concentration, i.e., for small values of $w_{11}-c_1c_0$. These dependences were not discussed in[16], but may be of interest, in particular, in connection with the somewhat unexpected results of the numerical calculations for an Ising model with nonmagnetic impurities in[6]:

$$T_c=2J/\ln\frac{2}{\varepsilon},\qquad \sigma_s=a\sqrt{\varepsilon},\qquad a=\left[\frac{3(1+c_0)^2}{(4+c_0)(1-c_0)}\right]^{1/2}; \tag{17a}$$

$$\chi_p(T)=\beta g^2c\frac{c+w_{11}\operatorname{th}\beta J}{c-(n-1)w_{11}\operatorname{th}\beta J},$$

$$\chi_p(T)\,|_{T-T_c\ll T_c{}^2/J}=\frac{g^2c_0(1+c_0)}{2J\varepsilon}\frac{1}{T-T_c}. \tag{17b}$$

Here $J = J_{11}$, $g = g_1$, $c = c_1$ and $\epsilon = w_{11}/c_1c_0 - 1 \ll 1$. Thus, in this approximation the phase transition with respect to the concentration is a second-order transition, and the Curie-Weiss constant increases without limit as $\epsilon \to 0$. The latter fact agrees qualitatively with the sharp increase in the susceptibility near T_c on increase of the concentration of nonmagnetic impurities, displayed in the numerical calculations of[6].

c) The cluster approximation. Mobile atoms. In describing alloys with an equilibrium distribution of atoms we shall again calculate the potential Ω (5a). As above, we shall introduce effective cluster Hamiltonians H_1' (for one site) and H_2' (for a pair of neighboring sites):

$$H_1'=-\sum_i\eta_1{}^i(h_i\sigma_1{}^z+\mu_i+n\nu_i); \tag{18a}$$

$$H_2'=-\sum_{ik}\eta_1{}^i\eta_2{}^k(J_{ik}\sigma_1{}^z\sigma_2{}^z+V_{ik})-\sum_i h_i^{(2)}(\eta_1{}^i\sigma_1{}^z+\eta_2{}^i\sigma_2{}^z) -\sum_i(\eta_1{}^i+\eta_2{}^i)[\mu_i+\nu_i(n-1)]. \tag{18b}$$

Here h_i is the same as in (14); $h_i^{(2)} = h_i - \varphi_i$; $n\nu_i$ is the renormalization (analogous to $n\varphi_i$) of the chemical potential μ_i by the interaction and, as for φ_i above, will be assumed to be proportional to the number n of neighbors. In accordance with this, this renormalization is written as $(n-1)\,\nu_i$ in the binary cluster (18b).

Arguing by analogy with the derivation of (13) – in particular, using the thermodynamic relation

$$\frac{\partial}{\partial\beta}(\beta\Omega)=E-\sum_i\mu_ic_i, \tag{19}$$

we obtain for the potential Ω:

$$\beta\Omega=-\frac{n}{2}\ln Z_2+(n-1)\ln Z_1. \tag{20}$$

Here,

$$Z_1=\sum_i x_iZ_1^{(i)},\qquad Z_2=\sum_{ik}y_iy_kZ_{ik}; \tag{21a}$$

$$x_i=\exp\{\beta(\mu_i+n\nu_i)\},\quad y_i=\exp\{\beta\mu_i+\beta(n-1)\nu_i\} \tag{21b}$$

and Z_{ik}, $Z_1^{(i)}$ are the same as in (13b), (14). An equation for ν_i and μ_i in terms of the concentrations is obtained from the consistency conditions for $\langle\eta_{\mathbf{r}}^i\rangle = c_i$, calculated in terms of the one-particle and binary clusters, or from the equivalent relations (5b) and the fact that Ω must be a minimum with respect to ν_i $(\partial\Omega/\partial\nu_i = 0)$:

$$x_i Z_1^{(i)} \Big/ \Big(\sum_k x_k Z_1^{(k)}\Big) = y_i \sum_k y_k Z_{ik} \Big/ \Big(\sum_{kl} y_k y_l Z_{kl}\Big) = c_i. \tag{22}$$

Here, since the relations (22) determine x_i and y_i only up to a common factor, these quantities can be normalized by one additional condition e.g., $\prod_i x_i = \prod_i y_i = 1$. From the relations (19), (20) and (8) we can also obtain an expression for the quantities w_{ik} introduced in (8) and (10):

$$w_{ik} = y_i y_k Z_{ik}/Z_2. \tag{23}$$

Finally, the consistency equations for the quantities $\langle\eta_{\mathbf{r}}^i \sigma_{\mathbf{r}}^z\rangle$ (or the conditions that minimize Ω with respect to the σ_i) have the previous form (12), (15), but the quantities w_{ik} are now determined by Eqs. (23), (22) and vary with T and H.

The relations (18)–(23) and (12) determine the thermodynamics of the system. So far, they have been derived only for the case when atomic order is absent and all the lattice sites are equivalent. Generalizations to the case of several sublattices (in particular, ordering alloys) are given below in Secs. 3 and 4.

In the case of a two-component alloy Eqs. (22) for $x_1 = 1/x_2$ and $y_1 = 1/y_2$ are easily solved, and for the quantity Ω, the chemical potential $\mu = \mu_1 = -\mu_2$ and the relative probabilities w_{ik} we have, from (21) and (23),

$$\beta\Omega = -\frac{n}{2}\ln\frac{Z_{12}(1+R)}{2c_1c_2} + \frac{n-1}{2}\ln\frac{Z_1^{(1)}Z_1^{(2)}}{c_1c_2}, \tag{24a}$$

$$\beta\mu = \frac{n}{2}\ln\left(\frac{R+c_1-c_2}{2c_2}\frac{Z_{12}}{Z_{11}}\right) - \frac{n-1}{2}\ln\left(\frac{c_1}{c_2}\frac{Z_1^{(1)}}{Z_1^{(2)}}\right), \tag{24b}$$

$$w_{12} = \frac{2c_1c_2}{1+R}, \quad w_{11} = c_1 - w_{12}, \quad w_{22} = c_2 - w_{12}. \tag{24c}$$

Here,

$$R = \sqrt{(c_1-c_2)^2 + 4c_1c_2z}, \quad z = Z_{11}Z_{22}/Z_{12}^2. \tag{25}$$

We note that for the one-dimensional case (n = 2) the results (20)–(25), in contrast to the case of fixed atoms, turn out to be exact even in the presence of a field H[3].

The magnetic properties in the para-phase and near the Curie point T_c can be studied by expanding the relations (24) and (12) in h_i. But for small h_i we can confine ourselves to the linear terms in (12), neglecting the dependence of w_{ik} on h_i. Therefore, the relations (16a), (16b) for T_c and $\chi_p(T)$ retain their form, but for the quantities $w_{ik}(T)$ we must substitute the expressions (24c), (25) with "paramagnetic" values of the quantities

$$Z_{ik} = 2\exp(\beta V_{ik})\,\mathrm{ch}\,\beta J_{ik}.$$

In this case it can be seen from the expression (24c) for w_{12} that if we introduce the energy parameter u by the relation

$$u = v + J, \quad v = V_{11} + V_{22} - 2V_{12}, \quad J = |J_{11}| + |J_{22}| - 2|J_{12}|, \tag{26}$$

then values $u < 0$ correspond to a tendency toward atomic ordering (alternation of atoms of different types) – as T is lowered the quantity w_{12} tends to its maximum possible value min (c_1, c_2). Positive u correspond to a tendency to phase separation: as $T \to 0$, $w_{12} \to 0$.

We shall also discuss, as above, the case of nonmagnetic impurities $(J_{12} = J_{22} = 0)$. The concentration dependence $T_c(c)$ can be found by substituting expression (24c) for w_{11} into (16a). The equation obtained is conveniently solved for the concentration $c(T_c)$:

$$c = \frac{\xi}{2\xi - 1 + z(\xi-1)^2}, \tag{27}$$

where

$$\xi = (n-1)\,\mathrm{th}\,\beta J, \quad z = e^{\beta v}\,\mathrm{ch}\,\beta J.$$

Eq. (27) is analogous to the corresponding equation for the case of a Heisenberg magnet, which was considered in detail in[18] and is discussed below taking into account the possibilities of phase separation or ordering in the alloy. Here we remark only that, if $u = v + J > 0$ – in particular, if $v = 0$, then in contrast to the case of fixed impurities Eq. (27) has a solution for arbitrarily small c (curve 6 in Fig. 3), although in reality for small c the curve (27) lies in a region that is unstable with respect to phase separation.

3. HEISENBERG MODEL

In the description of quantum systems – in particular, of the Heisenberg model, the cluster approximation encounters well-known formal difficulties at low T. Thus, in the original Bethe-Peierls-Weiss form (cf., e.g.,[15,19]), it gives an "anti-Curie point", i.e., vanishing of the magnetization at a certain $T = T_{ac}$. In the form used here[15,18] an anti-Curie point does not arise for a ferromagnet, but quantum spin-fluctuations in the cluster lead to incomplete saturation of the moment as $T \to 0$, which is absent in the exact solution or in the MAF:

$$\langle S^z\rangle_{T\to 0} \to S - 2^{-n} + O(n/2^{2n}). \tag{28}$$

However, it can be seen from (28) that for three-dimensional lattices with $n \geq 6$ this fictitious deviation from saturation is small, especially for larger $S \geq 1$, and is appreciable only when T is so low that other approximations, e.g., the spin-wave approximation, can be used to describe the system. But in the region of intermediate $T \lesssim T_c$, where the main change in the magnetization occurs, the above approximation clearly turns out to be appreciably more accurate than the MFA:

For a Heisenberg antiferromagnet the difficulty with the anti-Curie point remains[15,18]. It is shown below, however, that for large S or n this point lies well below the Néel point T_N, so that the approximation used (just as in the analogous treatment of the tunneling effects in KH_2PO_4[10]) clearly has a wide range of applicability. The question of the anti-Curie point for ferrites is discussed below.

With a view to application to real magnetic insulators, the majority of which are ferrites, we shall consider the general case of a Heisenberg ferromagnet with several spins per unit cell, situated in inequivalent positions. As above, we shall confine ourselves to substitutional alloys, taking only the nearest-neighbor interactions into account, and shall consider first the case of fixed atoms.

We denote the number of equivalent atoms in the unit cell of an impurity-free lattice by m_λ, the number of crystallographically equivalent bonds (interactions) linking an atom in a position λ with its neighbors in positions ν by $n_{\lambda\nu}$, and the ratio (analogous to w_{ik} in (8) and (9)) of the number of bonds going from atoms of type i in positions λ to atoms of type k in positions ν to the total number of bonds going from atoms in positions

λ to positions ν by $w_{ik}^{\lambda\nu}$. In analogy with (9), the sum over k of the quantities $w_{ik}^{\lambda\nu}$ equals $c_{i\lambda}$—the concentration of atoms of type i at sites λ, i.e., equals the ratio of the number of such sites occupied by atoms of type i to the total number of such sites. For a pure ferrite, in which each of the atoms i occupies a definite position λ, we have: $c_{i\lambda} = \delta_{i\lambda}$; $w_{ik}^{\lambda\nu} = \delta_{i\lambda}\delta_{k\nu}$.

In this notation the expression that generalizes (13a) for the free energy F per unit cell takes the form

$$\beta F=-\frac{1}{2}\sum_{\lambda\nu ik} m_\lambda n_{\lambda\nu} w_{ik}^{\lambda\nu}\ln Z_{ik}^{\lambda\nu}+\sum_{\lambda i} m_\lambda (n_\lambda-1)c_{i\lambda}\ln Z_1^{i\lambda}. \qquad (29)$$

Here $n_\lambda = \sum_\nu n_{\lambda\nu}$ is the total number of bonds of the atom λ, and the partition functions Z_{ik}, Z_1 and the corresponding Hamiltonians H_{ik}, H_1 are given by the expressions

$$Z_1^{i\lambda}=\mathrm{Sp}\, e^{-\beta H_1^{i\lambda}},\quad H_1^{i\lambda}=-S_i^z h_{i\lambda}, \qquad (30a)$$

$$Z_{ik}^{\lambda\nu}=\mathrm{Sp}\, e^{-\beta H_{ik}^{\lambda\nu}},\quad H_{ik}^{\lambda\nu}=-J_{ik}^{\lambda\nu}\mathbf{S}_i\mathbf{S}_k-V_{ik}^{\lambda\nu}-h_{i\lambda}^{(\nu)}S_i^z-h_{k\nu}^{(\lambda)}S_k^z, \qquad (30b)$$

where $V_{ik}^{\lambda\nu}$, as above, is the non-exchange part of the interactions, and the effective fields h are defined by analogy with the quantities h in (14), (18):

$$h_{i\lambda}=g_{i\lambda}H+\varphi_{i\lambda},\quad \varphi_{i\lambda}=\sum_\nu n_{\lambda\nu}\varphi_{i\lambda}^{\nu},\quad h_{i\lambda}^{(\nu)}=h_{i\lambda}-\varphi_{i\lambda}^{\nu}. \qquad (31)$$

According to (31), the quantity $\varphi_{i\lambda}^{\nu}$ has the meaning of the mean effective field acting on atom i in position λ, due to its neighbor in position ν. The total field $\varphi_{i\lambda}$ is obtained, as usual, by summing the contributions from all neighbors. Equations for the quantities $\varphi_{i\lambda}^{\nu}$ can be obtained from the consistency conditions or by minimizing F, after which the average spin $\langle S_{i\lambda}^z\rangle$ can be found, e.g., in terms of its value in a one-particle cluster:

$$\partial F/\partial\varphi_{i\lambda}^{\nu}=0, \qquad (32a)$$

$$\langle S_{i\lambda}^z\rangle=b(S_{i\lambda},\ \beta h_{i\lambda}), \qquad (32b)$$

where

$$b(S,\ x)=(S+{}^1/_2)\,\mathrm{cth}\,(S+{}^1/_2)x-{}^1/_2\mathrm{cth}\,(x/2)$$

is the Brillouin function.

The quantities Z_1 in (30) are simply calculated, but to find Z_{ik} it is necessary to diagonalize the matrix of the pair Hamiltonian H_{ik}, which has the form

$$(H_{ik}^{\lambda\nu})_{jm,j'm'}=\delta_{mm'}\Big[\frac{1}{2}\delta_{jj'}[S_i(S_i+1)+S_k(S_k+1)-j(j+1)]J_{ik}^{\lambda\nu}$$
$$-mh_+^{i\lambda,k\nu}-X_{jj'}^{ik}(m)h_-^{i\lambda,k\nu}\Big]. \qquad (33)$$

Here j and m are the values of the total moment and its projection for a pair of spins S_i, S_k;

$$h_\pm^{i\lambda,k\nu}={}^1/_2(h_{i\lambda}^{(\nu)}\pm h_{k\nu}^{(\lambda)}),$$

and the operator $X^{ik} = S_i^z - S_k^z$ has the following nonzero matrix elements:

$$X_{jj}^{ik}(m)=m\frac{(S_i-S_k)(S_i+S_k+1)}{j(j+1)}, \qquad (34a)$$

$$X_{j,j-1}^{ik}(m)=X_{j-1,j}^{ik}(m)=\left[\frac{(j^2-m^2)[(S_i+S_k+1)^2-j^2][j^2-(S_i-S_k)^2]}{j^2(4j^2-1)}\right]^{1/2}. \qquad (34b)$$

If the spins are equal in magnitude ($S_i = S_k$), then for $J > 0$ and $h_- = 0$ these expressions go over into the results for the ferromagnet, and for $J < 0$ and $h_+ = 0$ they go over into the results for the antiferromagnet[18].

We shall consider the behavior of F for small values of the quantities h, i.e., for small fields in the paramagnetic region or near magnetic phase-transition points. Then the expansion of F in powers of h can be written in the form

$$F(h)-F(0)=-\frac{\beta}{6}\sum_{\lambda\nu ik} m_\lambda n_{\lambda\nu} w_{ik}^{\lambda\nu}[fh_+^2+2\tilde f h_+h_-+gh_-^2]_{i\lambda,k\nu}$$
$$+\frac{\beta}{6}\sum_{\lambda i} m_\lambda (n_\lambda-1)c_{i\lambda}S_i(S_i+1)h_{i\lambda}^2. \qquad (35)$$

Here, subscripts $i\lambda$, $k\nu$ are implied in all quantities in the square brackets, and the functions f, $\tilde f$ and g have the form

$$f^{i\lambda,k\nu}=f(S_i,S_k,\beta J)=\frac{1}{2Z_0}\sum_{j=|S_-|}^{S_+}\exp\left\{\beta J\left[\frac{1}{2}j(j+1)-r\right]\right\}j(j+1)(2j+1),$$
$$\tilde f^{i\lambda,k\nu}=\tilde f(S_i,\ S_k)={}^1/_2 S_-(S_++1), \qquad (36a)$$

$$g^{i\lambda,k\nu}=g(S_i,S_k,\beta J)=\frac{1}{\beta J}\left[\exp(-\beta Jr)\frac{(S_++1)^2}{Z_0}-1\right],\quad S_i=S_k,$$

$$g^{i\lambda,k\nu}=-\frac{1}{\beta J}+\frac{S_-^2(S_++1)^2}{Z_0}\sum_{j=|S_-|}^{S_+}\exp\left\{\beta J\left[\frac{1}{2}j(j+1)-r\right]\right\}$$
$$\times\frac{2j+1}{j(j+1)}\left[\frac{1}{2}+\frac{1}{\beta Jj(j+1)}\right],\quad S_i\neq S_k. \qquad (36b)$$

In the formulas (36),

$$S_\pm=S_i\pm S_k,\quad J=J_{ik}^{\lambda\nu},\quad 2r=S_i(S_i+1)+S_k(S_k+1),$$

and Z_0 is the partition function of a binary cluster in the absence of fields (h = 0):

$$Z_0=Z_0(S_i,S_k,\beta J)=\sum_{j=|S_-|}^{S_+}\exp\left\{\beta J\left[\frac{1}{2}j(j+1)-r\right]\right\}(2j+1). \qquad (37)$$

The relations (35)–(37) enable us to find the Curie or Néel point (for second-order transitions) and the paramagnetic susceptibility.

First we shall discuss by means of (35)–(37) the question of Curie and anti-Curie points for pure, impurity-free ferrites. In this case, as has been noted, the quantities w_{ik} and $c_{i\lambda}$ in (29) and (35) are replaced by unity, and the summation over i and k disappears. We start with the simplest case of a two-sublattice model of a ferrite, in which each spin S_1 or S_2 interacts only with the n nearest spins of the other sublattice (a structure of the NaCl or CsCl type). Then the indices λ, ν in (29) take two values, 1 and 2; $m_\lambda = 1$; of all the $n_{\lambda\nu}$, only $n_{12} = n_{21} = n$ and $n_1 = n_2 = n$ are nonzero. The partition function Z_{12} contains spins S_1 and S_2 from different sublattices and, according to (31),

$$\varphi_1=n\varphi_1^{(2)},\quad \varphi_2=n\varphi_2^{(1)},$$

$$h_1^{(2)}=g_1H+(n-1)\varphi_1^{(2)},\quad h_2^{(1)}=g_2H+(n-1)\varphi_2^{(1)}.$$

The equation for the Curie points can be obtained from (35) by equating the denominator of the magnetic susceptibility to zero, or, which is the same thing, by finding the point at which, for H = 0, the quadratic form (35) of φ_1 and φ_2 ceases to be positive-definite:

$$D(T)=\left[r_{12}-\left(1-\frac{1}{n}\right)f_{12}\right]\left[r_{12}-\left(1-\frac{1}{n}\right)g_{12}\right]-S_-^2(S_++1)^2/4n^2=0. \qquad (38)$$

Here $S_\pm = S_1 \pm S_2$; f, g and r are the same as in (36), and for the usual case of anti-polarized sublattices $J = J^{12} < 0$.

If the spins of the sublattices are equal ($S_- = 0$), then in the absence of a field (H = 0) Eqs. (32) for $\varphi_\pm = \frac{1}{2}(\varphi_1 \pm \varphi_2)$ decompose. Then for a ferromagnet ($J > 0$) the transition point is determined by the zero of the first square bracket in (38) and for an antiferromagnet ($J < 0$) is determined by the zero of the second[1]:

$$J>0:\quad S(S+1)=(1-1/n)f(S,\ S,\ \beta_c J), \qquad (39a)$$

$$J<0:\quad S(S+1)=(1-1/n)g(S,\ S,\ \beta_N J). \qquad (39b)$$

To elucidate the question of the anti-Curie points for ferrites (J > 0) it is sufficient to study the signs of the left-hand side of (38) at high and low T. If these signs are different, Eq. (38) has one solution – one Curie point (three or more solutions do not arise, as can be shown). But if the signs are the same, then for the large $n \geq 6$ under consideration this indicates the existence of a second solution in addition to $T_c \sim T_c^{MFA}$, namely, an anti-Curie point $T_{ac} < T_c$. Investigating the expressions (38) and (36), we can convince ourselves that for large T we shall have D(T) > 0, and the condition for absence of an anti-Curie point (D(0) < 0) takes the form

$$S_- - 1 > \frac{1}{n}\left[2+\frac{S_-(1+S_-)}{S_2(1+S_2+S_-)}\right], \tag{40}$$

where it is assumed that $S_- = S_1 - S_2 > 0$. It can be seen from (39) that if $S_- \leq 1$ then a T_{ac} exists for all S_2, and if $S_- = 3/2$ then for n = 6 the anti-Curie point T_{ac} disappears for $S_2 \geq 3/2$, and for n = 8 disappears for $S_2 \geq 1$. If $S_- \geq 2$ and $n \geq 6$, there is no anti-Curie point.

We shall show, however, that if T_{ac} does exist, then for the fairly large values of n and S that are characteristic for most ferrites, it lies much lower than the temperatures T_C or T_N of the real transitions. We shall consider, e.g., the case of an antiferromagnet ($S_- = 0$). Discarding small terms $\sim\exp(-\beta_{ac}J) \sim 10^{-2}$ in (38), we obtain $T_{ac} \approx J/4$, and the Néel temperature for large n and S can be estimated by means of the MFA. As a result, we find

$$T_{ac}/T_N \approx 3/4nS(S+1) \ll 1.$$

An analogous estimate is valid for the ratio T_{ac}/T_c in ferrites.

As a second illustration we shall discuss the case of an impurity-free yttrium iron garnet, $Y_3Fe_5O_{12}$. According to the accepted ideas[21,22], here also there are two sublattices (the so-called a- and d-sublattices) of Fe atoms with spin S = 5/2, but in addition to the inter-sublattice interaction $J_{ad} < 0$ there are also intra-sublattice interactions J_{aa} and J_{dd}. The quantities m and n in (29) have the following values: $m_a = 2$, $m_d = 3$, $n_{aa} = 8$, $n_{ad} = 6$, $n_{da} = 4$, $n_{dd} = 4$, $n_a = 14$, $n_d = 8$. The temperature dependence of the magnetization, following from (32), is presented in Fig. 1. In the variables T/T_C used this curve is determined by only two parameters: $t_a = J_{aa}/J_{ad}$ and $p_d = J_{dd}/J_{ad}$. As noted by Belov[22], the experimental determination of p_a and p_d gives an appreciable discrepancy between the results of magnetic measurements, processed by the MFA method, which give $p_a \sim p_d \gtrsim 0.3$-0.4, and the more consistent methods (high-temperature expansions for the susceptibility, NMR, the method of spin waves), which give much smaller p_a, $p_d \lesssim 0.1$.

It can be seen from Fig. 1 that use of the latter data, especially those obtained from high-temperature expansions, gives a good description of M(T) down to $T \gtrsim 0.2T_C$. The subsequent parts of the curves, depicted by dashed lines, correspond to the fictitious decay of M(T) as T_{ac} is approached. The form of M(T) is extremely sensitive to the values of p_i, as is illustrated by the curves 3 and 4. With increasing p_a and p_d the spins in each of the sublattices tend to become antiparallel. Thus, when $p_a \approx 0.14$ and $p_d \approx 0.17$ (and even more so for the larger p_a and p_d used in the MFA), the ferromagnetic transition in the given approximation is already disappearing. We note also that, although the dependence of M on T/T_C is described entirely satisfactorily by the curves 1 and 2, the absolute values of J_{ad} obtained by comparing the calculated and experimental values of T_C ($|J_{ad}| = 0.094T_C$ $\sim 50°$) turn out to be larger than those usually used[22] ($|J_{ad}| \sim 35$-$40°$). We note, finally, that the structure considered, in which all couplings J_{ad}, J_{aa} and J_{dd} are antiferromagnetic, seems to be one of those least likely to favor accuracy of the cluster approximation. Therefore, Fig. 1 clearly gives an adequate idea of the possibilities of applying the method to real crystals (see also the papers[23,24] on the application to EuS and FeF_2).

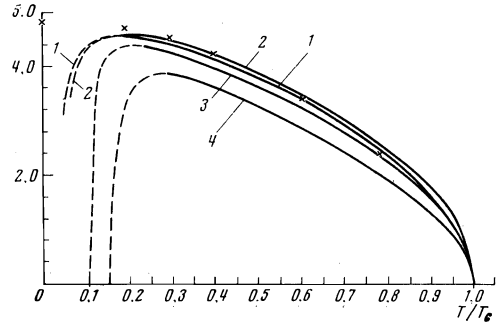

FIG. 1. Temperature dependence of the magnetization M(T) (in Bohr magnetons per molecule) in the cluster approximation for impurity-free $Y_3Fe_5O_{12}$. Curves 1 and 2 correspond to the use of the data of the high-temperature expansions of [22] for $p_a = J_{aa}/J_{ad}$ and $p_d = J_{dd}/J_{ad}$, and curve 3 corresponds to NMR data [22]. Curve 4 illustrates the sensitivity of the results to increase of p_d. The experimental points (X) are taken from [22]. Curve 1–$p_a = 0$, $p_d = 0$; 2–$p_a = 0.03$, $p_d = 0$; 3–$p_a = 0.02$, $p_d = 0.09$; 4–$p_a = 0$, $p_d = 0.2$.

Turning to the discussion of solid solutions, we shall confine ourselves for brevity to the simplest case of one-sublattice ferromagnets in sc, bcc or fcc lattices. Then in (29) $m_\lambda = 1$, the indices λ and ν disappear and this relation takes the form (13) (or (20), (21) for mobile atoms), but the partition functions Z_{ik}, Z_1 are given now by the expressions (30). Accordingly, the general character of the results turns out to be the same as for Ising model. Thus, e.g., for a two-component alloy the equation for T_C has, in place of (16a), the form

$$\left(\gamma_1 - w_{11}f_{11} - w_{12}\frac{f_{12}+2\tilde{f}_{12}+g_{12}}{2}\right)\left(\gamma_2 - w_{22}f_{22} - w_{12}\frac{f_{12}-2\tilde{f}_{12}+g_{12}}{2}\right) - \frac{1}{4}w_{12}{}^2(f_{12}-g_{12})^2 = 0, \tag{41}$$

where $\gamma_i = c_iS_i(S_i+1)(1-1/n)^{-1}$. In particular, for nonmagnetic impurities ($S_2 = 0$) the quantity $\gamma_2 = f_{22} = 0$ and $f_{12} = f_{12} = g_{12} = \frac{1}{2}S(S+1)$, and the equation obtained for T_C by equating the first bracket in (41) to zero differs from (39a) only by multiplication of the left-hand side of (39a) by $(1 + w_{12}/nw_{11})$[18].

For a comparison with other methods, we shall consider a case that has been discussed in a number of papers – that of a completely disordered alloy of two magnets with spin $\frac{1}{2}$ in an sc lattice: $w_{ik} = c_ic_k$, $S_1 = S_2 = \frac{1}{2}$, n = 6. The results of the different approximations for the dependence $T_c(c)$ in this case are given in Fig. 2.

It can be seen, first, that in the pure case (c = 0) the cluster approximation (CA) gives the value, $T_c^{cl}(0)$, closest to the results of the numerical calculation[25]. True, the great accuracy obtained here is clearly somewhat fortuitous. Thus, in an impurity-free fcc lattice the values of T_c^{cl}/T_c^{MFA} for $S = \frac{1}{2}$ and 1 are equal to 0.825 and 0.875 respectively, whereas the decoupling approximation of[26] gives 0.743 and 0.863 respectively, and the numerical calculations of[27] give 0.679 and 0.747, i.e., the CA results lie, as usual[10], approximately midway between the MFA and the exact results.

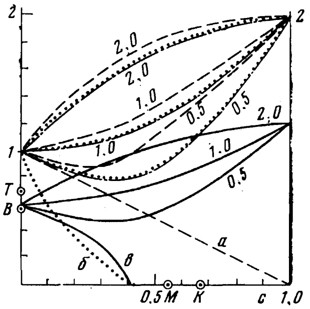

FIG. 2. Curie temperature $T_c(c)$ of an alloy of two Heisenberg magnets with spin 1/2 in an sc lattice, in units of $T_c^{MFA}(0) = (3/2)J_{11}$. The upper curves correspond to the values $J_{22} = 2J_{11}$ and $J_{12} = \frac{1}{2}J_{11}$, J_{11} and $2J_{11}$; the dashed curves correspond to the MFA, the dotted curves to the CPA [12], the solid curves to the cluster approximation, and the dashed-dotted curve to $T_c^{cl}(c)/T_c^{cl}(0)$; ⊚T is the value of $T_c(0)$ in the decoupling approximation [16] and ⊚B is the same from the numerical calculations of [25]; the lower curves are for nonmagnetic impurities ($J_{22} = J_{12} = 0$): a—MFA; b—CPA [12]; c—cluster approximation; ⊚M is the critical concentration $c_0 = c(T_c = 0)$ according to [13]; ⊚K is the same, from [14].

It can be seen also that if the interaction constants in the alloy are of the same order, the general character of the concentration dependence turns out to be approximately the same in the MFA and CPA as in the CA. True, because of the large difference in the values of T_c for the pure substances, the quantities $T_c^{cl}(c)$ go appreciably below T_c^{MFA} and T_c^{CPA}. If this difference did not exist, i.e., if we plotted the quantity $T_c(c)/T_c(0)$ along the ordinate axis for each of the approximations, the curves for the CPA and the CA would almost merge. Therefore, if the authors of[12] had substituted the "effective constant" J(c) that they found in the CPA not into the MFA formulas but, e.g., into the decoupling approximation[26] (which seems closer in spirit to the CPA than does the MFA), the differences from the CA would clearly be appreicably smaller.

In the case of widely different constants—in particular, for nonmagnetic impurities, the results of the different approximations, as can be seen from Fig. 2, are very noticeably different. The values of the critical concentrations c_0 for disappearance of the magnetism, found in different low-temperature approximations[13,14], are also given in the Figure. Inasmuch as all the approximations under consideration are different variants of the self-consistent field method, which in all known cases overestimates T_c[10], it may be thought that at low T too the CA gives the values of T_c and c_0 closest to the true values.

The case of mobile atoms can be treated in complete analogy with Sec. 2(c). In particular, in the one-sublattice case the results have the previous form (20)–(25), but Z_{ik}, $Z_1^{(i)}$ are now given by the expression (30), and the equation for φ_i has a form analogous to (32a): $\partial\Omega/\partial\varphi_i = 0$. For a two-component alloy the tendency toward phase separation or ordering at low T is determined by the sign of the parameter $u = v + J$, where v is the same as in (26) and $J = J_{11}S_1^2 + J_{22}S_2^2 - 2J_{12}S_1S_2$ (it is assumed that $J_{ik} \geq 0$; otherwise, the term $J_{ik}S_iS_k$ is replaced by $|J_{ik}|S_k(S_i + 1)$, where $S_i \geq S_k$). For an alloy of a ferromagnet with nonmagnetic impurities the curve $T_c(c)$ is given as before by (27), but ξ and z now have the form

$$\xi=(n-1)\left[\frac{f(S,S,\beta J)}{S(S+1)}-1\right],\quad z=e^{\beta v}\frac{Z_0(S,S,\beta J)}{(2S+1)^2},\tag{42}$$

where v, f, Z_0 are the same as in (26), (39a) and (37).

4. PHASE SEPARATION IN ALLOYS. ORDERING OF MAGNETIC ALLOYS

We shall use the relations (24) to consider the problem of the phase separation of a two-component alloy of Heisenberg or Ising magnets. For nonmagnetic alloys this problem has been solved earlier by the MF method[20].

The conditions for equilibrium of two phases A and B with different concentrations c_1^A and c_1^B can be written, in the thermodynamic variables usually used, in the following form[28]:

$$\mu(\alpha_A, T)=\mu(\alpha_B, T),\tag{43a}$$

$$\Omega(\alpha_A, T)=\Omega(\alpha_B, T).\tag{43b}$$

Here $\alpha = c_1 - c_2$ is the concentration difference, in terms of which the quantities c_1 and c_2 in each of the phases can be conveniently expressed: $2c_{1,2} = 1 \pm \alpha$.

The equilibrium curve (43) is studied most simply using the isotherms $\mu(\alpha, T)$ in the (μ, α)-plane, which, as is well known[28], are analogous to the usual p(V, T) isotherms (e.g., the van der Waals isotherms) used in the description of the gas-liquid transition. The presence of a "hump," i.e., a minimum and a maximum, in the curve $\mu(\alpha)$ corresponds to the region of phase separation. The positions of these extrema, which are determined by the relation $\partial\mu/\partial\alpha = 0$, indicate the boundary of stability of the alloy, analogous to the point with $\partial p/\partial V = 0$ in a liquid or gas[28]. The equilibrium curve can be found graphically from the condition that the areas cut off in the lower and upper humps of the curve $\mu(\alpha)$ by the horizontal μ = const be equal, which is derived here in complete analogy with the gas-liquid case, using (43b).

For simplicity we shall confine ourselves to the paramagnetic region, in which z in (25) does not depend on α; in particular, for an alloy with nonmagnetic impurities z is given by formula (42). Then it can be seen from (24a) that Ω is an even function of α. Therefore, a solution of (43b) is $\alpha_A = \alpha = -\alpha_B$, i.e., the phase-separation curve, as in the MFA[20], is found to be symmetric in c_1 and $c_2 = 1 - c_1$. Furthermore, we can see from (24b) that $\mu(\alpha) - \mu(0)$ is odd in α, i.e., the curve $\mu(\alpha)$ has mirror symmetry about the point $\alpha = 0$, $\mu = \mu(0)$. Therefore, (43a) gives the equation $\mu(\alpha) = \mu(0)$ for α. Expressing z(T) in terms of α by this relation, we obtain the equation of the equilibrium phase-separation curve $T = T_d(\alpha)$:

$$z(T_d)=\frac{4\alpha^2(1-\alpha^2)^{2/n}}{[(1+\alpha)(1-\alpha)^{2/n}-(1-\alpha)(1+\alpha)^{2/n}]^2}=\frac{(c_1-c_2)^2}{[c_1(c_2/c_1)^{1/n}-c_2(c_1/c_2)^{1/n}]^2}\tag{44}$$

We also give the equation for the instability curve $T = T_{dc}(\alpha)$, which is determined by the equation $\partial\mu/\partial\alpha = 0$ and bounds the region of states that are metastable with respect to phase separation:

$$z(T_{dc})=1+\frac{(n-1)}{(n-2)^2c_1c_2}.\tag{45}$$

The critical phase-separation point T_d^c at which the curves (44) and (45) touch corresponds to $\alpha = 0$, $c_1 = c_2 = \frac{1}{2}$ (see Fig. 3).

In order to compare the results (44) and (45) with the results of the MFA[20] we shall consider the case of nonmagnetic alloys ($J_{ik} = 0$). The curve obtained for $T_d(c)$ lies below the corresponding MFA curve (Fig. 3). In particular, the critical point for phase separation is equal to

$$T_d^c=v/2\ln\frac{n}{n-2}<(T_d^c)_{\text{MFA}}=nv/4.\tag{46}$$

The shaded region in Fig. 3 corresponds to the region of metastable states, which was not considered in[20]. In addition, Fig. 3 also shows phase-separation curves for an alloy of a magnet with nonmagnetic impurities for $u = v + J = J$ (curve 4) and for $u = J/2$ (curve 7). It can be seen that in the case of magnetic alloys the MFA, according to which the phase separation in the paraphase does not depend on J and is determined entirely by the quantity v (which in this case should be positive), can give a qualitatively incorrect description.

We shall also discuss the above-mentioned question of the relative behavior of the phase-separation curves $T_d(c)$ and the Curie points $T_c(c)$ in alloys with nonmagnetic impurities. In the absence of impurities (c = 1) the points T_c for not too large $v \lesssim JS^2$ lie appreciably above T_d^c. But with decreasing c the quantity $T_c(c)$ falls off more rapidly than $T_d(c)$ (see Fig. 3). By studying Eqs. (27), (44) and (45), with ξ and z from (42), we can convince ourselves that, for small c and all u > 0, as T is lowered phase separation occurs first, and the curve $T_c(c)$ lies somewhat below $T_{dc}(c)$, i.e., in the region of instability.

In the discussion of ordering alloys we shall confine ourselves for simplicity to the case of two-sublattice ordering of nearest neighbors in an sc or bcc lattice. In the presence of order, the mean fields φ_i and ν_i in (11) and (19) acting on an atom will be different in the different sublattices. This leads to an increase in the number of variables φ_i, ν_i in (18)–(23); in the case of two-sublattice ordering the number is doubled. In accordance with this, the potential Ω per pair of neighboring atoms here takes the form, in place of (20),

$$\beta\Omega = -n \ln Z_2 + (n-1) \sum_\lambda \ln Z_\lambda,$$
$$Z_2 = \sum_{ik} y_{i1} y_{k2} Z_{ik}^{12}, \qquad Z_\lambda = \sum_i x_{i\lambda} Z_1^{i\lambda}. \tag{47}$$

Here the sublattice index λ takes the values 1, 2; $x_{i\lambda}$ and $y_{i\lambda}$ are given by formulas (21b) with ν_i replaced by $\nu_{i\lambda}$. The partition functions $Z_{ik}^{\lambda\nu}$ and $Z_1^{i\lambda}$ depend on the indices λ and ν only through the fields $\varphi_{i\lambda}$ (31)—before the ordering appears, all the lattice sites are equivalent. The equations for $\varphi_{i\lambda}$ have the form $\partial\Omega/\partial\varphi_{i\lambda} = 0$, and $x_{i\lambda}$ and $y_{i\lambda}$ are determined from the conditions $\varphi\Omega/\varphi\nu_{i\lambda} = 0$ and from the constancy of the chemical potentials μ_i:

$$\frac{1}{Z_2} y_{i\lambda} \sum_{\substack{k \\ \nu\neq\lambda}} y_{\nu k} Z_{ik}^{\lambda\nu} = \frac{1}{Z_\lambda} x_{i\lambda} Z_1^{i\lambda} = c_{i\lambda}, \qquad \left(\frac{x_{1i}}{x_{2i}}\right)^{n-1} = \left(\frac{y_{1i}}{y_{2i}}\right)^n. \tag{48}$$

As in Sec. 2(c), the quantities $x_{i\lambda}$ and $y_{i\lambda}$ for each λ can be normalized by the condition

$$\prod_i x_{i\lambda} = \prod_i y_{i\lambda} = 1,$$

and the $c_{i\lambda}$ are connected by the relation $c_{i1} + c_{i2} = 2c_i$.

The relations given determine the thermodynamics of the system. As usual, there is always the "disordered" solution $\nu_{i1} = \nu_{i2}$, $\varphi_{i1} = \varphi_{i2}$, but below the transition point T_{ord} a solution corresponding to ordering appears: $\nu_{i1} \neq \nu_{i2}$, $\varphi_{i1} \neq \varphi_{i2}$. In particular, if the ordering occurs in the paramagnetic phase, i.e., $T_{ord} > T_c$, the transition in the two-component alloy is found to be second-order, and the equation for T_{ord} has a form analogous to (45):

$$z(T_{ord}) = 1 - (n-1)/n^2 c_1 c_2. \tag{49}$$

Here z, as in (44) and (45), denotes the combination of (25) with $Z_{ik} = Z_0(S_i, S_k)$ from (37). For nonmagnetic alloys ($J_{ik} = 0$), z = exp(βv) and (49) goes over into the result of the quasi-chemical approximation[20]. For low T and all u < 0, the curves (49) arrive at the point $c = c_0' = 1/n$. Fig. 4 shows examples of the curves (49) for two characteristic regions of parameters: u = v + J ~ −J and |u| ≪ J.

We shall also discuss, as above, the case of an alloy of a ferromagnet with nonmagnetic impurities. The curves $T_c(c)$ in this case have been discussed in detail in[18]. For the u < 0 under consideration all these curves arrive at the point $c = c_0 = S(n-1)(2nS-3S-1)^{-1}$ as T → 0. But, as noted in[18], for a certain interval of values of v ($-JS(S+2) \leq v < -JS^2$) the dependence $T_c(c)$ for small $c - c_0$ has a bulge on the left (curve 4 in Fig. 3), i.e., there is not only an upper, but also a lower Curie point T_{cL}. Physically, the appearance of magnetic order on increase of T is possible here because, from (24c), the probability w_{11} of finding neighboring magnetic atoms then increases sharply. Therefore, the gain in energy in the magnetic ordering as T increases turns out to be greater than the usual thermodynamic entropy loss, which also, of course, increases with increasing T.

Equation (27) for T_c is only valid, however, in the absence of atomic ordering, i.e., if the T_c found from it is higher than T_{ord} from (49). Figure 4 illustrates the relative behavior of the curves $T_c(c)$ and $T_{ord}(c)$ for the two above-mentioned characteristic regions of the parameters v and j. For comparison, the MFA curves for $T_c(c)$ and $T_{ord}(c)$, which respectively depend only on J and only on v but not on their sum u, are also given. It can be seen that, if the quantity u is not too small, the whole low-temperature part of the curve (27), including the region with T_{cL}, lies below the ordering curve, i.e., is not realized. Therefore, the stipulations in[18] that points T_{cL} are obviously unrealizable are, as a rule, valid. However, if u = 0, then $T_c(c)$ and $T_{ord}(c)$ have the form of the curves 5 and 6 in Fig. 4. Therefore, in a certain narrow range of u (in the case n = 8, S = 1, for $|u| \lesssim 0.02J$), the point T_{cL} for certain $c \sim \frac{1}{2}$ is found to lie above $T_{ord}(c)$ (the dotted curves in Fig. 4), i.e., the existence of a lower Curie point is possible in the given model.

True, it must be borne in mind that the presence of a solution T_{cL} of Eq. (27), i.e., a transformation of the

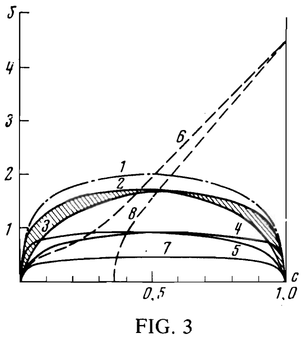

FIG. 3

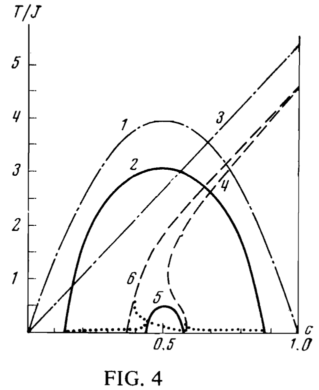

FIG. 4

FIG. 3. Phase-separation curve $T_d(c)$, instability curve $T_{dc}(c)$ and Curie temperature $T_c(c)$ of binary alloys with n = 8, S = 1 and u = v + J ⩾ 0. A) $J_{11} = J_{12} = J_{22} = 0$, v ≠ 0: 1–$T_d$/v (MFA); 2–$T_d$/v (CA); 3–$T_{dc}$/v (CA). B) $J_{12} = J_{22} = v = 0$, $J_{11} = J \neq 0$; 4–T_d/J (CA); 5–T_{dc}/J (CA); 6–T_c/J (CA). C) $J_{12} = J_{22} = 0$, $J_{11} = J$, V = −J/2; 7–T_d/J (CA). D) $J_{12} = J_{22} = 0$, $J_{11} = J = -v$: 8–T_c/J (CA).

FIG. 4. Ordering temperatures $T_{ord}(c)$ and Curie temperatures $T_c(c)$ of an alloy of a ferromagnet with nonmagnetic impurities: n = 8, S = 1, $J_{12} = J_{22} = 0$, $J_{11} = J \neq 0$ and $u = v + J \leqslant 0$. A) v = −2J: 1–T_{ord} (MFA); 2–T_{ord}(CA); 3–T_c(MFA); 4–T_c(CA). B) v = −J: 5–T_{ord} (CA); 6–T_c(CA). The dotted curves indicate schematically (on an enlarged scale) the behavior of $T_{ord}(c)$ and $T_c(c)$ in the CA for small u = v + J ($-0.02J \lesssim u < 0$).

point $\sigma = 0$ in $\Omega(\sigma)$ from a maximum into a minimum as T is lowered, does not yet necessarily imply the disappearance of the magnetic order; it is necessary, in addition, that $\Omega(\sigma)$ here have no other, deeper, minima with $\sigma \neq 0$ (cf., e.g., Sec. 25b in[10]). In addition, in real alloys at low T the mobility of the atoms tends to zero and their distribution "freezes" and ceases to be an equilibrium distribution. Furthermore, as a rule, for appreciable dilution $c \lesssim \frac{1}{2}$ in metals the character of the occupation of the electronic bands is changed[7] and this can substantially alter the exchange interactions. Thus, it is evident that in Fe-Al alloys even the sign of the interaction changes – the effective coupling becomes antiferromagnetic[29]. Therefore, the applicability of the model used (with constant J and S) to real alloys is not too clear. Nevertheless, the treatment given illustrates the possibility of a highly unusual form of phase diagrams for magnetic alloys, analogous to some of the dependences that have been observed[29]. Therefore, if we take into account the above-mentioned concentration dependence of the interactions by some method or another (e.g., as in[29]), the given method may turn out to be substantially more accurate than the MFA in the description of phenomena in magnetic alloys – in particular, those discussed in[29].

5. CONCLUSION

In conclusion, we present certain considerations on the connection of the CA results with the exact results for the models considered.

As has been noted, this approximation is one of the variants of the self-consistent field method. Therefore, as for other approximations of the self-consistent field method – in particular, the MFA, the accuracy of the CA becomes worse in the presence of large fluctuations of the quantities being considered. As emphasized in[8], in the description of alloys these fluctuations are great for low concentrations (when there is an appreciable difference in the interactions – e.g., for nonmagnetic impurities). This can be seen clearly in, e.g., the MFA in Sec. 2(a), where the sum over $\mathbf{r}'$ of the quantities $J_{ik}(\mathbf{r}-\mathbf{r}')\eta^k_{\mathbf{r}'}\sigma^z_{\mathbf{r}'}$ is replaced by the average $J^0_{ik}c_k\sigma_k$: such a replacement – neglect of fluctuations – is possible only when many particles of a given type lie in the sphere of influence of the potential $J_{ik}(\mathbf{r}-\mathbf{r}')$, and this is certainly not fulfilled for small c_k. Therefore, the dependence on the concentrations c_i for small c_i is obviously described incorrectly in the CA, as in the MFA. Thus, e.g., for the dependence $T_c(c)$ for low concentrations c_2 of nonmagnetic impurities a linear decrease with c_2 is obtained (Figs. 3, 4), whereas there are arguments that for small c_2 the quantity T_c in this case can remain constant as a consequence of the effects of fluctuations of the impurity distribution[5].

In this article, we have confined ourselves throughout for simplicity to the simplest (two-particle) cluster and to interactions between nearest neighbors only. If increase of the number of particles in the cluster does not lead to taking new effects into account, the accuracy of the approximation increases extremely slowly[10]. In certain cases, however, such an expansion of the cluster is necessary for an adequate description of the phenomena, e.g., in the description of orderings of the type found in Cu_3Au in an fcc lattice[20], in the description of systems of the type KH_2PO_4, $NaH_3(SeO_3)_2$, and so on[10,11]. It is often reasonable to describe the interaction with non-nearest neighbors by the MFA, because of their large number[10]. Both of the generalizations mentioned will be illustrated in a treatment of systems of the type $K(H_xD_{1-x})_2PO_4$ in another paper.

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[1)] The corresponding equations (2.4a, b) in [18] contain errors.

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122