

## A NEW TYPE OF MAGNETIC ORDERING IN SOME TRANSITION-METAL ALLOYS

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The nature of the magnetic ordering in a number of binary ferromagnetic alloys of the type Ni-Mn, Ni-Fe, Pt-Mn, Pd-Fe, etc. is investigated. A characteristic of these alloys is that the exchange interaction between atoms of the first component or between these atoms and those of the second component is ferromagnetic, whereas the interaction between atoms of the second component is antiferromagnetic. A Heisenberg ferromagnetic crystal with a pair of impurity atoms which interact antiferromagnetically is considered as the simplest element of such an alloy. The ground-state problem for such a system is solved exactly. In particular, regions of variation of the exchange parameters are determined in which the state of the system with maximum spin is unstable and goes over to a state with smaller spin. The results of the investigation of the behavior of a pair of impurity atoms in a ferromagnetic matrix can provide a qualitative explanation of the magnetic structure of the indicated alloys.

## 1. PRESENTATION OF THE PROBLEM

A number of transition-metal alloys (including Ni-Mn, Ni-Fe, Pd-Fe, Pt-Mn, and others) have strange magnetic properties. They are all ferromagnetic in a broad range of concentrations  $c$  of the second component from zero to some concentration  $c_0$  beyond which the spontaneous moment in the system disappears. Figure 1 shows the average saturation magnetic moment per atom of the alloy as a function of the concentration  $c$ .<sup>[1]</sup> This is a typical curve characteristic of all the above alloys with  $c_0$  changing from alloy to alloy and having values of 27 percent for the disordered Ni-Mn and Pt-Mn alloys and 75 percent for the Ni-Fe and Pd-Fe alloys.<sup>[1-4]</sup>

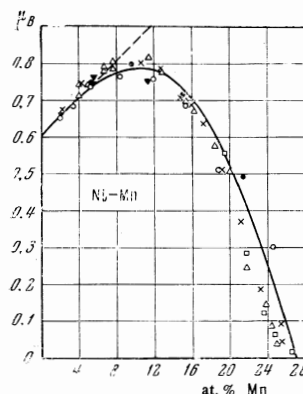
In order to explain the concentration dependence of the total magnetic moment, frequent use is made of ideas concerning the concentration dependence of the individual magnetic moments, it being assumed that the magnetic moments of the atoms of both components are collinearly oriented. This has, however, led to an improbably rapid change of the atomic magnetic moment of the second component within a very narrow range of concentrations, not only in the magnitude of the moment but also in the sign of its projection on the direction of the spontaneous magnetization (see for example the work of Loshmanov<sup>[5]</sup> on Ni-Mn with the attempt to interpret in this manner the data of neutron diffraction investigations). Obviously, the explanation of the course of the concentration dependence of the spontaneous moment of an alloy should be sought in the peculiarities of its magnetic structure.

It is important to note that all the alloys mentioned above have a cubic lattice and the following characteristic of their exchange interaction:

$$I_{11} > 0, \quad I_{12} > 0, \quad I_{22} < 0, \quad (1.1)$$

where  $I_{11}$  is the exchange integral between nearest neighbors in the solvent matrix,  $I_{12}$ —between the atoms of the second component and the atom of the matrix, and  $I_{22}$  is the exchange integral between the atoms of

FIG. 1. Dependence of the average magnetic moment per atom of the alloy  $\mu_B$  for disordered Ni-Mn alloys on the manganese concentration.<sup>[1]</sup>



the second component which are nearest neighbors. By virtue of the condition  $I_{12} > 0$  for small concentrations of the second component their atomic spins are directed along the ferromagnetic ordering in the matrix. For larger concentrations the atoms of type 2 are not only surrounded by the atoms of the matrix but also by their own atoms, and there appears thus a competition between the ferromagnetic interactions tending to line up their spins along the ferromagnetic ordering of the matrix and  $I_{22}$  interactions tending to orient the spins antiparallel to the type-2 neighbors. Sidorov and Doroshenko<sup>[2]</sup> were the first to draw attention to this circumstance and proposed that there exists in the indicated alloys an inhomogeneous noncollinear magnetic "structure" in which the atomic spins are turned at various angles (depending on their surroundings) relative to the direction of the spontaneous magnetic moment and the degree of this "turning" varies with changing concentration. By means of statistical methods they were able to calculate the concentration dependence of the total  $z$  projection of the atomic spins in such a structure and to obtain curves of the average moment which are in good agreement with the experimental ones (Fig. 1) when an appropriate choice is made of some phenomenological parameter. This conception also led to the explanation of a series of other ano-

malties in the properties of these alloys; however, it suffers from two deficiencies: first, it employs the concept of atomic spins as classical vectors, and, secondly, it contains no energy conditions indicating for what relation between the exchange interactions such an inhomogeneous ferromagnetic structure is in fact possible.

In this paper we attempt to set up a quantum theory of the ground state of a system of spins in the Heisenberg model under condition (1.1). In view of the fact that it is impossible to carry out a calculation for arbitrary concentration  $c$ , we consider first one very simple element of such an alloy: a pair of type-2 atoms which are nearest neighbors in a ferromagnetic matrix. It turns out that the ground-state problem of such a system can be solved exactly, and then using the obtained results one can make qualitative assertions about the structure of the indicated alloys. As the solvent crystal we have chosen a simple cubic lattice, since a detailed investigation of the single impurity problem is in this case available.<sup>[6,7]</sup>

## 2. A DIATOMIC "MOLECULE" IN A FERROMAGNETIC MATRIX

It is convenient to split the spin Hamiltonian of a ferromagnetic crystal containing two replacement impurity atoms which are nearest neighbors into two parts:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1, \quad (2.1)$$

$$\mathcal{H}_0 = -I \sum_n \sum_{\Delta} (S_n S_{n+\Delta}) - g\mu_0 H \sum_n S_n^z, \quad (2.2)$$

$$\begin{aligned} \mathcal{H}_1 = & -2I_{22}(S'_1 S'_2) + 2I(S_1 S_2) - 2I_{12} \sum_{i=1,2} \sum_{\Delta} (S_i S_{i+\Delta}) \\ & + 2I \sum_{i=1,2} \sum_{\Delta} (S_i S_{i+\Delta}) - g\mu_0 H (S_1^z + S_2^z - S_1^z - S_2^z), \end{aligned} \quad (2.3)$$

in which  $\mathcal{H}_0$  describes an ideal crystal and  $\mathcal{H}_1$ —the perturbation introduced in it by a pair of impurity atoms. Here  $\sum_n$  denotes summation over all lattice sites,  $\sum_{\Delta}$ —over  $z$  nearest neighbors;  $S_n$  denotes the spin operator of an atom of the matrix having spin  $S$ , and  $S'_1$  and  $S'_2$  are the spin operators of the impurity atoms having spin  $S'$  (Fig. 2). The prime in the sum  $\sum_{\Delta}$  means that in summing over nearest neighbors of the impurity atom 1 (or 2) the second impurity atom is not included; finally,  $H$  denotes a magnetic field applied along the spontaneous magnetic moment of the crystal, directed along the  $z$  axis.

The problem consists in finding the ground state of the system described by the Hamiltonian (2.1). It is well known that the operator of the total spin commutes with the exchange Hamiltonian; consequently, the ground state of our system should be characterized in addition to an energy also by a magnitude of the  $z$  projection of the total spin  $S^0$  (the  $z$  projection of the total spin also commutes with the Zeeman energy). The spectrum of possible values of  $S^0$  runs through the values:  $(N-2)S + 2S'$ ,  $(N-2)S + 2S' - 1$ ,  $(N-2)S + 2S' - 2$ , etc. The spectrum of eigenvalues of the system can correspondingly be classified by the eigenvalues of  $S^0$ . We shall denote the energy of the state

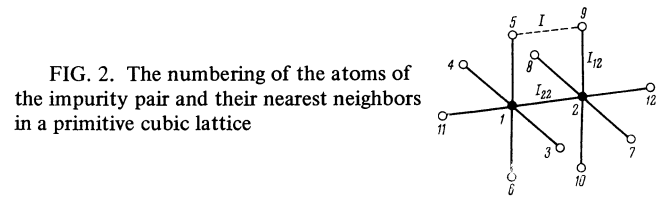


FIG. 2. The numbering of the atoms of the impurity pair and their nearest neighbors in a primitive cubic lattice

with  $S^0_{\max} = (N-2)S + 2S'$  (when all the spins of the system are "parallel") by  $E_0$ , and the energies of the states with  $S^0 = S^0_{\max} - 1$ ,  $S^0_{\max} - 2$ , etc. by  $E_1$ ,  $E_2, \dots$  respectively.

In order to determine the energy of the ground state, we should in principle find the eigenvalues of the energy  $E_0, E_1, E_2, \dots$  and compare them with one another. The state with total spin  $S^0_{\max}$  corresponds to a single energy level  $E_0$ , whereas states with smaller total spin correspond to entire energy bands (for example, to spin waves in an ideal ferromagnet). If one of the levels  $E_1$  will be below  $E_0$  and below all the remaining levels  $E_2, E_3, \dots$ , then precisely it will correspond to the ground state of the system. We shall restrict ourselves to a calculation of  $E_0$  and  $E_1$  and show that for certain values of the parameters of the exchange Hamiltonian one of the levels  $E_1$  can have an energy lower than  $E_0$ . Consequently in a certain range of parameters a ground state can exist<sup>1)</sup> with  $S^0 = S^0_{\max} - 1$ .

We denote the wave functions of the system which correspond to the eigenvalues  $E_0, E_1, \dots$ , by  $\Psi_0, \Psi_1, \dots$ . It is readily seen that the function  $\Psi_0$  corresponding to the state with parallel spins corresponds to the energy

$$\begin{aligned} E_0 = & -I[Nz - 4(z-1) - 2]S^2 - 4I_{12}(z-1)SS' - 2I_{22}(S')^2 \\ & - g\mu_0 H[(N-2)S + 2S']. \end{aligned} \quad (2.4)$$

In order to find  $E_1$ , one must solve the Schrodinger equation

$$\mathcal{H}\Psi_1 = E_1\Psi_1, \quad (2.5)$$

for this purpose we expand  $\Psi_1$  in a series of wave functions  $|j\rangle$  of single-particle spin deviations localized on the crystal sites  $j$ <sup>[6,8]</sup>:

$$\Psi_1 = \sum_{j=1}^N c_j |j\rangle. \quad (2.6)$$

The functions  $|j\rangle$  are obtained by the operator  $S_j^-$  acting on the wave function  $\Psi_0$ :

$$|j\rangle = (2S_j)^{-1/2} S_j^- \Psi_0. \quad (2.7)$$

Since the  $|j\rangle$  constitute a complete set of functions describing the state of the system with  $S^0 = S^0_{\max} - 1$ , the expansion (2.6) for  $\Psi_1$  is exact.

Equation (2.5) corresponds to an equivalent system of equations for  $c_j$ :

$$\sum_j \langle i | \mathcal{H} | j \rangle c_j = E_1 c_i, \quad (2.8)$$

<sup>1)</sup>In principle it may turn out that in another range of parameters  $E_2 < E_1 < E_0$ . However, in view of the fact that the study of this problem requires a knowledge of the value of  $E_2$  (and subsequently values of  $E_3, E_4$ , etc may be required), we shall not study the loss of stability of the state with spin  $S^0 = S^0_{\max} - 1$ , concentrating all our attention on the loss of stability of the state with  $S^0 = S^0_{\max}$ .

where the matrix elements of the Hamiltonian (2.1) can be calculated using the definition (2.7) for the functions  $|j\rangle$  as well as the definition of the function  $\Psi_0$ :

$$S_j^+\Psi_0 = 0, \quad S_j^-\Psi_0 = S_j\Psi_0, \quad (2.9)$$

where  $S_j = S$  for the sites of the matrix and  $S'$  for the sites occupied by impurity atoms. Thus we find that Eq. (2.8) is

$$\sum_j (\mathcal{E} - g_{10}H - 2ISz)\delta_{ij} + 2IS \sum_{\Delta} \delta_{i+\Delta,j} c_j - \sum_j V_{ij}c_j = 0, \quad (2.10)$$

where  $V_{ij}$  is a  $12 \times 12$  symmetric perturbation matrix with nonzero elements (see Fig. 2):

$$\begin{aligned} V_{11} = V_{22} &= 2IS[(z-1)\epsilon + \xi], & V_{12} &= -2IS\xi, \\ V_{33} = V_{44} = \dots &= V_{12,12} = 2IS\rho, \\ V_{13} = V_{14} = V_{15} = V_{16} &= V_{1,11} = V_{27} = V_{28} = V_{29} \\ &= V_{2,10} = V_{2,12} = -2IS\gamma. \end{aligned} \quad (2.11)$$

Here the quantities  $\epsilon$ ,  $\rho$ ,  $\gamma$ , and  $\xi$  are perturbation parameters:

$$\epsilon = \frac{I_{12}}{I} - 1, \quad \rho = \frac{I_{12}}{I} \frac{S'}{S} - 1, \quad \gamma = \frac{I_{12}}{I} \sqrt{\frac{S'}{S}} - 1, \quad (2.12)$$

$$\xi = \frac{I_{22}}{I} \frac{S'}{S} - 1. \quad (2.13)$$

It is characteristic that the parameters  $\epsilon$ ,  $\rho$ , and  $\gamma$  characterize the interaction of one of the impurity atoms with the matrix and coincide with those which appear in the theory of isolated impurities in ferromagnets,<sup>[6,7]</sup> whereas the new parameter  $\xi$  characterizes the interaction between the two impurity spins.

Another notation has been introduced in Eq. (2.10):

$$\mathcal{E} = E_1 - E_0. \quad (2.14)$$

It is readily seen that the expression in square brackets in (2.10) is the reciprocal Green's function  $[G^{0-1}]_{ij}$  of single-particle excitations of an ideal ferromagnet. Taking this into account, we write Eq. (2.10) in the compact form:

$$\sum_j (\delta_{ij} - \sum_n G_{in}^0(\mathcal{E}) V_{nj}) c_j = 0, \quad (2.15)$$

where

$$G_{in}^0(\mathcal{E}) = \frac{1}{N} \sum_k \frac{e^{ik(i-n)}}{\mathcal{E} - \epsilon_k} \quad (2.16)$$

( $\epsilon_k$  is the energy of the spin wave in an ideal crystal).

The spectrum of possible values of the energy  $\mathcal{E}$  in a system in the state  $\Psi_1$  is determined by the zeros of the determinant of the system of equations (2.15):

$$D(\mathcal{E}) = \det|1 - G^0(\mathcal{E})V|, \quad (2.17)$$

which indeed has dimensions of  $12 \times 12$ . In order to factorize the determinant, one must use symmetry theory. A diatomic "molecule" in a primitive cubic lattice lowers the point symmetry of the crystal to the group  $D_{4h}$  (with a center of symmetry at the middle of the line joining the atoms 1 and 2). In calculating the determinant we can go over to a representation of symmetrized combinations of wave functions  $|j\rangle$  which transform like the bases of the irreducible representations of the point group of the symmetry of the system. It is simplest of all to use the symmetry by setting up the unitary transformation matrix which effects the transition from the site representation to the sym-

metrized combinations, as was first done in the work of Wolfram and Callaway<sup>[6]</sup> in the analysis of an impurity atom in a ferromagnet. In our case one can set up from the twelve localized functions  $|1\rangle, |2\rangle, \dots, |12\rangle$  symmetrized combinations transforming in accordance with the following irreducible representations<sup>[9]</sup>:  $\mu = A_{1g}, A_{2u}, B_{1g}, B_{2u}, E_g, E_u$  of the group  $D_{4h}$  which also determine the sought unitary matrix (braces denote groups of columns of the unitary matrix which give rise to combinations transforming according to the given group representation):

$$U = \begin{pmatrix} a & 0 & 0 & a & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -a & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & b & 0 & 0 & b & 0 & b & b & d & 0 & 0 & d \\ 0 & b & 0 & 0 & b & 0 & b & b & -d & 0 & 0 & -d \\ 0 & b & 0 & 0 & b & 0 & -b & -b & 0 & -d & d & 0 \\ 0 & b & 0 & 0 & b & 0 & -b & -b & 0 & d & -d & 0 \\ 0 & b & 0 & 0 & -b & 0 & b & -b & -d & 0 & 0 & d \\ 0 & b & 0 & 0 & -b & 0 & b & -b & d & 0 & 0 & -d \\ 0 & b & 0 & 0 & -b & 0 & -b & b & 0 & d & d & 0 \\ 0 & b & 0 & 0 & -b & 0 & -b & b & 0 & -d & -d & 0 \\ 0 & 0 & a & 0 & 0 & a & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & a & 0 & 0 & -a & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \quad (2.18)$$

$\underbrace{\hspace{1.5cm}}_{A_{1g}} \quad \underbrace{\hspace{1.5cm}}_{A_{2u}} \quad \underbrace{\hspace{1.5cm}}_{B_{1g}} \quad \underbrace{\hspace{1.5cm}}_{B_{2u}} \quad \underbrace{\hspace{1.5cm}}_{E_g} \quad \underbrace{\hspace{1.5cm}}_{E_u}$

where  $a = 1/\sqrt{2}$ ,  $b = 1/\sqrt{8}$ , and  $d = 1/2$ .

If one introduces the rectangular matrices  $T(A_{1g})$ ,  $T(A_{2u})$  etc., corresponding to the columns joined by the braces, then  $U$  can be represented in the form of a symbolic sum<sup>[10]</sup>

$$U = \sum_{\mu} T(\mu). \quad (2.19)$$

The determinant  $D(\mathcal{E})$  separates into a product of factors

$$D(\mathcal{E}) = \prod_{\mu} \{1 - (T^+(\mu)G^0(\mathcal{E})T(\mu))(T^+(\mu)VT(\mu))\}, \quad (2.20)$$

corresponding to the various irreducible group representations. In our case

$$\begin{aligned} D(\mathcal{E}) &= D(A_{1g}, \mathcal{E})D(A_{2u}, \mathcal{E})D(B_{1g}, \mathcal{E}) \\ &D(B_{2u}, \mathcal{E})D^2(E_g, \mathcal{E})D^2(E_u, \mathcal{E}), \end{aligned} \quad (2.21)$$

where  $D(A_{1g}, \mathcal{E})$  and  $D(A_{2u}, \mathcal{E})$  represent third-rank and  $D(B_{1g}, \mathcal{E})$ ,  $D(B_{2u}, \mathcal{E})$ ,  $D(E_g, \mathcal{E})$ , and  $D(E_u, \mathcal{E})$  first-rank determinants. The squares in the last two factors are due to the fact that the representations  $E_g$  and  $E_u$  are two-dimensional. Individual factors in (2.21) denote the corresponding factors in the product (2.20).

It turns out that only  $D(A_{2u})$  includes the parameter  $\xi$  (2.13); the other factors in (2.21) include only  $\epsilon$ ,  $\rho$ , and  $\gamma$ . Since  $I_{12} > 0$ , then the zeros of these factors will determine the values of the energy  $\mathcal{E}$  only in the region  $\mathcal{E} > 0$ , the position of these levels not depending on the value of the exchange integral  $I_{22}$  (which comes in only through  $\xi$ ). It is hence clear that only the factor  $D(A_{2u})$  which depends on  $I_{22} < 0$  can in principle yield a solution with  $\mathcal{E} < 0$ , i.e.,  $E_1 < E_0$ . In this case the state with  $S^0 = S_{\max}^0 - 1$  would be energetically advantageous compared with the state  $S^0 = S_{\max}^0$ .

The quantity  $D(A_{2u})$  represents a  $3 \times 3$  determinant of the form:

$$= \det \left[ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} - 2IS \begin{pmatrix} T & R & X \\ R & W & Y \\ X & Y & Z \end{pmatrix} \begin{pmatrix} \varepsilon(z-1) + 2\xi & -2\gamma & -\gamma \\ -2\gamma & \rho & 0 \\ -\gamma & 0 & \rho \end{pmatrix} \right]. \quad (2.22)$$

Here the latter matrix represents  $T^*(A_{2u})VT(A_{2u})$  and that preceding it— $T^*(A_{2u})G^0T(A_{2u})$  where  $G^0$  is a  $12 \times 12$  block of the complete Green's matrix for an ideal ferromagnet; for brevity we have used the notation:

$$\begin{aligned} T &= G_{11}^0 - G_{13}^0, & R &= 2(G_{31}^0 - G_{32}^0), & X &= G_{31}^0 - G_{34}^0, \\ Y &= 2(G_{32}^0 - G_{38}^0), & Z &= G_{11}^0 - G_{11,12}^0, \\ W &= G_{11}^0 + G_{34}^0 + 2G_{32}^0 - G_{31}^0 - G_{38}^0 - 2G_{30}^0. \end{aligned} \quad (2.23)$$

A relation exists between the different matrix elements of the Green's function of an ideal crystal of cubic symmetry:

$$\sum_{\Delta} G_{n,m+\Delta}^0(\mathcal{E}) = \frac{1}{2IS} \delta_{nm} + \left( z - \frac{\mathcal{E} - g\mu_0 H}{2IS} \right) G_{nm}^0(\mathcal{E}), \quad (2.24)$$

by the use of which one can decrease the number of independent  $G_{nm}^0$  appearing in (2.23) to three which must be calculated numerically. These are conveniently chosen as  $G_{11}^0$ ,  $G_{32}^0$  (they are tabulated in<sup>[6]</sup>) and  $G_{39}^0$  (which we have calculated on a computer). The remaining problem reduced to the analysis of the solutions of Eq. (2.22).

### 3. THE ENERGY OF THE GROUND STATE

First of all let us obtain the condition under which one of the roots  $\mathcal{E}$  of the equation

$$D(A_{2u}, \mathcal{E}) = 0 \quad (3.1)$$

passes through zero and becomes negative. For this purpose we substitute in expression (2.22)  $T, R, W, X, Y,$  and  $Z$  for the value  $\mathcal{E} = 0$ , using calculated values of  $2ISG_{nm}^0(0)$ . Equation (3.1) will then yield the relation between all the parameters determining the solution  $\mathcal{E} = 0$ . Figure 3 shows the results of a numerical solution of this equation. The curves plotted in the plane  $I_{12}/I$  and  $I_{22}/I$  for three values of  $S'/S = 4, 1,$  and  $1/4$  separate the regions of values of the exchange parameters  $I_{12}/I$  and  $I_{22}/I$  for which the state  $S^0 = S_{\max}^0$  is stable (this region turns out to be below the corresponding curve). In the remaining region the state  $A_{2u}$  with a total spin  $S^0 = S_{\max}^0 - 1$  lies below the energy of the state with parallel spins. As is seen from the Figure, the regions of stability of the states with  $S^0 = S_{\max}^0$  depend very appreciably on the ratio of the spins  $S'/S$ . The smaller this ratio, the more stable (with other conditions the same) this state.

In the general case the roots of Eq. (3.1) can only be found numerically; however, for very low-lying

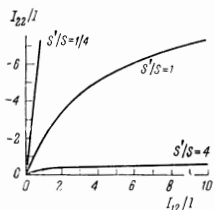


FIG. 3. Stability regions of the state with maximum spin of the system  $S_{\max}^0$  for various ratios of the atomic spins.

levels one can obtain an approximate analytic expression by the use of the asymptotic form of the Green's functions (2.16) for large  $|\mathcal{E}|$  such that

$$4ISz/|\mathcal{E}| \ll 1, \quad (3.2)$$

where  $4ISz$  is the width of the spin-wave band of an ideal crystal. Under this condition

$$G_{nm}^0(\mathcal{E}) = \frac{1}{\mathcal{E}} \delta_{nm} + \frac{2IS}{\mathcal{E}^2} \left[ z\delta_{nm} - \sum_{\Delta} \delta_{n,m+\Delta} \right] + \dots, \quad (3.3)$$

where the  $\delta_{nm}$  and others are Kronecker symbols for a discrete argument. To an approximation accurate up to square terms in  $1/\mathcal{E}$  we obtain the solution of Eq. (3.1):

$$\frac{\mathcal{E}}{4ISz} = \frac{\xi}{z} + \frac{z+1}{2z} \varepsilon + \frac{1}{2}. \quad (3.4)$$

The last two terms here are of the order of unity; thus condition (3.2) is fulfilled for  $|\xi| \gg z$ , and  $\mathcal{E}$  is negative for negative  $\xi$ . Taking into account the definition of  $\xi$  (2.13), one can write an approximate expression for the energy of a level lying very deep below the band and belonging to the state  $A_{2u}$ , and for the condition of its appearance:

$$\mathcal{E} \approx 4I_{22}S', \quad |I_{22}S'/IS| \gg z - 1. \quad (3.5)$$

Such a level appears for strong negative exchange interaction of the spins of the impurity pair.

In the general case the position of the energy of the ground state can only be obtained by numerical solution of (3.1). Figure 4 shows the results of such calculations for the case  $S' = S = 1/2$ . The solid curves show the dependence of the energy of the ground state on the parameter  $I_{22}/I$  for fixed values of the parameter  $I_{12}/I$ .

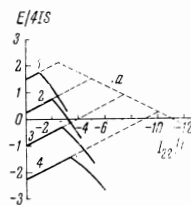


FIG. 4. The energy of the ground state of a crystal containing an impurity diatomic "molecule" as a function of  $I_{22}/I$  for the case  $S' = S = 1/2$  and for values of the parameter  $I_{22}/I$ : 1 - 0.5; 2 - 1.0; 3 - 1.5; 4 - 2.0.

Each curve consists of an ascending and descending branch. The ascending branch (together with the dashed continuation) yields the energy  $E_0$  of the state with maximum spin  $S_{\max}^0$  calculated in accordance with Eq. (2.4). The descending curve gives the energy  $E_1$  of the state with spin  $S_{\max}^0 - 1$  calculated on the basis of the solution of Eq. (3.1). It is seen that on increasing  $|I_{22}|$  the state of the system with  $S^0 = S_{\max}^0 - 1$  lies below the state with parallel spins, the difference in the energy increasing with increasing  $|I_{22}|$ . Thus the points of inflection correspond to a loss of stability of the state with  $S^0 = S_{\max}^0$ . The position of these points in the plane of the variables  $I_{12}/I$  and  $I_{22}/I$  has been depicted in Fig. 3 (on Fig. 4 the zero of the energy corresponds to  $E_0^0 = -NizS^2$ —the energy of the ground state of an ideal crystal). The dashed line intersecting the prolongation of the straight lines for the energies  $E_0$  corresponds to the classical configuration for which the spins of the impurity atoms are antiparallel. The energy of such a classical state is given by the formula

$$E_{\text{Kl}} = -I[Nz - 4(z-1) - 2]S^2 + 2I_{22}(S')^2. \quad (3.6)$$

The dashed line *a* on Fig. 4 corresponds precisely to this formula for  $S' = S = 1/2$ . We note that the energy of the true quantum-mechanical state with total spin  $S_{\text{max}}^0 - 1$  lies appreciably lower than the energy of the classical state with the same value of the total spin and strictly antiparallel orientation of the spins of the impurity pair. This result shows that in this problem the treatment of the spins as classical vectors gives no satisfactory solution of the ground-state problem.

#### 4. THE WAVE FUNCTION OF THE STATE WITH TOTAL SPIN $S_{\text{max}}^0 - 1$

We have shown that for certain values of the perturbation parameter the ground state of our system is the state with  $S^0 = S_{\text{max}}^0 - 1$ . Its wave function transforms in accordance with the irreducible representation  $A_{2U}$  and the coefficients  $c_j$  of the wave function are determined from Eq. (2.15) which we shall rewrite in the form

$$c_i = \sum_{nj} G_{in}^0(\mathcal{E}) V_{nj} c_j. \quad (4.1)$$

Since the matrix  $V_{nj}$  is a  $12 \times 12$  matrix, it is clear that in order to determine all the  $c_i$  one must solve a system of twelve equations for  $c_1, c_2, \dots, c_{12}$ ; then the other  $c_i$  with  $i > 12$  are automatically determined by relation (4.1). However, in each concrete state symmetry imposed relationships exist between the twelve values  $c_1, c_2, \dots, c_{12}$ . Since the state which interests us transforms in accordance with the  $A_{2U}$  representation, we find at once from the form of the matrix  $U$  (2.18) [more accurately, from the form of a part of it—the rectangular  $T(A_{2U})$  matrix] that in this state

$$\begin{aligned} c_1 &= -c_2, \quad c_{11} = -c_{12}, \\ c_3 &= c_4 = c_5 = c_6 = -c_7 = -c_8 = -c_9 = -c_{10}; \end{aligned} \quad (4.2)$$

thus there are only three independent coefficients, for example,  $c_1, c_3$ , and  $c_{11}$ .

In order to determine these coefficients it is convenient to make further use of the theory of the representations of the symmetry group. We use  $C$  to denote the column of coefficients  $c_1, c_2, \dots, c_{12}$ . Then, making use of the property of the unitary matrix  $UU^* = 1$ , we write (4.1) in the symbolic form:

$$C = G^0(\mathcal{E}) U \cdot U^* V U \cdot U^* C. \quad (4.3)$$

We take further account of the "additivity" of the unitary matrix  $U$  (2.19); then, making use of the theorem on the vanishing of the matrix elements between states belonging to different irreducible representations<sup>[9]</sup> we obtain from (4.3) an equation for the state  $A_{2U}$  of interest to us:

$$\begin{aligned} & T^+(A_{2U}) C(A_{2U}) \\ &= T^+(A_{2U}) G^0(\mathcal{E}) T(A_{2U}) \cdot T^+(A_{2U}) V T(A_{2U}) \cdot T^+(A_{2U}) C(A_{2U}) \end{aligned} \quad (4.4)$$

[in obtaining this equation we have multiplied the preceding Eq. (4.3) on the left by  $T^+(A_{2U})$ ].

Carrying out the indicated matrix multiplications, and using relations (4.2), we represent Eq. (4.4) in the following form:

$$\begin{pmatrix} c_1(A_{2U}) \\ c_2(A_{2U}) \\ c_{11}(A_{2U}) \end{pmatrix} = 2IS \begin{pmatrix} T & R & X \\ R & W & Y \\ X & Y & Z \end{pmatrix} \begin{pmatrix} \varepsilon(z-1) + 2\xi & -2\gamma & -\gamma \\ -2\gamma & \rho & 0 \\ -\gamma & 0 & \rho \end{pmatrix} \begin{pmatrix} c_1(A_{2U}) \\ c_3(A_{2U}) \\ c_{11}(A_{2U}) \end{pmatrix}, \quad (4.5)$$

where all the symbols have been previously encountered in Sec. 2. The determinant of this system coincides with (2.22) and vanishes by virtue of condition (3.1), as it should.

Knowing  $c_1, c_3$ , and  $c_{11}$ , one can calculate arbitrary  $c_i$  using Eq. (4.1). Proceeding analogously with the aid of the unitary matrix, one can readily obtain for any site

$$\begin{aligned} c_i(A_{2U}) &= 2IS \{ [\varepsilon(z-1) + 2\xi] (G_{i1}^0 - G_{i2}^0) - \gamma(G_{i3}^0 + G_{i4}^0 + G_{i5}^0 \\ &+ G_{i6}^0 - G_{i7}^0 - G_{i8}^0 - G_{i9}^0 - G_{i10}^0) ] c_1(A_{2U}) + [\rho(G_{i3}^0 + G_{i4}^0 + G_{i5}^0 + G_{i6}^0 \\ &- G_{i7}^0 - G_{i8}^0 - G_{i9}^0 - G_{i10}^0) - 4\gamma(G_{i1}^0 - G_{i2}^0) ] c_3(A_{2U}) \\ &+ [\rho(G_{i11} - G_{i12}^0) - \gamma(G_{i1}^0 - G_{i2}^0) ] c_{11}(A_{2U}) \}. \end{aligned} \quad (4.6)$$

One can readily verify that the  $c_i$  determined by this expression satisfy the symmetry relations (4.2), and  $c_1, c_3$ , and  $c_{11}$  satisfy Eq. (4.5). We note that in expression (4.6) the values  $G_{ij}^0(\mathcal{E})$  are taken with the value  $\mathcal{E} < 0$  satisfying Eq. (3.1). The state  $A_{2U}$  has an energy  $\mathcal{E} < 0$  in the range of parameters of interest. The Green's function  $G_{ij}^0(\mathcal{E})$  (2.16) decreases, as is well known, exponentially with the distance  $|R_i - R_j|$  for negative arguments. It is seen from (4.6) that  $c_i(A_{2U})$  also decreases exponentially with the distance from the impurity molecule, i.e. the state  $A_{2U}$  which belongs to a discrete level is localized.

In order to determine fully the coefficients  $c_i(A_{2U})$ , one must take into account the normalization relationship  $\sum_j |c_j(A_{2U})|^2 = 1$ . Using Eq. (4.1), one can represent it in the form [we have taken into account that for  $\mathcal{E} < 0$   $\text{Im } G_{ij}^0(\mathcal{E}) = 0$ ]

$$1 = - \sum_{lmip} c_l^*(A_{2U}) V_{lm} \frac{dG_{mi}^0}{d\mathcal{E}} V_{ip} c_p(A_{2U}). \quad (4.7)$$

This form is convenient in that only  $c_j$  for sites 1 through 12 enter in it. Taking into account the symmetry of the  $A_{2U}$  state, Eq. (4.7) for this state can be written in matrix form:

$$\begin{aligned} 1 &= -C^*(A_{2U}) T(A_{2U}) \cdot T^+(A_{2U}) V T(A_{2U}) \cdot T^+(A_{2U}) \frac{dG^0}{d\mathcal{E}} T(A_{2U}) \\ &\quad \times T^+(A_{2U}) V T(A_{2U}) \cdot T^+(A_{2U}) C(A_{2U}). \end{aligned} \quad (4.8)$$

After partial multiplication of the matrices, we obtain

$$\begin{aligned} 1 &= -(2IS)^2 (\sqrt{2} c_1^* \cdot \sqrt{8} c_3^* \cdot \sqrt{2} c_{11}^*) \begin{pmatrix} \varepsilon(z-1) + 2\xi & -2\gamma & -\gamma \\ -2\gamma & \rho & 0 \\ -\gamma & 0 & \rho \end{pmatrix} \\ &\quad \times \begin{pmatrix} T' & R' & X' \\ R' & W' & Y' \\ X' & Y' & Z' \end{pmatrix} \begin{pmatrix} \varepsilon(z-1) + 2\xi & -2\gamma & -\gamma \\ -2\gamma & \rho & 0 \\ -\gamma & 0 & \rho \end{pmatrix} \begin{pmatrix} \sqrt{2} c_1 \\ \sqrt{8} c_3 \\ \sqrt{2} c_{11} \end{pmatrix}. \end{aligned} \quad (4.9)$$

Here  $T'$  etc. denotes the derivative  $dT(\mathcal{E})/d\mathcal{E}$  at the point  $\mathcal{E} = \mathcal{E}_{A_{2U}}$  etc. Simultaneous solution of the system (4.5) with this equation makes it possible to determine  $c_1, c_3$ , and  $c_{11}$ . A knowledge of these coefficients yields the average value of the  $z$  projection of the atomic spins on an arbitrary site:

$$\langle \Psi_i^* | S_i^z | \Psi_i \rangle = S_i - |c_i(\mathcal{E})|^2, \quad (4.10)$$

where  $S_i = S'$  for  $i \neq 1, 2$  and  $S_i = S'$  for  $i = 1$  or  $2$ .

Let us consider certain special cases of the solution of the system of equations (4.5) and (4.9). Under the

condition  $|\xi| \gg z$  when we have a very deep level  $\mathcal{E}_{A_{2U}}$  (3.4) the use of the asymptotic form of expressions (3.3) yields in the second approximation in  $1/\xi$  the solution

$$|c_1|^2 \approx \frac{1}{2} \left( 1 - (z-1) \frac{(1+\gamma)^2}{4\xi^2} \right),$$

$$|c_3|^2 = |c_{11}|^2 \approx \frac{(1+\gamma)^2}{4\xi^2} |c_1|^2 \approx \frac{(1+\gamma)^2}{8\xi^2}. \quad (4.11)$$

In the limit  $|\xi| \rightarrow \infty$  we have  $|c_1|^2 = 1/2$ ; thus the state of the system with total spin  $S_{\max}^0 - 1$  corresponds in this limit to a change of the total spin projection on the pair by exactly one unit. In particular, for  $S' = 1/2$  the average value of the spin projection on an impurity atom is obviously zero; this corresponds exactly to the spin state of an isolated pair. For finite  $\xi$  the spin cancellation on the impurity is less than  $1/2$ , so that for  $S' = 1/2$  the average value of the  $z$  projection of the impurity spin has a small component in the direction of the spontaneous moment of the crystal; there is at the same time a small deviation of the spin projections on the nearest neighbors. The state  $A_{2U}$  is thus in this case highly localized. On decreasing  $\xi$ , its localization decreases.

Let us now consider the other limit when the value of  $\xi$  corresponds to the limit of the appearance of the ground state  $A_{2U}$ , i.e., when  $\mathcal{E}_{A_{2U}} \rightarrow -0$ . Results are obtained particularly easily in the case of the special model with  $S' = S$  and  $I_{12} = I$ . Then the value of  $\xi$  which yields  $\mathcal{E}_{A_{2U}} = 0$  turns out to be  $\xi = -3$ . One can readily show that in this instance

$$|c_1|^2 = -\frac{1}{8\xi^2} \frac{1}{(2IS)^2 [dT/d\xi]_{\xi=0}}; \quad (4.12)$$

with the following relation obtaining:

$$\left[ \frac{d}{d\xi} T \right]_{\xi=0} = \frac{1}{2ISz} G_{11}^0(0). \quad (4.12)$$

Analogous formulas can also be obtained for  $|c_3|^2$  and  $|c_{11}|^2$ ; the numerical values of the spin cancellations obtained from them are:

$$|c_1|^2 = 0.33; \quad |c_3|^2 = 0.01; \quad |c_{11}|^2 = 0.02. \quad (4.14)$$

The total cancellation on a complex consisting of the impurity pair and its ten neighbors is 0.78; thus in this case too the state  $A_{2U}$  turns to be localized to a considerable extent.

We note in conclusion that such large average values of the cancellation of the  $z$  projections of the impurity spins (up to  $1/2$ ) make it impossible to employ in this problem the Holstein-Primakoff formalism which we have in this case avoided.

## 5. QUALITATIVE ANALYSIS OF THE SPIN STATE OF AN ALLOY

The above results of an investigation of a ferromagnetic crystal containing a diatomic impurity "molecule" can be summed up briefly as follows. For not too large values of the exchange coupling between the impurity atoms  $|I_{22}|$  the ground state of the crystal corresponds to the maximum value of the total spin  $S_{\max}^0$ , i.e., to complete "parallelism" of the spins of the impurity and of the matrix. At a certain critical value of the parameter  $I_{22}$  (with the other parameters

fixed) such a state becomes unstable and the ground state of the system corresponds to the spin  $S_{\max}^0 - 1$ . This state is localized and is characterized by cancellations of the  $z$  projections of the spins on the impurity atoms and atoms of the matrix near the impurity "molecule"; the total cancellation of the spin projections over the crystal should be equal to unity. With increasing  $|I_{22}|$  the degree of localization of the cancellation increases; however, for some  $|I_{22}|$  the system can in principle go over into states with values of the spin smaller than  $S_{\max}^0 - 1$  (this question which requires an analysis of the levels of many-particle deviations in the system has not been investigated). Physically it is clear that for  $S' > 1/2$  the state with  $S_{\max}^0 - 1$  will be the ground state in not too broad a range of variation of  $|I_{22}|$ . The state with  $S_{\max}^0 - 1$  will apparently remain the ground state for  $|I_{22}|$  increasing without limit only when  $S' = 1/2$  (with  $I_{12}$  of the order of  $I$ ). One can assume that the principal features of the ground state with  $S_{\max}^0 - 1$  (nonuniform distribution of cancellations of spin projections over the crystal and their localization near the impurity "molecule") will also be retained in states with  $S^0 < S_{\max}^0 - 1$ .

It would also be possible to consider analogously other multi-atom "molecules" in the crystal: "threes," "fours," etc. The results of the investigation of certain types of these defects in the special model ( $S' = S$ ,  $I_{12} = I$ ) are as follows:

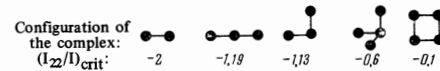


FIG. 5

Here we have indicated the critical values of  $I_{22}/I$  for which the state with parallel spins becomes unstable. These results are purely illustrative; however, a tendency can be traced in them: the more atoms in the impurity complex, the less stable the state with parallel spins. Since in the crystal  $I_{22}$  (as well as other parameters) are fixed, this means that in the presence of various types of isolated "molecules" a portion of these (molecules with smaller numbers of atoms) can be with parallel orientation of spins, whereas others already correspond to a smaller value of the total spin. This makes it possible to formulate some ideas concerning the structure of alloys of the type Ni-Mn, about which we have written at the beginning of the article, for small concentrations of the second component.

When the concentrations are so small that the atoms of the second component can be assumed to be isolated from one another, their spins are oriented parallel to the spin ordering in the matrix and a simple law of mixing operates for the average magnetic moment of the alloy, so that for  $S' > S$  the average moment of the alloy increases linearly with increasing concentration. With increasing concentration there appears a certain number of "twos," "threes," etc., and if in one of these "molecules" the condition of "parallelism" of the spin is violated, it will contribute a smaller contribution to the total spin of the crystal (compared with the case of complete parallelism of the spins). Thus,



for concentrations when there will be many such molecules in the alloy, a sharp decrease of the spontaneous magnetic moment of the alloy will commence. With further increasing concentration the number of molecules with a large number of atoms increases sharply and this ensures a rapid decrease of the average moment with the concentration.

It is thus possible to explain the nature of the curve on Fig. 1 within the framework of the Heisenberg model of ferromagnetism, without assuming a concentration dependent change of the atomic magnetic moments and taking into account only a decrease of the quantum-mechanical average projections of the atomic spins on the direction of the spontaneous moment of the crystal. The magnitude of the  $z$  projection of the atomic spin in an alloy changes from atom to atom and depends on the surroundings in which a given atom finds itself (i.e., on whether it constitutes a part of a "twosome," "three-some," etc). The quantum mechanical averages of the perpendicular projections of the atomic spins vanish at the same time. Of course, for high concentrations of the second component one cannot separate in the alloy isolated atoms (they join each other to produce long chains of various configurations), and the best description of such an alloy would be a statistical description in which it is assumed that the magnitude of the  $z$  projection of a given atom of the second component in the alloy is determined by the number of atoms of the same type in the nearest surroundings, i.e. by the number of couplings of the type  $I_{22}$ , and the value of this quantity averaged over the ensemble of atoms is obtained with account of the probability of the appearance of each type of neighborhood for a given concentration. Precisely such a program has been carried out in the work of Sidorov and Doroshenko<sup>[1,2]</sup> who expressed the concentration dependence of the average moment of this type of alloys by means of a phenomenological parameter—the concentration  $c_0$ . However, their phenomenological approach did not reveal the connection between the spin state of the system and the energy parameters—the magnitudes of the

exchange interactions; this we have partly filled in through this study.

As a general conclusion we find that the indicated alloys have a collinear magnetic structure but with a nonuniform distribution of the  $z$  projections of the atomic spins over the crystal, which depends on the concentration. The spontaneous moment of the crystal provides a quantization axis in the system which is unique for all the magnetic moments of the alloy.

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