Magnetic State of Components of Fe-Mn Alloys and Mixing energy: First-Principles Calculation

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Abstract - **Methods of first-principles computer simulation have been used to calculate the magnetic moments at the component atoms and the energies of mixing in disordered substitutional fcc and bcc solid solutions of manganese in iron. It has been established that the energies of mixing in alpha- and gamma-solid solutions have not only different magnitudes but even different signs. It is shown that in alpha- solid solutions there is a thermodynamic anomaly at a manganese concentration of approximately 1.5 at. %, namely, a change in the concentration dependence of the energy of mixing caused by a reorientation of magnetic moments at manganese atoms. With increasing Mn content in dilute solutions, there occurs a continuous variation of the orientation of magnetic moments of manganese atoms from strictly antiparallel with respect to the ferromagnetic iron matrix to predominantly parallel one.**

***Index Terms*—Fe-Mn, mixing energy, LMTO, thermodynamics, magnetic moments.**

I. INTRODUCTION

A topical and important problem of solid-state physics is the calculation of the energy of atomic interaction in solid solutions. In recent years, packets of computer programs have been developed which make it possible to calculate properties of substitutional solid solution using the method of a supercell that was developed for the investigation of metallic glasses [1]. In this method, a self-consistent calculation of the electronic-band structure is performed for a model crystal formed by periodically repeating in space a certain unit cell (a selected part of the disordered material under consideration).

Note that a similar quantity is measured or calculated by indirect methods in thermochemistry [2]. We speak of the energy (heat) of mixing of components in a solution E_{mix}, which for a binary solution at T = const is the difference between the energy (enthalpy) of the solution and the energies of pure components B and C taken in appropriate proportions. For example, in a simple thermochemical approximation we have

$$E_{mix} = A \cdot x_B \cdot x_C \qquad (1)$$

where $A = zN(2\varepsilon_{BC} - \varepsilon_{CC} - \varepsilon_{BB})/2$ is the energy of interchange between the atoms of types B and C. Thus, the heat of mixing is directly expressed through the energies of interaction ε_{ij} of atoms of types i and j. If we assume that the change in entropy upon the dissolution of components reduces to the configurational entropy for a disordered distribution of atoms, we obtain the so-called model of regular solutions [3]. In this case, the parameter A should be independent of concentration but can change with temperature. In the next approximation, the model of subregular solutions is used, according to which $A = A_1 \cdot x_A + A_2 \cdot x_B$.

The heats of mixing or the parameters A are experimentally measured by determining pressures of saturated vapors or using the electrochemical and calorimetric methods [2], but for terminal solutions and, especially, for nonequilibrium phases the parameter A can be roughly estimated from the boundary concentrations of phases being in a stable or metastable equilibrium. But even if such measurements are conducted, they usually refer to high temperatures and the extrapolation of experimental results into the range of low temperatures is always associated with a risk of errors.

Table I gives thermodynamic parameters A^{γ} and A^{α} for the gamma- and alpha solid solutions of manganese in iron according to various literature data. Here,

$$A = \frac{\Delta G_{ex}}{x_A x_B} = \frac{E_{\text{mix}}}{x_A x_B} - T\frac{\Delta S_{\text{ex}}}{x_A x_B} \qquad (2)$$

where ΔG_{ex} is the excess free energy of mixing with respect to the ideal solid solution. In this equation, the temperature-independent term corresponds to the energy of mixing and the coefficient at T is expressed through the excess entropy of mixing, which frequently turns out to be independent of temperature.

The data of different authors for E^{α}_{mix} and E^{γ}_{mix}, correspondingly, for A^{α} and A^{γ} differ substantially not only in magnitude but even in sign. For the fcc alloys, the preference can be given to the data of [5] obtained in experiments with a galvanic cell. However, the measurements in this investigation were carried out at 1073-1273 K; therefore, the behavior of A^{γ} below 1073 K remains uncertain. In essence, we have no criterion that could help us to select some works as being most reliable.

Since the conduction of an accurate experiment at low temperatures appears to be difficult, it is natural to turn to a computer simulation of the quantity of interest. As was already noted above, the modern computation methods permit one to determine the energy of mixing with a sufficiently high accuracy, at least at the absolute zero temperature. Thus, in [10] and [11] independent calculations of the energy of mixing for bcc Fe-Cr alloy were performed using the LMTO and EMTO methods. The results of both calculations coincide to an accuracy of 600 J/mol. Moreover, in both calculations there was revealed a region of small chromium contents (below 6 at. %) in which the energy of mixing has a negative sign.

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Table I. Thermodynamic properties of Fe-Mn alloys

N	A^{γ} (J/mol)	A^{α} (J/mol)	$\Delta^{0}G_{Mn}^{\alpha\rightarrow\gamma}$ (J/mol)	Ref.
1	$+4960$	$+480$		[3]
2	$-21800+19.08\,T$	$-3370-16.43\,T-1500\,S_m$	$-1800+1.276\cdot T$	[4]
3	$730-10\cdot T$	$19450-12.81T-1500\,S_m$	$-1800+1.276\cdot T$	[5]
4	$-18870+16.987\cdot T$	$4100\,x_{Fe}+5188\,x_{Mn}+(4.486\,x_{Fe}+1.506\,x_{Mn})\,T$	$1477-0.514\,T-2.742\times10^{-2}\,T^2+1.6534\times10^{-6}\,T^3$	[6]
5	$-15000+7.3\cdot T$			[7]
6	$(-13390\,x_{Fe}+24270\,x_{Mn})\times(1-T/1100)$			[8]
7	$A^{\gamma}=A^{\alpha}$	$A^{\gamma}=A^{\alpha}$	$-30805+23.103\,T$	[9]

This circumstance permits us to assume that the suggested method of computer simulation of the energy of mixing with the use of a TB-LMTO packet of programs that was developed by Andersen et al. [12] makes it possible to calculate this quantity for the ground state to an accuracy of 600 J/mol.

The aim of this work is to calculate the energy of mixing of bcc and fcc Fe--Mn alloys at 0 K and to estimate the local magnetic moments at manganese and iron atoms, since an analysis of these quantities helps one to understand the nature of the concentrational dependence of the energy of mixing.

II. COMPUTATION TECHNIQUE

The calculations were performed using a TB-LMTO-ASA packet of programs, version 4.7. For the simulation of various concentrations, we used a supercell consisting of 54 iron atoms for the bcc lattice and of 32 atoms for the fcc lattice; some of these were randomly replaced by manganese atoms. In this way, we performed a simulation of alloys with manganese content from 0 to 50 at. %. In the approximation of the local spin density with the use of a Barth--Hedin exchange-correlation potential [13], we calculated the total energy, density of electronic states, and magnitudes of the magnetic moments at isolated atoms for the ferromagnetic and antiferromagnetic states of the system. The errors related to the use of the atomic-sphere approximation (ASA) were corrected by the introduction of the so-called combined correction [12, 14]. In all cases, we used the LMTO basis including s, p, and d functions for each atom in the supercell. While integrating over the Brillouin zone, we employed a grid in the k space consisting of 8 ×8 × 8 nodes, which ensured, according to the data of control tests, an accuracy of the calculation of the total energy no worse than 0.5 mRy. When simulating the Fe--Mn system, we found, using several computational experiments, that the allowance for topologically inequivalent variants of arrangement of impurity atoms in the iron matrix leads to substantial changes in the energy and parameters of the system. This circumstance forced us to develop a technique of averaging of the results of calculations over the possible variants of arrangement of impurity atoms. We wrote a computer program which, for a given number of impurity atoms in the cell, enumerates all possible ways of their arrangement, dividing the configurations analyzed into groups. One group includes all impurity-atom configurations that can be obtained from one another via symmetry operations allowed for a given crystal lattice. Correspondingly, the configurations of impurity arrangement entering into different groups cannot be reduced to one another by symmetry operations (irreducible variants).

The number of configurations entering into a given group determines the relative probability of the appearance of a corresponding irreducible variant. For example, from the seven groups for the case of two impurity atoms two groups contain 324 configurations each; two groups, 216 configurations each; two groups, 162 configurations; and one group, 27 configurations. For each composition, we selected several main irreducible variants whose total fraction exceeded 50%. The configurational averaging of the calculation results reduced to the averaging of electronic and magnetic characteristics of the selected irreducible variants in accordance with their probabilities, which permitted us to perform this procedure with a reasonable consumption of the computational time.

We investigated the concentration dependence of the total energy of the system and energy of mixing of the alloy, which was calculated by the following scheme. The energy of mixing is determined by subtracting the total energies of the components (taken with corresponding weights) from the total energy of the composition under study:

$$E_{\text{mix}} = E_{\text{tot}} - x\cdot E_{Fe} - (1-x)\cdot E_{Mn} \tag{3}$$

where E_{tot} is the total energy of the alloy of composition $Fe_{1-x}Mn_x$, and E_{Fe} and E_{Mn} are the total energies of the corresponding elements (all taken per atom). In the calculations, we used experimental values of the lattice parameters of disordered Fe-Mn alloys borrowed from [15]. In a number of cases, including pure Fe and Mn, the calculations were also performed, to estimate the effect of lattice parameters on the computational results, for lattice parameters both greater and smaller than the experimental ones.

III. CALCULATION RESULTS AND DISCUSSION

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The results of the calculation energy of mixing for FCC

Fe-Mn solutions are presented on the Fig.1.

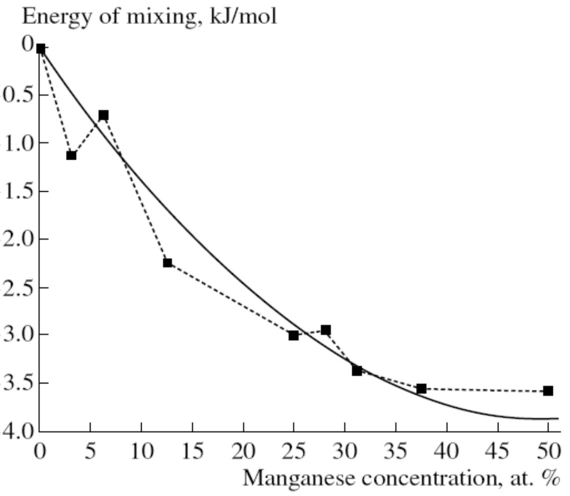

Fig.1 Concentration dependence of the energy of mixing for γ-solid solutions of the Fe-Mn system: dot line - calculation; solid line - approximate curve described by Eq. (4).

Note, first of all, that the E_{mix} values are negative. This means that these alloys have a tendency to ordering. The absolute value of the energy of mixing increases as the manganese concentration increases to 50%. The concentration dependence of E_{mix} can be described by the equation

$$E^{\gamma}_{\text{mix}}(0) = -15500\ x_{Fe}\ x_{Mn}\ \text{(J/mol)}, \qquad (4)$$

characteristic of regular solutions. Thus, $A^{\gamma}(0)$ = -15500 J/mol. Let us compare this result with the data given in Table 1. Approximately the same value (but for the temperature range of 800-1000 ^{0}C) was obtained in [7] by emf measurements. Note also the results of measurements at 1450 ^{0}C: $\Delta H^{\gamma} \simeq -(18000 \pm 5000)\ x_{Mn}\ x_{Fe}$ J/mol [2]. We can suppose that the energy of interchange in the temperature range of 0—1450 ^{0}C is virtually independent of temperature and is equal to -15500 ± 700 J/mol.

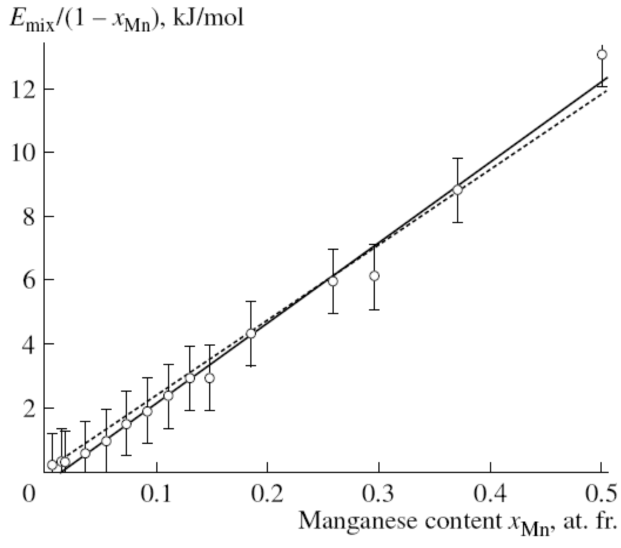

Fig.2 Energy of mixing for bcc solid solutions of the Fe-Mn system: empty circles - calculation; solid line- approximate curve in the range of concentrations above 1.5 at. %; and dotted line - approximate straight line passing through the origin.

The solid solutions of manganese in α-iron have a positive energy of mixing. Fig.2 displays the results of calculations in $E_{\text{mix}}/(1-x_{Mn})$ versus x_{Mn} coordinates.

It is seen that the equation of the straight line

$$E^{\alpha}_{\text{mix}}/(1-x_{Mn}) = 25200\ (x_{Mn} - 0.015) \qquad (5a)$$

with a rather high accuracy approximates the obtained dependence at $x_{Mn} > 0.015$. Below, we will show that all points lying on this line correspond to the case where the magnetic moments of iron and manganese atoms mainly coincide in direction, i.e., they have a ferromagnetic orientation. At manganese concentrations above 0.015, the straight line should intersect the abscissa axis; i.e., the energy of mixing should change its sign, as was observed earlier for Fe-Cr alloys [10]. However, at $x_{Mn} < 0.015$ a more stable configuration is that in which the magnetic moments of impurity atoms turn out to be antiparallel to the matrix moments. Three points near zero that deviate from the straight line refer just to this situation. If we draw a straight line through the origin, its equation

$$E^{\alpha}_{\text{mix}}/(1-x_{Mn}) = 23700\ x_{Mn} \qquad (5b)$$

approximates the results of calculations at $x_{Mn} > 0.015$ slightly worse, but corresponds better to the model of regular solutions. Thus, the energy of interchange in the α-phase can be assumed to be $A^{\alpha}(0)$ = 23700 J/mol.

The results of our calculations did not confirm most data for the energy of mixing given in literature (see Table 1). In some cases, the difference is not only in magnitude but even in sign. The only investigation whose results are close to our is that by Hillert and Waldenstrom [5] (A^{α} = 19000 J/mol). The thing is that no experimental study of the heat of mixing in the bcc Fe-Mn alloys have ever been performed, since the solubility range in this system is very limited both in concentration and temperature. The experiments at low temperatures for such systems are virtually impossible. Therefore, all the authors used the diagram of equilibrium of the α- and γ-phases in these alloys and the thermodynamic conditions of their equilibrium, which reduce to the equality of the chemical potentials of the components in the two phases. If we assume that both α- and γ-solutions are close to regular, the equilibrium conditions can be described by two equations [3]:

$$\begin{aligned} &{}^{o}G^{\gamma}_{Mn} + A^{\gamma}\cdot(1-x^{\gamma}_{Mn})^2 + RT\cdot\ln x^{\gamma}_{Mn} = \\ &\qquad {}^{o}G^{\alpha}_{Mn} + A^{\alpha}\cdot(1-x^{\alpha}_{Mn})^2 + RT\cdot\ln x^{\alpha}_{Mn} \end{aligned} \qquad (6a)$$

$$\begin{aligned} &{}^{o}G^{\gamma}_{Fe} + A^{\gamma}\cdot(1-x^{\gamma}_{Fe})^2 + RT\cdot\ln x^{\gamma}_{Fe} = \\ &\qquad {}^{o}G^{\alpha}_{Fe} + A^{\alpha}\cdot(1-x^{\alpha}_{Fe})^2 + RT\cdot\ln x^{\alpha}_{Fe}. \end{aligned} \qquad (6b)$$

From the first equation, we can derive the parameter A^{α} as

$$A^{\alpha} = \frac{({}^{o}G^{\gamma} - {}^{o}G^{\alpha})_{Mn} + A^{\gamma}\cdot(1-x^{\gamma}_{Mn})^2 + RT\cdot\ln\left(\dfrac{x^{\gamma}_{Mn}}{x^{\alpha}_{Mn}}\right)}{(1-x^{\alpha}_{Mn})^2} \qquad (7)$$

and calculate its values at various temperatures, given the differences in the free energies of the γ- and α-phases of manganese $({}^{o}G^{\gamma} - {}^{o}G^{\alpha})_{Mn}$, energies of mixing for the γ-phase, and the equilibrium boundary concentrations x^{γ}_{Mn} and x^{α}_{Mn}. Eq. (4) permits us to calculate the temperature dependence of A^{α} using reliable (as is confirmed by our results for 0 K) data given in [5] and [3]:

$$A^{\gamma}(T) = -15000 + 7.3 \cdot T \text{ J/mol};$$
$$\Delta^{o}G_{Mn}^{\alpha-\gamma} = -1800 + 1.276\, T \text{ J/mol.} \quad (8)$$

In this calculation, we also used the data on the equilibrium concentrations of manganese in the α- and γ- phases borrowed from [9,17]. The results are given in Fig.3.

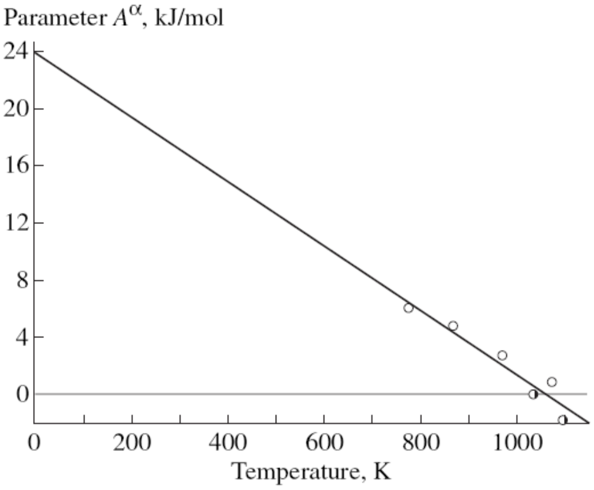

Fig.3 Calculation of the temperature dependence of the parameter A^{α} based on the experimental data on the boundary concentrations of manganese upon the γ-α phase equilibrium in the Fe-Mn system. The data were borrowed from : ○ – [17], ◑ – [9].

Below 1060 K, the parameter A^{α} becomes positive and sharply increases with decreasing temperature. A linear extrapolation of the A^{α} values to 0 K gives a value $A^{\alpha}(0)$ =24000 J/mol, which is close to the results of computer calculations. We, of course, can doubt if the temperature dependence of $A^{\alpha}(T)$ is linear, but the coincidence of data obtained at T = 0 K speaks in favor of such a dependence, i.e.,

$$A^{\alpha}(T) = 23700 - 22.36 \cdot T \text{ J/mol.} \quad (9)$$

We have also noted above that the positive sign of the energy of mixing reflects the tendency of the components to surround themselves by atoms of the same kind. In the approximation of regular solutions [3], which is quite applicable for the Fe-Mn alloys with a manganese content greater than 2 at. %, the temperature--concentration boundary (dome) of immiscibility is determined by the equation

$$T = \frac{A^{\alpha}}{R} \frac{1 - 2x_{Mn}^{\alpha}}{\ln\left((1 - x_{Mn}^{\alpha}) / x_{Mn}^{\alpha}\right)} \,. \quad (10)$$

The results of calculations of the immiscibility diagram using values of A^{α} specified by Eq. (9) are shown in Fig. 4.

In this diagram, a spinodal line is also drawn, at which the coefficient of interdiffusion is equal to zero. Its equation is as follows:

$$T = 2A^{\alpha}\, x_{Mn}^{\alpha}\, (1 - x_{Mn}^{\alpha}) / R \,. \quad (11)$$

The validity of the immiscibility diagram can be confirmed by the results of [18], where the phase separation in the α-phase was established experimentally.

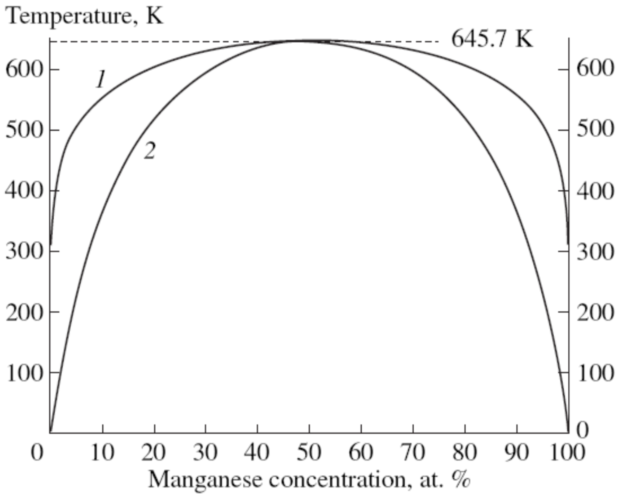

Fig.4 Calculated diagram of phase separation and the spinodal curve for Fe--Mn α-solid solutions.

IV. MAGNETIC MOMENTS OF ATOMS IN THE BCC FE-MN SOLID SOLUTIONS

The magnetic properties of ferromagnetic bcc Fe-Mn alloys have been studied insufficiently. Note in particular the controversy between the existing data on the magnitude of the local magnetic moment at impurity manganese atoms both in the absolute value (which changes from $0.0 \pm 0.2\ \mu_B$ [19] to $1.0 \pm 0.2\ \mu_B$ [20]) and in the direction (cf., e.g., +0.77 μ_B parallel to the magnetic moment at the atoms of the iron matrix according to [21] and -0.82 μ_B according to [22]). In [23], it was shown by direct calculations in terms of the LMTO method that the states with a parallel and antiparallel orientations of the magnetic moments at the impurity manganese atoms in the iron lattice are stable and degenerate in energy. This permitted the authors of [23] to suppose that it is the fluctuations between the two above states with the opposite spins that are responsible for the discrepancies in the experimental data. In this connection, it was of interest to test the above assumption by performing a similar investigation of the concentration dependence of magnetic moments in dilute bcc Fe-Mn alloys using first-principles calculations. Note that in [24] there was made a similar attempt with the use of the KKR method in the coherent-potential approximation. However, the results obtained in [24] only poorly agreed with the available experimental data.

The results of our calculations given in Fig. 5 permitted us to refine the conclusions made in [23]. As follows from Fig. 5, at small manganese contents (less than 1.5 at. %) a strictly antiparallel arrangement of magnetic moments of manganese and iron atoms is realized, since the magnitude of the average moment at Mn atoms coincides with the absolute value of the moment. Our calculation, contrary to that of [23],

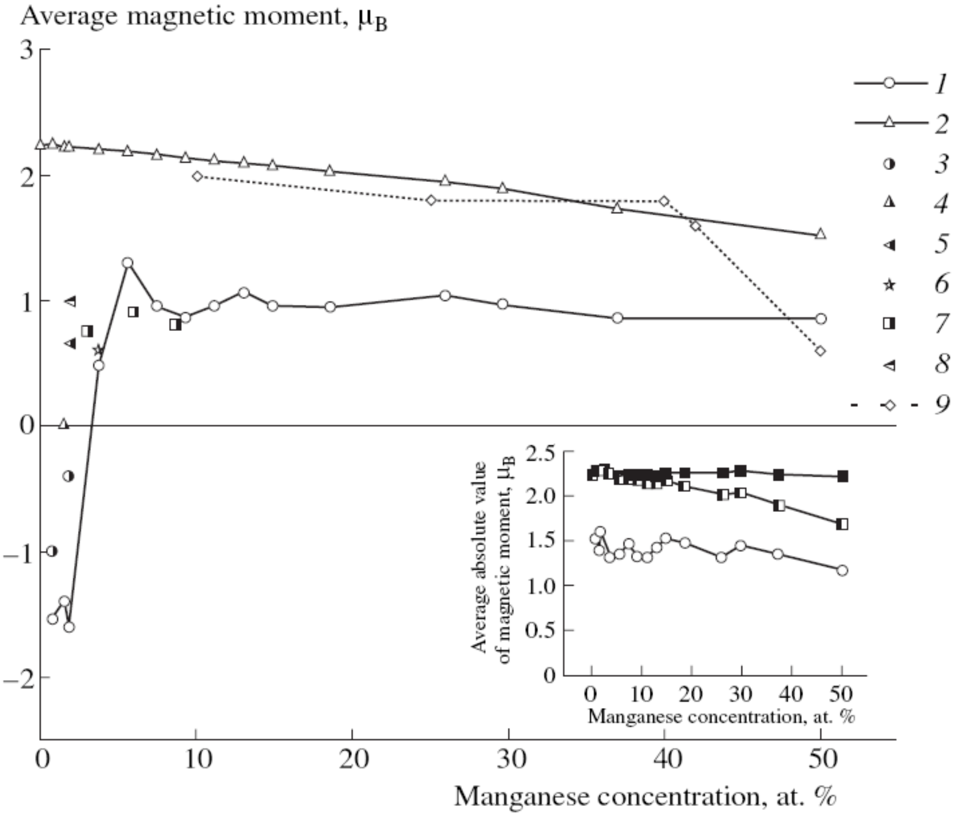

Fig.5 Magnetic moments in Fe--Mn alloys: (a) average magnetic moment per alloy atom: (2) - this work; (9) - experimental data of [21, 24]; (b) average magnetic moment of Mn atoms: (1) - this work; (3)--(8) experimental data borrowed from (3) [22], (4) [19], (5, 8) [20], (6) [25], and (7) [21]. The inset displays the results of calculation of the absolute values of magnetic moments of Fe atoms (upper curve), Mn atoms (lower curve), and the average absolute values of magnetic moments per alloy atom. The experimental data refer to room temperature.

showed that the antiparallel orientation of the magnetic moment of manganese is nevertheless energetically more favorable. However, the energy required for the reversal of the magnetic moment at the manganese atom is indeed small. Therefore, even a slight increase in the Mn content to 1.5 at. %, which leads to an increase in the magnetic interaction between its atoms in the solution, violates the stability of a given configuration. Such a behavior agrees with the more general results obtained by Izyumov and Medvedev (cited by [26]) which indicate a principle possibility of a reorientation of the spin of an impurity atom in the case of an initial antiparallel spin arrangement under the effect of thermal activation. The origin of the instability of the antiparallel ordering of manganese magnetic moments in our case can easily be understood if we assume that the magnetic interaction between the manganese atoms dissolved in iron is antiferromagnetic. Then, in the case of a strictly antiparallel ordering with respect to the ferromagnetic matrix the magnetic moments of any pair of manganese atoms will be parallel and their magnetic energy will increase. To avoid an increase in the magnetic energy, some manganese atoms (probably, nearest to one another) begin to change the orientation of the moment from antiparallel to parallel orientation. The number of such atoms increases monotonically with increasing Mn concentration. According to our calculations, at a Mn concentration of 2 at. % the number of atoms in parallel and antiparallel configurations becomes approximately equal, so that there is observed a zero value of the average magnetic moment at manganese atoms. As the Mn content increases further, approximately to 6--8 at. %, the parallel orientation gradually becomes dominating. However, beginning from 8 at. % Mn, the average magnetic moment of Mn atoms becomes stabilized at a value on the order of 1 μ_B, which is substantially lower than the observed average absolute value of the magnetic moment equal to approximately 1.4 μ_B (see inset in Fig. 5). The same is held for the magnetic moments at iron atoms. This suggests that the sign of the energy of magnetic interaction between magnetic moments of Mn and Fe atoms can change depending on their spacing, which is caused by Friedel oscillations of the electron density. Then, the related frustration effects transform the solid solution into a state of the spin-glass type, which agrees well with the conclusions obtained in studies of iron--manganese alloys by the Mossbauer method [27].

The results obtained in our work permit us to understand the origin of discrepancies between the available experimental data [19-22, 25] in both the magnitude and direction of the magnetic moment of manganese atoms at small Mn concentrations. It appears to be related to the spread in the composition of the samples. Note also that the ability of impurity manganese atoms to form stable and almost degenerate in energy states with parallel and antiparallel orientations in the bcc lattice of iron leads to a deviation of the concentration dependence of the average magnetic moment from the linear dependence. In this relation, the Fe-Mn alloys differ from Fe-Cr atoms that were studied in our previous works [10], which can be referred to classical Slater--Pauling systems with a linear dependence of the average magnetic moment of an alloy on its composition.

V.CONCLUSIONS

(1) The calculations performed suggest that at 0 K the solid solutions of manganese in fcc and bcc iron are close in behavior to regular solutions but have energies of mixing that differ in the magnitude and sign of the interchange energy and, correspondingly, in the energy of mixing: A^{γ}_{Fe-Mn} = -15.5 kJ/mol, A^{α}_{Fe-Mn} = +23.7 kJ/mol. It may be assumed that the fcc solutions are apt to ordering, whereas the bcc alloys have a tendency to phase separation.

(2) The published thermodynamic data obtained in experimental studies of the heat of mixing give, when being extrapolated to zero temperature (0 K), values of the energy of mixing differing not only in magnitude bur even, in some cases, in sign. The calculation data agree with the results obtained in [9] for the fcc and bcc solutions.

(3) Near 1.5 at. %, the BCC solid solutions exhibit a thermodynamic anomaly - a change in the concentration dependence of the energy of mixing - which is caused by a reorientation of magnetic moments of manganese atoms.

(4) With increasing Mn concentration in dilute solid solutions, there occurs a continuous variation of the orientation of magnetic moments of manganese atoms, namely, their deviation from the strictly antiparallel orientation relative to the ferromagnetic iron matrix to predominantly parallel, which apparently corresponds to the formation of a phase of the spin-glass type.

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