The formation and ordering of local magnetic moments in Fe-Al alloys

A.K. Arzhnikov*, L.V. Dobysheva, M.A. Timirgazin

Physical-Technical Institute, Ural Branch of Russian Academy of Sciences, Kirov str. 132, Izhevsk 426001, Russia

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* Corresponding author: e-mail arzhnikov@otf.pti.udm.ru, Phone +07-3412-218988, Fax +07-3412-250614

With density functional theory, studied are the local magnetic moments in Fe-Al alloys depending on concentration and Fe nearest environment. At zero temperature, the system can be in different states: ferromagnetic, antiferromagnetic and spin-spiral waves (SSW) which has a minimum energy. Both SSW and negative moment of Fe atoms with many Al atoms around them agree with experiments. Magnetization curves taken from literature are analysed. Assumption on percolation character of size distribution of magnetic clusters describes well the experimental superparamagnetic behaviour above 150 K.

1 Introduction. The alloys Fe-Al attracts the attention of researchers as a perspective material in an extreme technology. They possess the properties such as good refractoriness, oxidizing and corrosion resistance, relatively low density, good ductility at room temperature. Intensive study of magnetic properties was firstly initiated by a development of non-destructive control methods, as the magnitudes of all the above properties correlate with magnetic characteristics in these alloys. Afterwards, unusual behavior of magnetic properties generated a separate interest to their study. Mainly the attention is focused on the concentration range from 25 to 50 at.% of Al for quasiordered and from 40 to 60 at.% of Al for disordered alloys. Reliably enough, it was established that in higher and lower concentration ranges the alloys are in the ferromagnetic and paramagnetic states, correspondingly, and in the intermediate region more complicated states are realized. To the beginning of the 80-s a majority of researchers have been convinced that at low temperature the magnetic state is a spin glass in this region. But a row of experimental data that had been then considered as an evidence for the spin glass, had, as a matter of fact, another nature, which has been revealed later. For example, the thermomagnetic hysteresis in these alloys is a consequence of a solely magnetic hysteresis [1].Recently, the neutron powder diffraction has shown that at low temperature the magnetic order is governed by spin-density waves [2]. At high temperature the alloys are superparamagnetic [3].

A row of discrepancies in studies of magnetic properties of these alloys has given an impetus to our paper. Here, a theoretical analysis of the superparamagnetic behavior in the experimental data available is conducted, collinear and spiral magnetic structures are studied with the help of the density-functional theory.

2 Superparamagnetic behavior. Magnetization curves of the alloy with 34 at.% Al as a function of the applied magnetic field and temperature have been received in the Ref. [3]. Higher than the blocking temperature of 150 K the magnetization curves join each other, which is typical for the paramagnetic behavior. Besides, the magnetization increases rather quickly at low magnitude of the parameter $h/T \approx 10^3 A/m/K$, but does not reach the saturation up to $5 \times 10^4 A/m/K$, which is an evidence for different by size magnetic clusters that do not interact. Note that the system is structurally homogeneous, so the clusters are governed by magnetic interactions. Using the Arrhenius formula for the relaxation time $t$ one can estimate the up-
per limit for the number of atoms in clusters. It is an order of \( n_{\text{max}} \approx 10^4 \) atoms (the characteristic time of magnetic measurement at which the detection of largest clusters is possible equals \( t = t_0 \times \exp\{-n_{\text{max}}E_a/KT\} \approx 10^{-2} \) s, where \( E_a \approx 7 \times 10^{-25} \) J/at is energy of the magnetocrystalline anisotropy in iron, \( t_0 \approx 10^{-6} \) c is the spin-lattice relaxation time, \( T = 150K \) is a blocking temperature).

Assuming that the alloy contains clusters of two types, we succeeded in describing the magnetization curves with clusters of 6 nm diameter (6500 atoms in the cluster) and 3 nm diameter (600 atoms in the cluster). 20 % of all atoms belong to the 6 nm clusters and 80 % of all atoms belong to the 3 nm clusters. The average magnetic moment of an Fe atom is 0.33\( \mu_B \). This description has however essential shortcomings. First, there is no physical or chemical mechanism which could be responsible for just these cluster sizes (as authors of Ref.\[3\] assure, the sample was homogeneous). Second, with such size distribution of clusters, magnetization at weak fields should be proportional to \( h/T \), which is not corroborated by experiment (see insert in Fig.\[1\]).

More naturally looks the assumption about a continuous size distribution as this is in the case of hierarchy of the cluster size distribution in disordered percolation task [4,5]. In this case, density of the number of clusters consisting of \( n \) Fe atoms divided by total number of lattice sites is equal to \( \omega_n = x(\tau - 2)n_{\text{min}}^{-\tau}n^{-\tau} \), where \( \tau \) is a critical exponent [4,5], \( n_{\text{min}} \) is a minimal cluster size and \( x \) is concentration of Fe atoms. As the magnetic moment of a cluster is large, one can use classical concepts and calculate the magnetization per iron atom (see Ref.\[6\]):

\[
M = m_{\text{av}}(\tau - 2)n_{\text{min}}^{-\tau} \times \int_{n_{\text{min}}}^{\infty} n^{1-\tau}[\text{cth}(nm_{\text{av}}h/kT) - kT/nm_{\text{av}}h] \, dn
\]

Here \( m_{\text{av}} \) is average magnetic moment of an Fe atom in a cluster.

Scaling relations [5] allow us to write \( \tau = \delta^{-1} + 2 \), where \( \delta \) determines the magnetization behavior \( M \propto \)}
$(h/T)^{1/8}$ at $h/T \to 0$. In the insert to Fig. 1 shown is a least-squares adjustment of the experimental data with $\delta = 1.49$. From the above interrelation between coefficients we receive $\tau = 2.67$. Further, using this $\tau$, we have conducted fitting in the whole range of the parameter $h/T$ (Fig. 1). The best agreement with experiment have been achieved at $n_{\text{min}} = 62$ atoms and $n_{\text{av}} = 0.44 \mu_B$.

We must note that the coefficient $\tau$ obtained does not coincide by magnitude with the coefficient in the classical percolation theory ($\tau = 2.2$ [5]). To our opinion, the reasons are the following: first, the sample in the experiment was quasiorordered, that is, had a strong short order; second, it did not reach the percolation threshold; third, the interactions between the atomic magnetic moments, that govern the geometry of magnetic clusters, are connected with the chemical configurations of the atoms disposition in a very complicated way.

3 Dependence of Fe magnetic moments on the closest atomic environment. To understand the peculiarities of the magnetic interaction in the Fe-Al alloys we have conducted first-principles calculations of the periodical systems $\text{Fe}_{38}\text{Al}_{16}$ (29.6 at.\% Al), $\text{Fe}_{31}\text{Al}_{5}$ (31.3), $\text{Fe}_{34}\text{Al}_{20}$ (37.0), $\text{Fe}_{10}\text{Al}_{6}$ (37.5) and $\text{Fe}_{9}\text{Al}_{7}$ (43.8). These systems have been chosen so that to cover that interesting intermediate concentration region from 29 to 44 at.\% Al and to receive many different chemical configurations of the iron nearest environment. The calculations have been conducted by FP LAPW method with the WIEN2k program package [7]. The detailed description of the models and approximations used is given in [8].

One of the main results consists in the following: there are two solutions with collinear magnetic moments found for all the concentrations studied. One of them has Fe local magnetic moments all of a direction, the other has both positive and negative moments depending on environment. Namely, the magnetic moments at Fe atoms with 6 and more Al atoms in nearest environment direct oppositely to those of the rest iron atoms. In the following, we call the first as the solution of a ferromagnet type (FM), and the second as that of an antiferromagnet type (AFM). The AFM states are slightly lower by energy than the FM ones in $\text{Fe}_{31}\text{Al}_{5}$, $\text{Fe}_{34}\text{Al}_{20}$ and $\text{Fe}_{10}\text{Al}_{6}$; in $\text{Fe}_{38}\text{Al}_{16}$ and $\text{Fe}_{9}\text{Al}_{7}$ the FM state is more preferable. The Fe average magnetic moment in the AFM solutions as a function of Al concentration agrees rather well with experimental data (Fig. 2). Fig. 2 shows the iron magnetic moments in all the systems studied, in the aggregate, depending on nearest environment. One can see that direction and magnitude of the magnetic moments in AFM solutions are rather accurately determined by chemical composition of the iron nearest environment, and only small variations can be imputed to different structure, concentration or environment in more distant coordination spheres.

Similar results have been also obtained earlier for disordered alloys using a two-band Hubbard model [10]. This behavior of local magnetic moments gives grounds for usage of the Jaccarino-Walker model for interpretation of experiments. The main idea of the Jaccarino-Walker model asserts that the local magnetic moment at a transition-metal atom is determined by chemical composition of the nearest environment and only weakly depends on the overall concentration. Using this model authors of Refs. [9,11] have described combination of magnetic and Mossbauer experimental data in disordered and partly disordered Fe-Al alloys. Surely, the models describing the magnetic order in terms of closest environment cannot pretend to be very precise in the transition-metal alloys. Nevertheless, this model

![Figure 2](image2.png) Average magnetic moment of Fe atoms as a function of Al concentration. Circles denote the first-principles results, squares are for experimental data from Ref. [9]. Triangle shows the moment obtained from analysis of superparamagnetic behavior.

![Figure 3](image3.png) The local magnetic moment of Fe atoms as a function of number of Al atoms in the nearest environment.
4 Spiral magnetic structures. Recently, neutron diffraction studies [2] have shown that quasierorder Fe-Al alloys have spin-density waves with [111] direction at temperature lower than 100 - 150 K. Such study, as authors of Ref.[2] themselves admit, cannot distinguish the spin-density wave with a collinear structure (SDW) and the spin-spiral wave (SSW). SDW in Cr have been rather long ago known and well studied. A nesting in the Fermi surface [13] is considered the most justified mechanism for appearance of SDW in Cr. This mechanism looks impossible for the Fe-Al alloys. First, the Fermi surface of iron does not have nesting; second, the alloys have a disorder in the atomic disposition, which makes the influence of the Fermi surface on the SDW formation very problematic. That is why we think that the oscillations in the experiment come from SSW and consider the conditions of their appearance in the systems $F_{9}A_l7$ and $F_{10}A_l6$. The calculation is conducted with use of a non-collinear-magnetic version of WIEN2k package [14,15]. The SSW in $F_{9}A_l7$ has been considered earlier in [10]. They have received that the SSW with [001] direction and the wave vector $q = 0.44a_0^{-1}$ possesses the minimum energy (here $a_0$ is a bcc lattice parameter). We have received the same result for $F_{10}A_l7$. For $F_{10}A_l6$ the minimal by energy SSW direction coincides the experimental one [11]. The difference between the collinear and the SSW solutions is less than 7 mRy/cell which is a small value and allows transitions from SSW to a collinear state at small energy of an external excitation (magnetic field or temperature). We must note that wavelength of the SSW received in both our and Ref. [16] calculations is $4a_0$, while the experimental value observed at these concentrations is $7a_0$ [2].

We did not take into account the spin-orbit interaction in our calculations, so it cannot be responsible for the appearance of the SSW as this usually occurs in the magnetics on the basis of rare-earth elements and actinides. To our opinion, the main reason of the SSW appearance as the ground state is a competition of the two collinear magnetic states FM and AFM that are close by energy.

5 Conclusions. At temperatures higher than 150 K the alloy with 34 at.% of Al is a typical superparamagnetic [5]. The best theoretical description of experimental magnetization curves is obtained with assumption that cluster distribution by size obeys a scaling law with minimum size clusters as $\approx 60$ magnetic atoms, and with the average local magnetic moment of Fe atom is $m_{av} = 0.44\mu_B$.

Our study has shown a potential possibility of existence of few types of magnetic order in Fe-Al alloys: collinear structures (FM and AFM) and spin-spiral waves (SSW). The energy of SSW is lower than those of the FM and AFM structures. The difference in energy between these states does not exceed 7 mRy/cell. This allows the system to transform from one magnetic structure to another at weak external influence (magnetic field or temperature). The character of the thermal or field transition from SSW to a collinear state is, however, unclear in actual disordered alloys: is it a kind of phase transition or the transition occurs through a row of continuous reconstructions of the electron structure in local regions?

The average Fe magnetic moments theoretically calculated in structures with AFM ordering (Fig.2) are close to the experimental data from direct magnetization measurements and from the analysis of the superparamagnetic behavior. This fact allows researchers to use for interpretation of experimental data a modified Jaccarino-Walker model, with a dependence of the magnetic moment on the closest environment similar to Fig.5.

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References

[1] E. P. Elsukov, E. V. Voronina, A. V. Korolyov, and A. E. Yelsukova, Hyper. Interact. 168, 1079 (2006).
[2] S. Kirkpatric, Rev. Mod. Phys. 45, 243 (1973).
[3] E. V. Voronina, E. P. Yelsukov, A. V. Korolyov, and A. E. Yelsukova, Hyper. Interact. 117, 87 (1992).
[4] A. K. Arzhnikov and L. V. Dobyshева, (presented for publication to J. of Exper. and Theor. Phys.)
[5] E. P. Elsukov, E. V. Voronina, A. V. Korolyov, A. E. Elsukova, and S. K. Godovikov, Phys. Met. Metallogr 104, 35 (2007).
[6] A. K. Arzhnikov and L. V. Dobyshева, J. Magn. Magn. Mater. 117, 87 (1992).
[7] K. Szymanski, D. Satula, L. Dobrzynski, E. Voronina, E. P. Yelsukov, and T. Miyanaga, Phys. Rev. B 72, 104409 (2005).
[8] H. Sato and A. Arrott, Phys. Rev. 114, 1427 (1957).
[9] A. W. Overhauser, Phys. Rev. 128, 1437 (1962).
[10] R. Laskowski, G. K. H. Madsen, P. Blaha, and K. Schwarz Phys. Rev. B 69, 140408(R) (2004).
[11] K. Szymanski, D. Satula, L. Dobrzynski, E. Voronina, E. P. Yelsukov, and T. Miyanaga, Phys. Rev. B 72, 104409 (2005).
[12] H. Sato and A. Arrott, Phys. Rev. 114, 1427 (1957).
[13] A. W. Overhauser, Phys. Rev. 128, 1437 (1962).
[14] R. Laskowski, G. K. H. Madsen, P. Blaha, and K. Schwarz Phys. Rev. B 69, 140408(R) (2004).
[15] J. Kunes and R. Laskowski Phys. Rev. B 70, 174415 (2004).
[16] J. Bogner, W. Steiner, M. Reissner, P. Mohr, P. Blaha, K. Schwarz, R. Krachler, H. Ipser, and B. Sepiol, Phys. Rev. B 58, 14922 (1998).