Formation of hyperfine fields in alloys

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This work deals with the analysis of experimental data on the average magnetization of $Fe_{1-x}Me_x$ (Me=Sn,Si) disordered alloys, the average and local hyperfine fields (HFF) at the Fe nuclei. The effect of the metalloid concentration on the HFF is studied with the help of the results of first-principles calculations of ordered alloys. The disorder is taken into account by means of model systems. The dependences obtained correspond to those experimentally observed. Experimental data on the ratio of the average HFF at Fe nuclei to the average magnetization in alloys with sp-elements show that the ratio decreases proportionally with the metalloid concentration. This change in the ratio is bound up with three factors. First, the contribution of the valence electron polarization by the neighboring atoms, that is positive (unlike the polarization by the own magnetic moment), increases with the change of the disorder degree (increase of concentration). Second, the appearance of the impurities, i.e. metalloid atoms, in the nearest environment of Fe leads to the orbital moment increase. And, finally, the change of the disorder degree, as in the first case, results in an increase in the orbital magnetic moment and its positive contribution to the HFF. The value and the degree of the influence of these contributions to the HFF is discussed.

In the opinion, even in this case the experimental spectra may provide more reliable and complete information without the use of phenomenological models and restriction to the nearest environment. One should then analyze the HFF peculiarities from the "first-principles" calculations. This work is devoted to such an analysis of the hyperfine magnetic fields, magnetization and local magnetic moments and their interrelation in the disordered $Fe_{1-x}Sn_x$, $Fe_{1-x}Si_x$ alloys. Here the magnetic characteristics of clusters with a given impurity configuration in disordered alloys are taken from the first-principles calculations of the translationally invariant systems, supposing the interaction between the clusters to be not significant because of small free length of electron in these alloys. Nowadays, there is no possibility to conduct these calculations for the disordered systems, moreover, it should be noted that even calculations of the ordered alloys often do not give the required agreement with experiment and reveal only the main features of the HFF and LMM behavior.

The calculations were performed by the full-potential linearized augmented plane wave method (FLAPW) using the WIEN-97 program package [5]. The results are presented in Table 1.

The systems were simulated on a BCC lattice which in the disordered alloys under consideration is retained within a wide concentration range [1]. The lattice parameters were chosen in accordance with the experimental values for $x=3.125$ at.%. and $x=6.25$ at.%. It should be mentioned that even at small concentrations the BCC lattice is somewhat distorted due to the repulsion/attraction by the Sn/Si atom of the surrounding Fe atoms. As shown in our paper [6], the changes in magnetic characteristics because of this relaxation are insignificant. Though the results in Table 1 were obtained with allowance for this relaxation, we do not discuss it here.

1. AVERAGE AND LOCAL MAGNETIC MOMENTS.

Fig.1 presents the experimental data and the calculated averages of the magnetic moment per one Fe atom. The average magnetic moment $M = \sum_i M_d^i + M_{int}$, where $M_d^i$ is the spin magnetic moment over the muffin-tin (MT) sphere of the i-th Fe atom (hereinafter we will refer to this value as local magnetic moment, LMM), $M_{int}$ is the spin magnetic moment over the unit cell with-
out the MT-spheres. The main contribution to the LMM comes from the d-electrons that are almost entirely inside the MT-sphere, whereas $M_{int}$ is formed by the s- and p-electrons and has a small negative value as compared to the LMM. We do not take into account the contribution of the orbital magnetic moment that is about 0.045 $\mu_B$ in our calculations. In experiments this value is 1.572 times larger and comprises 0.08 $\mu_B$ [7]. It is believed that the inclusion of the orbital polarization in the exchange-correlation potential [8] improves the agreement between the calculations and the experimental values, but here we didn’t use such a potential supposing that the calculated value can be multiplied by the factor close to two. The main reason for the neglect of the orbital contribution lies in the fact that its variations with concentration and configuration of metalloid atoms are small as compared to M even with allowance of the actual value and amounts less than 1 % (see the last but one column in Table 1), whereas the Mdi variations range up to 15 %. Fig.1 displays a rather good agreement of the magnetic moment with the experimental data, though the theoretical values of the magnetic moment are somewhat higher than the experimental ones. We believe that the disorder, which is not taken into account here, reduces the magnetization by 2-3 % [9]. Let us mention some peculiarities of the magnetic moments formation.

A. The magnetic moment does not depend on the metalloid type and, as shown in Ref.10, is governed by the lattice parameter, a. At equal concentrations, the lattice parameter of the Sn alloy is greater than that of the Si alloy, so the magnetic moment in the first case is greater.

B. The LMM of the Fe atom closest to the impurity is of the smallest among others value (Table 1). As noted in Ref.10, this difference is defined by the competition between two mechanisms: the LMM reduction due to flattening of the d-band because of the s-d hybridization that is the strongest near the impurity, and the LMM increase due to narrowing of the d-band because of a decrease of the wave function overlap. There also exists third mechanism of the LMM reduction due to the difference in the impurity-potential screening by d-electrons (the difference in pushing out the impurity levels by the bands with spin up and down), which was revealed in this work by a comparison of the number of d-electrons within the MT-sphere for different Fe-atom positions (there are more d-electrons near the impurity, Table 1).

C. The LMMs are concentration dependent. So the LMM of the Fe atom closest to the Si atom is 2.181 $\mu_B$ at x=3.125 at. % ($Fe_{31}Si$), and 2.262 $\mu_B$ at x=6.25 at. % ($Fe_{15}Si$). This LMM increase with concentration holds in general for all the non-equivalent positions (Table 1). However, in spite of the LMM increase, the average magnetic moment in the $Fe_{1-x}Si_x$ system somewhat decreases 2.238 $\mu_B$ at x=3.125 $\mu_B$ (Fig.1). This is the result of a higher probability of finding a Fe atom with a neighboring impurity, which increases the number of Fe atoms having lower LMM values.

2. HYPERFINE MAGNETIC FIELDS AT NUCLEI.

The program package WIEN-97 allows one to calculate the interaction between the nucleus magnetic moment and the spin and orbital magnetic moments of the electron subsystem. The spin dipole contributions are small (2 \( \div \) 3 kGs), they are suppressed due to the symmetry relations, and the main contribution comes from the spin polarization at the nucleus (Fermi-contact interaction) and the orbital magnetic moment. The Fermi-contact interaction may be divided into $H_{i}^{core}$ (the core-electron polarization) and $H_{i}^{vol}$ (the valence-electron polarization), and hence, the resulted field at the i-th site contains three terms: $H_{i} = H_{i}^{core} + H_{i}^{vol} + H_{i}^{orb}$. For the core-electron polarization the simple relation $H_{i}^{core} = \gamma_{s} M_{d_{i}}$ is satisfied, where $\gamma_{s}$ does not depend to a high accuracy on neither the metalloid type nor its concentration, and is determined only by the approximation for the exchange-correlation potential. Here we use the GGA approximation [11] which gives $\gamma_{s} \approx 123kGs/\mu_B$. In our opinion just this simple expression between the LMM and Hcore makes it possible to use phenomenological models neglecting the effect of the atoms in the second, third, etc. coordination spheres. Really, from Table 1 one can see that the main distinctions in LMM at a certain concentration are connected with the presence or absence of the metalloid atom in nearest environment. So, this also determines the variations in $H_{i}^{core}$. Though the experiments showed that the proportionality between the magnetic moment and HFF is not as good as we found, and the proportionality coefficient essentially decreases with concentration. As we shall see later this is connected with the other two contributions to the HFF.

The proportionality $H_{i}^{orb} = \gamma_{orb} M_{i}^{orb}$ is fulfilled in a somewhat worse way, but still rather satisfactorily. Note, however, that $\gamma_{orb}$ is positive and about five times larger in magnitude than $\gamma_{s}$. Hence, if the changes of $M_{i}^{orb}$ affect the magnetic moment only slightly, the changes in Horbi may amount to 20 kGs even at low concentrations (see Table 1). The nature of these changes in disordered alloys is discussed in more detail in Ref.12. Here we men-
tion only the main features. The $H_i^{val}$ increases along with the $M_i^{orb}$ increase with concentration. The $H_i^{val}$ takes the largest value at the atom closest to the metalloid atom. The increase of $H_i^{val}$ with allowance for the actual values of $M_i^{orb}$, that are twice as large as the calculated one, comprises 15±20 kGs even at low concentrations as compared to that in pure Fe. On the strength of the qualitative character of the last statement, we can say about the tendency of the variations. Finally, as shown in [10], the orbital contribution increases also with disorder (that is, with concentration).

The $H_i^{val}$ behaves in a more complicated way. This is primarily associated with strong delocalization of the s- and p-like electrons that interfere at sites with different magnetic and charge properties, and therefore the $H_i^{val}$ behavior cannot be in fact quantitatively predicted. However, we succeeded in revealing some qualitative regularities supported by experimental evidence. First of all, we analyzed the valence contribution using the simple functional dependence of the magnetic moment screening in the RKKY (Ruderman - Kittel - Kasuya - Yosida) theory, as it was done in Ref.9: $H_i^{val} = A + B \sum_j M_j^{orb} \cos(2k_j r / T + \phi) / r^3$. Such a simplified treatment of $H_i^{val}$ is hardly justified in our case, but we hope to have determined the main qualitative dependences. Solving the inverse task for the ordered cluster of size 200 a.u. we receive the most probable values of A, B, T and $\phi$ in the alloys Fe15Sn and Fe31Sn. The corresponding functions of $B \cos(2k_j r / T + \phi) / r^3$ are shown in Fig.2. Of special interest is the fact that for both concentrations the spin polarization of electrons is positive for the I and II coordination spheres, which entirely contradict the results of a similar processing of the experimental data. This is due to the fact that during processing of the experimental data the difference between H0 (HFF at the nucleus of the Fe atom without the metalloid atoms in its nearest environment) and H1 (with one impurity atom in the nearest environment) was attributed to the changes in $H_i^{val}$, whereas in an alloy there are differences in the local magnetic moment that primarily affect $H_i^{core}$ and $H_i^{orb}$. Fig.3 presents the experimental H0 and H1 as a function of concentration. Table 1 shows that the difference between these quantities can be successfully explained by the LMM magnitude and hence by the core-electron polarization. However, if everything were determined only by $H_i^{core}$ we should expect an increase in H0 and H1 with concentration in accordance with the LMM increase, which is not the case, as for the Fe15Sn alloy the magnetic moment increases much more quickly than H0 and H1, and there is no increase at all for Si. In reality the expected increase is compensated by the decrease in magnitude of the configurationally averaged negative contribution $H^{val}$. Fig.4 gives the averaged values of $H^{val}$ of a disordered cluster of size 200 a.u. with a certain number of impurities in the first coordination sphere. The averaging was performed in assumption that the Fe atoms are distributed randomly and polarize the conductivity electrons at distance r according to the model function for concentrations 6.25 and 3.125 % (see Fig.2). The decrease of the averaged Hval with concentration is due to the positive values of the
RKKY polarization at the distance of the first and second coordination spheres (see Fig.2). Two main features in the behavior of the Hval averaged over configurations can be noticed. First, the magnitude of \( H_{\text{val}} \) at the Fe atom without impurities in nearest environment is less by 5-10 kGs than \( H_{\text{val}} \) at the Fe atom with one impurity in the environment, and second, the magnitude of the averaged \( H_{\text{val}} \) decreases with concentration for both configurations of the environment.

Thus, the use of the "first-principles" calculations makes it possible to explain the main peculiarities of the HFF behavior in the low-concentration disordered alloys \( Fe_{1-x}Me_x \). The difference between \( H_0 \) and \( H_1 \) \( H_0 - H_1 \approx -20 \) kGs consists of \( H_{\text{val}}^0 - H_{\text{val}}^1 \approx 7 \div 10 \) kGs, \( H_{\text{core}}^0 - H_{\text{core}}^1 \approx -15 \div -25 \) kGs and \( H_{\text{orb}}^0 - H_{\text{orb}}^1 \approx -5 \div -10 \) kGs. The decrease of the proportionality coefficient between the HFF and the magnetic moment with concentration results from the decrease of magnitude of \( H_{\text{val}} \) and increase of magnitude of \( H_{\text{orb}} \) that are opposite to the \( H_{\text{core}} \).

We believe that the general relations obtained here will be useful in processing the experimental data on the HFFs in disordered alloys of transition metals and non-magnetic impurities.

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TABLE I. The results of the calculations: Configuration of impurities in the Fe-atom environment, [nm...] denotes the number of metalloid atoms in the first (n), second (m) etc. spheres. Number of such Fe atoms in the unit cell, $N_{Fe}$. Number of d-electrons in the MT sphere, $N^d$. Magnetic moment, $M^d$, in the MT sphere. Contribution of the core-electrons polarization to the HFF, $H^{core}$. Contribution of the valence-electrons polarization to the HFF, $H^{val}$. Orbital magnetic moment, $M^{orb}$. Orbital contribution to the HFF, $H^{orb}$.

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Fe$_{31}$Sn, $a=21.804$ a.u.

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Fe$_{15}$Sn, $2a=21.985$ a.u.

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Fe$_{31}$Si, $a=21.604$ a.u.

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Fe$_{15}$Si, $2a=21.585$ a.u.