Formation of magnetic characteristics
and hyperfine fields in metal-metalloid alloys

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This work deals with the analysis of peculiarities of formation of the hyperfine fields (HFF) at the Fe nuclei in disordered alloys metal-metalloid using the "first-principles" calculations. Some phenomenological models and justification of their usage for the interpretation of the experimental HFF distributions are discussed.

Keywords: hyperfine field, magnetic moment, disordered alloy

1. Introduction

The development of technologies for preparing materials for modern electronics requires a detailed knowledge of different local physical quantities at the atomic level. In the experimental physics the possibility to measure the local characteristics at such a scale are very limited. Among few existing methods, of special accuracy are the nuclear ones (for example, the Mossbauer spectroscopy) that measure the hyperfine magnetic fields (HFF) at nuclei. It is widely believed that these techniques can reflect some chemical and topological features of the atomic surroundings of the excited nuclei. Indeed, in numerous studies the spectra are interpreted in terms of phenomenological models considering only the nearest atomic environment (see e.g. [1-3]). There is no doubt that such a description is often useful and efficient. We think, however, that there are some cases when such a simplified approach is not justified. Moreover, for the spectra of transition metals and alloys on their basis, the successful description within the framework of such models is rather an exception than a rule, and every time additional arguments are needed to justify these limitations.

In this work we analyze the peculiarities of formation of HFF in disordered alloys of Fe and metalloid using the "first-principles" calculations. One may consider an HFF as
a sum of three main terms: $H_{\text{core}}$, $H_{\text{val}}$ and $H_{\text{orb}}$ which are the core, valence and orbital contributions, respectively. This standard division is based on the physical features that determine the magnitude of these contributions, $H_{\text{core}}$ and $H_{\text{orb}}$ being mostly dependent on the topological and chemical peculiarities of the nearest neighboring only, whereas $H_{\text{val}}$ is significantly influenced by the atoms of the second and more distant spheres. At the same time, in disordered alloys the effect of the distant spheres on $H_{\text{val}}$ may be considerably suppressed due to the great localization of the valence electrons. Owing to this, in some cases [1-3] the HFF distributions can be successfully described by phenomenological models of the Jaccarino-Walker type where the magnitudes of the local magnetic moments (LMM) and HFF are taken to be dependent on the number of metalloid atoms in the nearest neighboring. Often such descriptions are surprisingly accurate and efficient. One must bear in mind, however, that the phenomenological models have fitting parameters, and there are various examples in the history of sciences when the accuracy and efficiency were illusory, being only a result of manipulation with the number and magnitudes of the parameters.

To avoid such a trap, one must realize how to remove the contradiction between the localized character of the description of HFF and the itinerant behavior of the d- and sp-electrons in metals. At present, the solid state theory based on the ”first-principles” calculations allows one not only to justify the use of some phenomenological models, but also to make them more reliable by defining the parameters from the ”first-principles” calculations.

In this paper, we analyze the behavior of $H_{\text{core}}$, $H_{\text{val}}$ and $H_{\text{orb}}$ using the ”first-principles” calculations performed for the ordered alloys $Fe_{100-c}Me_c$ ($Me = Si, Sn$), namely: $Fe_{31}Si$, $Fe_{15}Si$, $Fe_{31}Sn$, $Fe_{15}Sn$, $Fe_{26}Si_6$, $Fe_{25}Si_7$, $Fe_{24}Si_8$, $Fe_{23}Si_9$ and $Fe_{22}Si_{10}$, and experimental data [4]. The calculations were carried out by the full-potential linearized augmented plane wave method (FLAPW) using the WIEN-97 program package [5]. Some 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 of the alloys with corresponding concentrations
(c = 3.125, 6.25, 18.75, 21.875, 25, 28.125 and 31.25 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 magnetic of the surrounding Fe atoms. As shown in our paper [6], the changes in 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.

2. The local magnetic moment

Hereinafter, the local magnetic moment (LMM) at Fe atom \(i\) means the spin magnetic moment over the muffin-tin (MT) sphere, \(M^d_i\). The average magnetic moment over the unit cell is \(M = \sum_i(M^d_i + M^{orb}_i) + M^{int}\), where \(M^{orb}_i\) is the orbital magnetic moment, \(M^{int}\) is the spin magnetic moment outside 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 neglect \(M^{orb}\), as its variations with concentration and the metalloid atoms arrangement are small and amount to less than 1 \(\%\) [7]. The calculated values are two times less than the experimental ones. We believe that the actual changes of \(M^{orb}\) do not exceed twice the calculated ones. It should be noted that the neglect of \(H^{orb}\) requires some caution: in what follows we shall show that the changes in \(H^{orb}\) may be quite significant amounting to 10 \(\div 15 \%\) of the average HFF. Mention the principal features of the LMM formation.

A. The main peculiarities of the magnetic moment depend weakly on the metalloid type and, as shown in [8], 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 other values. As noted in [8], 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) [7].

C. The LMMs are concentration dependent. So the LMM of the Fe atom closest to the Si atom is $2.181 \, \mu_B$ at $c=3.125$ at.\% ($Fe_{31}Si$), and $2.262 \, \mu_B$ at $c=6.25$ at.\% ($Fe_{15}Si$) (Table 1).

At the same time, our "first-principles" calculations and the mathematical treatment [9-10] testify that, to an accuracy of $10 \div 15\%$, the LMMs in disordered alloys are independent of concentration and governed by the number of nearest metalloid atoms only.

D. It is natural to expect that, with a large number of nearest metalloid atoms the LMM will considerably decrease down to zero, due strong s-d hybridization [10].

3. 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), $H^{\text{core}} + H^{\text{val}}$, and the orbital magnetic moment. For the core-electron polarization the simple relation $H_i^{\text{core}} = \gamma^s M_d$ 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 $\gamma^s \approx 123kGs/\mu_B$. Due to the simple relation between the LMM and $H^{\text{core}}$ and owing to the possibility of the rough description of the LMM as a function of neighboring metalloids number discussed in Section 2 point C, if $H^{\text{val}}$ is not too large one can use the Jaccarino-Walker-type phenomenological models while interpreting the HFF distributions of disordered metal-metalloid alloys, but the accuracy in this case cannot be high.

The proportionality $H_i^{\text{orb}} = \gamma^{\text{orb}} M_i^{\text{orb}}$ is fulfilled in a somewhat worse way, but still rather satisfactorily. Note, however, that $\gamma^{\text{orb}}$ is positive and about five times larger in magnitude
than $\gamma^s$. Hence, if the changes of $M^{orb}_i$ affect the magnetic moment only slightly, the changes in $H^{orb}_i$ with allowance for the actual magnitude of $M^{orb}$ may amount to 20 kGs even at low concentrations (see Table 1).

$H^{val}_i$ 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 $H^{val}_i$ behavior cannot be in fact quantitatively predicted in disordered systems. However, we succeeded in revealing some qualitative regularities supported by experimental evidence. We analyzed this contribution using the simple functional relation

$$H^{val}_i = F_0 M_i + \sum_j F_j N_j,$$

(1)

where $F_0$ is a constant describing the polarization of the valence electrons of the Fe atom at site $i$ by its own magnetic moment, $F_j$ are factors describing the change of polarization at atom $i$ by the metalloid atom in sphere $j$, $\sum_j$ is summation over all coordination spheres ($j > 0$), $N_j$ is the number of metalloid atoms in sphere $j$. Fig.1 shows the values of $F_j$ for the calculations of different sets of alloys. The first curve was obtained by solving the equation system Eqn. (1) by the least-squares method with calculated values $H^{val}_i$ and $M_j$ for the alloys Fe$_{26}$Si$_6$, Fe$_{25}$Si$_7$, Fe$_{24}$Si$_8$, Fe$_{23}$Si$_9$ and Fe$_{22}$Si$_{10}$, the second curve was calculated for the data for the alloys Fe$_{31}$Si and Fe$_{15}$Si, the third curve was received for Fe$_{31}$Sn and Fe$_{15}$Sn alloys. One can see that $F_j$ is of oscillating nature and depends on the metalloid type and concentration. This dependence reveals itself mostly at close distances, which leads to an amazing conclusion: $H^{val}$ may be considered, to some extent, as a linear superposition of the changes in spin polarization by distant atoms, whereas the polarization by close atoms can hardly be regarded as linear because of a significant re-distribution of the charge density which is not linear.
FIG. 1. The parameters of the model (1), $F_j (kGs)$, as a function of sphere number

Thus, it is clear why the use of the simplest RKKY (Ruderman- Kasuya- Yosida- Kittel) interaction for the description of HFF resulted sometimes in reasonable conclusions for superlattice. First, for the realistic sp-electron densities, this interaction has an oscillation period close to our result ($2 \div 3$ interatomic distances, Fig.1). Second, the spin polarization by the distant metalloid atoms may be considered additive. In the superlattices (e.g. in the $DO_3$ type ordered alloy $Fe_{75\pm c}Si_{25\mp c}$), the possibility of a configuration of impurity (here, by an impurity is meant an atom of $Fe$ or $Si$ which appears at a ”wrong” site as compared to the totally ordered $Fe_3Si$ alloy) atoms arrangement around the $Fe$ atom with
large number of the impurity atoms in the second and third spheres may be high even at low concentration of the impurity atoms. In the light of the above, the models where the spin polarization is considered as an additive contribution from the RKKY polarization by the first sphere, are doubtful.

So far, our statements were mainly based on the "first-principles" calculations of the ordered alloys, while the disordered one were discussed. It should be mentioned that the problem of quantitative calculations of HFFs in disordered alloys remains unsolved, that is why we can examine the effect of disorder only qualitatively, using the model systems.

In our paper [8], the effect of disorder was investigated by averaging the RKKY interaction whose parameters were determined from the "first-principles" calculations. Now we realize that such an approach should be used with caution. However, the result of this paper [8] that the decrease of the HFF magnitude should be larger than the decrease in the magnetic moment with disordering (i.e. with the increase in metalloid concentration), holds true if the behavior of the polarization by the third and most distant spheres being averaged in disordered alloys, is similar to that of Fig.1 (the positive polarization by the third sphere).

Note that the decrease in $H_i/M_i$ is also determined by the increase in the positive contribution of $H_{orb}$ with the increase of the disorder degree [12]. It is difficult to separate these contributions and to answer unambiguously why the change of this ratio is experimentally observed.

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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. $N_{Fe}$ is the number of such Fe atoms in the unit cell.

|                 | $[nm...]$, $N_{Fe}$ | $M^d$, $\mu_B$ | $H^{core}$, kGs | $H^{val}$, kGs | $M^{orb}$, $\mu_B$ | $H^{orb}$, kGs |
|-----------------|---------------------|----------------|-----------------|----------------|-------------------|----------------|
| $Fe_{31}Sn$, a=21.804 a.u. | [1000], 8           | 2.246          | -277.50         | -37.59         | .0489             | 27.94          |
|                 | [0003], 8           | 2.507          | -310.35         | -30.94         | .0483             | 26.41          |
|                 | [0100], 6           | 2.432          | -300.17         | -34.84         | .0482             | 26.62          |
|                 | [0020], 6           | 2.425          | -299.79         | -22.39         | .0479             | 26.28          |
|                 | [0000], 2           | 2.391          | -295.13         | -34.34         | .0441             | 23.66          |
|                 | [0000], 1           | 2.423          | -299.68         | -24.17         | .0470             | 25.15          |
| $Fe_{15}Sn$, 2a=21.985 a.u. | [1003], 8           | 2.442          | -301.01         | -20.25         | .0548             | 29.77          |
|                 | [0200], 3           | 2.530          | -312.64         | -29.97         | .0535             | 29.08          |
|                 | [0040], 3           | 2.542          | -314.55         | -2.46          | .0550             | 29.38          |
|                 | [0000], 1           | 2.390          | -294.33         | -29.97         | .0450             | 23.32          |
| $Fe_{31}Si$, a=21.604 a.u. | [1000], 8           | 2.181          | -269.44         | -38.68         | .0497             | 28.27          |
|                 | [0003], 8           | 2.413          | -297.89         | -35.15         | .0471             | 25.55          |
|                 | [0100], 6           | 2.343          | -288.51         | -31.31         | .0446             | 24.46          |
|                 | [0020], 6           | 2.385          | -294.06         | -16.92         | .0468             | 25.32          |
|                 | [0000], 2           | 2.489          | -308.13         | -19.72         | .0485             | 26.44          |
|                 | [0000], 1           | 2.389          | -294.81         | -13.56         | .0451             | 24.28          |
| $Fe_{15}Si$, 2a=21.585 a.u. | [1003], 8           | 2.262          | -277.20         | -29.11         | .0594             | 32.38          |
|                 | [0200], 3           | 2.353          | -289.52         | -21.64         | .0456             | 24.44          |
|                 | [0040], 3           | 2.432          | -298.87         | 5.49           | .0509             | 27.31          |
|                 | [0000], 1           | 2.536          | -313.82         | -13.89         | .0496             | 26.83          |