Fe HYPERFINE FIELDS IN $\text{Fe}_{3-x}\text{V}_x\text{Si}$ ALLOYS

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The Mössbauer spectra of Fe in $\text{Fe}_{3-x}\text{V}_x\text{Si}$ alloys for $0 \leq x \leq 1$ shows that V occupies almost exclusively one of two Fe sites (the B site). As x increases the spectra of Fe on the other site (the A, C site) becomes increasingly complex as the number of their V 1st neighbors increases. Simulated Mössbauer spectra were calculated using moments obtained by a simple model from bulk magnetization and V NMR data. This model assumes a decrease in Fe(A, C) moments as the number of their Fe 1st neighbors decreases. Comparison of the Fe(B) field of the alloy with $x = 1$ to that of the alloy with $x = 0$ gives an estimated reduction in the on site 4s electron polarization of about 100 kOe or about 0.05 unpaired 4s electrons.

1. Introduction

Models based on the short-range interaction approach involving first nearest neighbor configuration interactions have been successfully used in explaining both the iron and impurity hyperfine fields in pseudobinary alloys of Fe_3Si with the transition metals Mn and V [1]. They are based on the assumption that (a) the atomic moment of an Fe atom in these materials is a function of the number of its first nearest neighbor Fe atoms and

(b) the observed hyperfine fields reflect both the contribution of the local moment and the spin polarization due to first neighbor moments. The models allow the interpretation of the magnetic hyperfine field data in terms of the electronic properties of the impurity atoms.

The intermetallic compound Fe_3Si is well ordered crystallographically in the face-centered cubic DO_3 type structure and ferromagnetic below about 800 K [2]. This structure (fig. 1) has four sites A, B, C and D. Fe occupies A, B and C sites, Si the D sites. Fe on B sites, Fe(B), has 8 Fe(A, C) first nearest neighbors, 1nn, and an atomic moment of $2.2\mu_B$, while Fe(A, C) has 4 Fe(B) + 4 Si(D) 1nn and a $1.35\mu_B$ atomic moment [3-5]. The internal fields of Fe(B) and Fe(A, C) nuclei at $T = 4.2$ K are 338 and 218 kOe, respectively [6,7]. Si(D) has 8 Fe(A, C) 1nn, essentially zero moment and an internal field of 37 kOe.

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Fig. 1. Unit cell of $\text{Fe}_{3-x}\text{V}_x\text{Si}$ alloys. The sites are represented by A, B, C and D. The A and C sites are equivalent and are occupied by Fe atoms, the B site is occupied by Fe and V, and the D site by Si.

Fig. 2. Spin-echo spectra of $\text{Fe}_{3-x}\text{V}_x\text{Si}$ for $x=0.15, 0.25, 0.5, 0.75$ and 0.9 at 1.3 K . The spectra are dominated by "V" resonance and no resolved lines due to Fe and Si nuclei are observed. This data is taken from ref. [2].

V introduced in Fe_3Si as an impurity replaced Fe randomly on the B sites and single phase solid solutions $\text{Fe}_{3-x}\text{V}_x\text{Si}$ form for $0 \leq x \leq 1$ with the lattice parameter increasing slightly with x and some $\text{B} \leftrightarrow \text{D}$ disorder [1]. Since the 3nn of B sites is composed of B sites, V(B) are 3nn of both Fe(B) and V(B) and shells of 12 Fe(B), 11 Fe(B) + 1 V(B), 10 Fe(B) + 2 V(B), etc., occur. The lines due to V nuclei with this variety of 3nn environments are clearly seen in spin-echo NMR spectra of alloys with $x \leq 0.25$ taken at 1.35 K . These lines, due to V with various numbers of V replacing Fe(B) in their 3nn shell, are clearly seen in fig. 2. Analysis shows that the internal field at such V nuclei is proportional to the average moment of its 1nn. These 1nn are Fe(A, C) atoms the moments of which are determined by the number of Fe atoms in their 1nn shell [1]. Although clearly seen in dilute alloys the NMR observation of the Fe(B) lines is impossible for alloys with $x \geq 0.04$ since the strong V resonance, shifting to lower frequencies as the V concentration increases, covers them. V(B) replaces Fe(B) atoms in the 1nn shell of the A, C atoms providing Fe(A, C) atoms which have 4, 3, 2, 1 or 0 Fe(B) 1nn. Again the very strong V resonance makes these lines unobservable in many NMR spectra. The work presented here, a Mössbauer study of the Fe internal fields, complements the NMR data and makes possible a comparison of the Fe fields in the Mn and V alloys.

2. Review of the local environment model and its application to related structures

Magnetization studies suggest that for small x the atomic moment of V in $\text{Fe}_{3-x}\text{V}_x\text{Si}$ is essentially zero and further, that the replacement of Fe(B) 1nn by V produces the same reduction in the Fe(A, C) moment as does the replacement of Fe(B) by Si in off-stoichiometric $\text{Fe}_{1-x}\text{Si}_x$ alloys [3].

Fig. 3 is a plot of the atomic moment of a Fe atom in Fe_3Si alloys as a function of the number of its Fe 1nn. This relationship and a similar one for Fe_3Al alloys was originally proposed by Friedman [8]. He also pointed out the proportionality of internal field and atomic moment for these alloy systems. Our recent measurements of saturation

Fig. 3. Magnetic moment at the Fe(A, C) sites (in μ_B) versus the number of Fe 1nn for the binary Fe-Si system. The moment of 8 Fe 1nn is $2.2\mu_B$. The solid line and closed symbols are taken by scaling the Fe moments with the corresponding hyperfine fields and the dashed line is a linear extrapolation.

Fig. 4. Experimental bulk magnetization (in μ_B per formula unit) for $\text{Fe}_{3-x}\text{V}_x\text{Si}$ alloys in the composition range $0 \leq x \leq 0.75$. The experimental results are shown by a solid line and open circle and the calculated values using the model described in fig. 3 by the dashed line and crosses. The nearly constant Fe(B) moment and the calculated average moments for B and A, C sites are also shown.

magnetization and internal fields in $\text{Fe}_{1-x}\text{Si}_x$, $\text{Fe}_{3-x}\text{Mn}_x\text{Si}$ and $\text{Fe}_{3-x}\text{V}_x\text{Si}$ alloys have strongly supported both the dependence of the Fe moment on its 1nn Fe atoms and the proportionality between the Fe hyperfine field and atomic moment. The saturation magnetization per formula unit for $\text{Fe}_{3-x}\text{V}_x\text{Si}$ alloys can be written

$$\sigma_0 = (1-x) 2.2 + x\mu(V) + (-0.07) + 2 \sum_{i=0}^4 P_i \mu_i, \quad (1)$$

where $\mu(V)$ is the moment of V (≈ 0), μ_i is the moment of an Fe(A, C) atom having i Fe(B) 1nn, P_i is the probability that an Fe(A, C) atom has i Fe(B) 1nn, and the Fe(B) and Si(D) moments are 2.2 and $-0.07\mu_B$, respectively. In general, for a concentration, x , of impurities randomly distributed on a sublattice, the probability, $P_n(m)$, of finding m impurities in a shell of n sites is

$$P_n(m) = \frac{n!}{m!(n-m)!} x^m (1-x)^{n-m}. \quad (2)$$

Since V randomly replaces the four Fe(B) 1nn of Fe(A, C) and x is the concentration of V on the B sublattice, the P_i 's are easily calculated [3].

Fig. 4 compares the measured composition dependence of the saturation magnetization of $\text{Fe}_{3-x}\text{V}_x\text{Si}$ alloys with one calculated as described above. The agreement over the composition range $0 \leq x \leq 0.75$ is good. It should be noted that for alloys with $0.5 \leq x \leq 0.75$ the values calculated using the model are lower than the measured values by a small amount underestimating the moment on some of the Fe sites in alloys with rather large V substitutions.

For the $\text{Fe}_{3-x}\text{T}_x\text{Si}$ ternary alloys, where $\text{T} = \text{V}, \text{Mn}, \text{Co}$, models based on the short-range interaction approach and involving 1nn configurations for the Fe(A, C) and Fe(B) atoms have been developed. The models successfully describe the detailed behavior of the magnetic moments and internal fields at all sites and thus division of the observed fields into contributions due to the spin polarization transferred from neighboring moments and the polarization resulting from the on-site moments is possible [1].

For systems involving transition metals, the in-

ternal field at a particular nucleus, H_{int} , is assumed to arise from three contributions: (1) a core polarization due to the exchange interaction between the on-site moment of the d electrons and the inner s shells, H_{cp} , (2) a spin polarization of the conduction s electrons due to the on-site moment of the atom itself, H_s , and (3) overall (transferred) conduction electron spin polarization due to the moments in neighboring shells, H_{sp} . Hence, we can write

$$H_{\text{int}} = H_{\text{cp}} + H_s + H_{\text{sp}}. \quad (3)$$

In general, the first two terms are proportional to the on-site moment, while the third term is usually expressed as a sum of terms involving the neighboring moments. As a first approximation, it is assumed that the transferred spin polarization at a nuclear site arises only from the moments in the 1nn shell and is given by

$$H_{\text{sp}} = A_{4s} n p \langle \mu \rangle_{1\text{nn}}, \quad (4)$$

where A_{4s} is the appropriate hyperfine coupling constant in units of kOe/μ_B , n is the number of 4s electrons involved in the hyperfine coupling, p is the exchange polarization of the 4s electrons by the 3d moments and $\langle \mu \rangle_{1\text{nn}}$ is the average moment per atom in the 1nn shell. Such an approach has proved successful in describing the internal field behavior for $\text{Fe}_{1-x}\text{Si}_x$, $\text{Fe}_{3-x}\text{V}_x\text{Si}$, $\text{Fe}_{3-x}\text{Mn}_x\text{Si}$ and $\text{Fe}_{3-x}\text{Co}_x\text{Si}$ [1,9]. For these systems, the atomic hyperfine coupling constants used were those calculated by Campbell [10].

The Fe magnetic moment is very sensitive to its 1nn atomic environment. The Fe(B) atoms in the $\text{Fe}_{1-x}\text{Si}_x$, $\text{Fe}_{3-x}\text{Mn}_x\text{Si}$ for $0 \leq x \leq 0.75$ and $\text{Fe}_{3-x}\text{V}_x\text{Si}$ for $0 < x < 0.1$ are always surrounded by 8 Fe(A, C) provided no atomic disorder is present. In this environment, Fe(B) preserves a constant moment of $2.2\mu_B$ regardless of the moment of the Fe(A, C) sites. Replacing Fe(B) atoms in the 1nn shell of an Fe(A, C) atom by elements to the left of Fe in the periodic table, V (with $0\mu_B$), Mn ($2.2\mu_B$) or with Si ($-0.07\mu_B$) reduces the Fe(A, C) magnetic moment in a linear manner [2], see fig. 3.

In Fe_3Si the values obtained for $H_{\text{cp}} + H_s$ and for H_{sp} at Fe(B) are -205 and -130 kOe, respectively [1].

3. Experimental and conclusions

The Mössbauer effect spectra for a series of $\text{Fe}_{3-x}\text{V}_x\text{Si}$ alloys are shown in fig. 5. Spectra for alloys with $x \leq 0.25$ were taken at room temperature and those with $x \geq 0.50$ were taken at 4.2 K. For purposes of comparison, the room temperature spectra were corrected to 4.2 K. Since the splittings in these spectra are due to magnetic hyperfine interactions. This correction can be accomplished by increasing the horizontal coordinates of each data point by the ratio of the measured magnetizations of the alloys at 4.2 K and room temperature, $M(4.2)$ and $M(\text{RT})$. $M(4.2)/M(\text{RT}) \approx 1.066$ for alloys with $x = 0, 0.2$ and 0.4 and 1.099 for the alloys with $x = 0.25$ [1].

We will first discuss the experimental spectra. The intensities of the outer lines, due to Fe(B) atoms, decrease with V concentration becoming negligible for $x = 0.9$. This behavior shows directly that the V is entering the Fe(B) site almost exclusively. The Fe(A, C) spectrum which is a single six line pattern in Fe_3Si where A, C sites have 4 Fe(B) + 4 Si(D) 1nn, increases in complexity as x increases, reflecting the variety of Fe(A, C) 1nn shells formed by V replacing Fe(B). If the model for the behavior of the Fe(A, C) moment is correct there are five different values of the Fe(A, C) moment and thus 5 values of the Fe(A, C) internal field and 30 lines contributing to the Mössbauer spectra. For the higher values of x the 1nn configurations with no Fe or few Fe predominate and the spectrum collapses into a single line representing an internal field near zero. For $x = 1$ this line shows a quadrupolar splitting of 0.7 mm/s.

The simulated spectra are calculated using the following assumptions:

- 1 All Fe sites are represented by a six line pattern with the intensities of the lines in the 3:2:1:1:2:3 ratios characteristic of powder patterns.
- 2 Two of the Fe(B) lines are the clearly resolved outer lines in each spectrum. Their intensities are decreased with concentration in proportion to the number of Fe on the B sites.
- 3 The splittings for the Fe(B) internal fields are obtained from the clearly resolved outer lines. These fields in alloys with $x = 0.00, 0.02, 0.04$

Fig. 5. Comparison of experimental and calculated Mössbauer spectra for $\text{Fe}_{3-x}\text{V}_x\text{Si}$ alloys for the compositions indicated. The data points are plotted to represent the experimental spectrum. The solid curve shows the spectrum calculated as described in the text.

0.25, 0.50, 0.75, 0.90 are (330 ± 10) , (325 ± 10) , (320 ± 10) , (305 ± 10) , (310 ± 10) and (310 ± 10) kOe, respectively.

- 4 There are as many as 5 Fe(A, C) internal fields and these fields are proportional to the Fe(A, C) atomic moments as determined from fig. 3.
- 5 The intensities of the Fe(A, C) lines are calculated from formula (2), assuming a random distribution of V on the B sites.
- 6 For all lines in alloys with $x = 0.00, 0.02, 0.04, 0.25$ and 0.50 line widths of $0.34, 0.41, 0.34, 0.41$ and 0.47 mm/s, respectively, were used. In al-

loys with $x = 0.75$ and 0.90 widths of 0.54 and 0.47 mm/s were used for all lines except the contributions near zero field which required a width of 0.81 mm/s. 0.81 mm/s widths were used for both lines in the $x = 1.00$ spectrum.

- 7 The measured isomer shifts, about 0.2 mm/s, relative to Fe in Fe metals, for Fe(B) and 0.14 mm/s for Fe(A, C) are used for the alloys with compositions near Fe_3Si ($x = 0, 0.2$ and 0.4). The spectra of these are simple enough to permit determinations from least-squares fits. No isomer shifts could be determined for alloys

with $x \geq 0.25$ and the shifts measured for Fe_3Si are used.

- 8 The spectrum for $x = 1$ is obviously two lines split by about 0.7 mm/s.

The simulated spectra do not attempt to include any of the following:

- 1 The effects of crystallographic disorder or errors in the concentrations of the alloys.
- 2 Second and more distant near neighbor effects except in-so-far as they affect a line's position in the spectrum.

In the regions of high and low x where least-squares computer fits of the experimental data to Lorentzian lines are possible the parameters used to calculate the simulated spectra agree well with those obtained by the least-squares computer fits. As can be seen in fig. 5, the overall agreement between the experimental and the simulated spectra are good, given the simplicity of the model.

The intensities of the Fe(B) lines agree with those required for a substitution of the V into B sites. The Fe(B) internal field in all alloys is nearly that of Fe in Fe metal. These values are higher than those calculated from eqs. (3) and (4) assuming that the contributions due to 4s electrons H_s , and H_{sp} (which depends on np), do not change. V substitutions into FeSi reduces the number of outer electrons and probably the number of 4s electrons. It is not unreasonable that both H_s and np are concentration dependent.

At the highest concentration ($x = 1$) where the average A, C moment is zero, H_{sp} becomes negligible. Since the internal field of Fe(B) in this alloy is about -310 kOe and H_{cp} is negative and should remain constant in the whole concentration range, a reduction of about 100 kOe in the positive contribution of the on site 4s spin polarization, H_s , is indicated, as one goes from Fe_3Si to Fe_2VSi . This loss corresponds to a reduction of about 0.05 in the unpaired 4s electrons. A hyperfine coupling constant of about 2000 kOe per 4s electron [10] was used to make this estimation.

The overall agreement between the experimental spectra and the Fe(A,C) portion of the simulated spectra is good, for $0 \leq x \leq 0.50$. The calcu-

lated spectrum for $x = 0.75$ and $x = 0.9$ underestimates the spectral contributions of the Fe(A,C) atoms which show larger internal fields and moments. This is the same region in which the model for the magnetization gives a value somewhat smaller than the experimental one. The Fe(A,C) atoms, which have 4 to 0 Fe(B) 1nn, have a moment which is nearly proportional to the number of the Fe 1nn. A spectral line from those Fe atoms with a 1nn shell completely filled by Si and V, and thus unable to support a moment, is clearly resolved for alloys with $x \geq 0.75$. Thus V affects the moment of its Fe 1nn in a manner very similar to that of Si and Al.

4. Summary

The Mössbauer spectra show directly the behavior of the Fe moments with V concentration which had been assumed to explain magnetization and V NMR data. In addition, the concentration dependence of the Fe(B) hyperfine fields together with the constancy of Fe(B) moments and variations of Fe(A,C) moments make it possible to estimate the change in the unpaired 4s spin density at Fe(B) between the Fe_3Si and Fe_2VSi alloys at about 0.05 electrons.

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