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## A Mössbauer investigation of ordered alloys with composition $\text{Ni}_3\text{Fe}_{1-x}\text{Sn}_x$ , $0 < x < 0.1$

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**Abstract.** Evidence is presented for believing that Sn atoms dissolved in  $\text{Ni}_3\text{Fe}$  lie mainly on Fe sites. We show that the hyperfine field at an Sn nucleus is determined by the moments in its first- and second-neighbour shells, and its magnitude is consonant with that found in other magnetic materials.

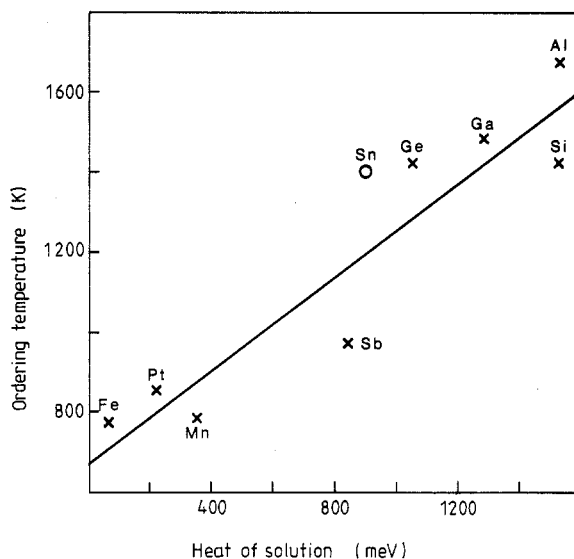
### 1. Introduction

The solubility of many elements in nickel exceeds 25%, and several of them form ordered alloys at that composition. In this, and a later paper, we are interested in compounds with the  $\text{Cu}_3\text{Au}$  ( $L1_2$ ) structure, in which the Au atoms lie on a simple cubic lattice, and the Cu atoms (in our case, Ni atoms), lie at the centres of the cube faces. The leading eight alloys listed in table 1 form the  $\text{Cu}_3\text{Au}$  ( $L1_2$ ) structure. The systematics of the ordering have been discussed by Pettifor (1986).

For our purposes, it will be relevant to consider the structure from the point of view of central pairwise interactions in the following way. Let us assume that both the heat of solution of metal B in metal A and the ordering of  $\text{A}_3\text{B}$  alloys in the  $L1_2$  structure can be associated with the breaking of B–B bonds and their replacement by A–B bonds. Then we may expect that the ordering temperature of the  $\text{A}_3\text{B}$  alloy will be correlated with the heat of solution of B in A. Miedema *et al* (1977) have given a semi-empirical formula which enables the heat of solution,  $H$ , of one metal dissolved in another to be predicted, and we have used this formula to deduce the values given in column 2 of table 1 for the heat of solution in nickel of the metals M of column 1. In column 3, we give the ordering temperature,  $T_c$ , of the alloy  $\text{Ni}_3\text{M}$ , and in figure 1 we have plotted  $T_c$  against the heat of solution. It can be seen that there is indeed a good correlation. The equation of the line in figure 1 is

$$T_c = aH + b \quad (1.1)$$

where, after converting  $T_c$  from K to meV,  $a = 0.050$  and  $b = 58$  meV. A simple first-neighbour interaction model predicts  $a = 0.25$  and  $b = 0$ . The observed value of  $b$  may be attributed to a band effect which is independent of solute, and the substantial



**Figure 1.** The ordering temperature of  $L1_2$  alloys of nickel plotted against the heat of solution. The point for tin, which does not form an  $L1_2$  alloy, is marked with an open circle.

**Table 1.** The table gives the heat of solution of ten elements in nickel, calculated using the methods of Miedema. The third column gives the ordering temperature of the  $Ni_3M$  alloy, and the fourth the interaction potential between element M and Fe when both are dissolved in Ni, using the method of Krolas (1981).

M	Heat of solution (meV)	$T_c$ (K)	M-Fe (meV)
Al	1534	1673	63
Ga	1286	1483	73
Ge	1054	1423	45
Mn	354	783	35
Pt	221	853	-19
Sb	845	973	65
Si	1530	1423	36
Fe	66	775	11
Cr	282	—	24
Sn	900	—	75

discrepancy in  $a$  may be due to interactions at greater distances than first neighbours (Inden 1977). Despite these uncertainties, we hold that figure 1 shows that the elements of table 1 form a group, whose members behave in a similar way and may be expected to substitute for each other, at least in low concentrations.

Krolas (1981) showed how the heats of solution of metals can be used to deduce the value of the interaction potential between B and C atoms when they are dissolved in a third metal A. We have used his procedure to deduce the interactions between an atom of the metals in column 1 and an iron atom when they are both dissolved in nickel. These values are given in column 4. It can be seen that, with the exception of platinum, they

are all positive, i.e. repulsive, and in fact are larger than the repulsive potential between pairs of iron atoms. This is a strong indication that when elements from the first column are dissolved in  $Ni_3Fe$ , they will tend to occupy iron sites, and may even raise the ordering temperature. The exceptional behaviour of Pt is no doubt connected with the existence of the ordered compound  $Pt_3Fe$ .

At the bottom of table 1, placed separately because neither forms the ordered compound  $Ni_3M$  with the  $Cu_3Au$  structure, we have given the data for Cr and Sn. The alloy  $Ni_3Fe_{1-x}Cr_x$  has been studied previously (Cranshaw 1988) where it was found that for  $x = 0.08$ , the concentration of Cr atoms on Fe sites was 6.1% and on Ni sites 0.8%. If this difference were to be attributed to a repulsive first-neighbour interaction between Fe and Cr atoms, its strength would need to be about 34 meV, in good accord with the prediction of 24 meV. However, the ordering temperature is lowered by about 8 K when  $x = 1\%$  (Marwick *et al* 1987). This is presumably connected with the fact that nickel and chromium form an ordered alloy with the  $Pt_2Mo$  structure rather than  $Cu_3Au$ . The ordered alloy  $Ni_3Sn$  has an HCP structure which closely resembles the  $L1_2$  structure, and Sn raises the ordering temperature of the  $Ni_3Fe$  alloy (Zemcik and Kreislerova 1980). The alloy obtained by dissolving Sn in  $Ni_3Fe$  is particularly interesting to Mössbauer physicists, because then both the  $^{57}Fe$  and the  $^{119}Sn$  are available for investigation.

Huffman and Dunmyre (1971) presented spectra of such an alloy containing 1% Sn. The  $^{57}Fe$  spectra showed components with a magnetic hyperfine field greater than that for a pure  $Ni_3Fe$  specimen, and they attributed these components to Fe atoms with 1 or 2 Sn atoms as near neighbours. The field increment for 1 Sn neighbour at He temperature was 1.7 T, and for 2 Sn neighbours 4.5 T, implying a very unusual degree of non-linearity.

For the  $^{119}Sn$  spectra, Huffman and Dunmyre expected two superimposed magnetic components arising from Sn atoms on Ni sites, which would have 4 Fe and 8 Ni neighbours, and Sn atoms on Fe sites, which would have 12 Ni neighbours. In the event, the spectra showed considerable line broadening, which they attributed to disorder in the sample, and they assumed the presence of Sn atoms with numbers of Fe neighbours between 0 and 4. To obtain a fit to their spectra it was supposed that Sn and 4 Fe neighbours corresponded to a field of +12.3 T, and Sn with no Fe neighbours corresponded to a field of +2.0 T.

Zemcik and Kreislerova (1980) presented spectra of  $^{119}Sn$  dissolved in  $Ni_3Fe$  at a concentration of 1%, and demonstrated the marked change which occurs on ordering. Spectra taken at a range of temperatures showed that  $T_c$  was raised by 10 K by the addition of the Sn. In later work, Kreislerova *et al* (1985) found that the saturation magnetisation increased by 4.5% on ordering the tin alloy compared with 5.2% for pure  $Ni_3Fe$ . The mean hyperfine field at  $^{57}Fe$  nuclei was found to increase by only 3.6% on ordering compared with an increase of 43% for the  $^{119}Sn$  field.

Kreislerova *et al* (1985) argue that neither the change in bulk magnetisation, nor the changes in the occupation of first-neighbour sites of the tin atom are sufficient to explain the pronounced dependence of the  $^{119}Sn$  field on ordering. The latter point follows if the concentration of Sn atoms is the same on Ni and Fe sites, for then the first-neighbour shell is occupied on the average by 9 Ni atoms and 3 Fe atoms in both the ordered and disordered states. Kreislerova *et al* (1985) supposed that the tin atoms entered only Ni sites, and then by assuming an empirical dependence of  $^{119}Sn$  field on the number of Fe neighbours they were able to reproduce the behaviour of the mean field as a function of order.

We have given reasons above for believing that Sn atoms would lie on Fe sites, and we provide here one additional argument that rests on the magnitude of the hyperfine

field. Following Delyagin and Kornienko (1971) and Balabanov and Delyagin (1970), Campbell and Blandin (1975) proposed an empirical rule for the hyperfine field,  $H_{\text{eff}}$ , at Sn in magnetic materials, namely

$$H_{\text{eff}} = -14 \mu_{\text{nn}} + 10 \mu_{\text{nnn}} \quad (1.2)$$

where  $\mu_{\text{nn}}$  and  $\mu_{\text{nnn}}$  are the mean moments in the first- and second-neighbour shells of the Sn atom. For Sn in Fe,  $\mu_{\text{nn}} = \mu_{\text{nnn}} = 2.2 \mu_{\text{s}}$ , and this rule predicts the value  $-8.8 \text{ T}$  for  $H_{\text{eff}}$ . For Sn in Ni, we have to take into account the reduction of Ni moment when the Ni atom has an Sn neighbour. The value of  $d\mu/dc$  for Sn in Ni is  $-4.2 \mu_{\text{s}}$  per atom (Sadron 1932, Marian 1937). If this loss is assumed to occur in the nickel atoms which are first neighbours of the tin atom,  $\mu_{\text{nn}} = 0.4 \mu_{\text{s}}$  and  $\mu_{\text{nnn}} = 0.7 \mu_{\text{B}}$ , leading to a prediction  $H_{\text{eff}} \approx 2 \text{ T}$ , in agreement with experiment. For  $\text{Ni}_3\text{Fe}$ , we may assume  $\mu_{\text{Fe}} \approx 3.0$ , and  $\mu_{\text{Ni}} \approx 0.7$ . If we suppose no changes in Ni moment occur, when Sn goes on an Fe site the predicted field is about  $+20 \text{ T}$ , and on a Ni site about  $-14 \text{ T}$ . Considering the observation by Huffman and Dunmyre (1971) of positive fields of  $12.3 \text{ T}$  these figures favour the assumption that Sn atoms lie on Fe sites.

Furthermore, equation (1.2) predicts that when an Sn atom dissolved in Fe has a non-magnetic atom in its first- or second-neighbour shell, the changes in hyperfine field,  $\Delta H_1$  and  $\Delta H_2$  will be  $+3.9 \text{ T}$  and  $-3.7 \text{ T}$  respectively. These are close to the values found when s-p elements are present in the first- and second-neighbour shells of an Sn atom dissolved in Fe (Cranshaw 1987b). This success gives grounds for hope that equation (1.2) may make helpful predictions in the case of Sn dissolved in  $\text{Ni}_3\text{Fe}$ .

During the course of this work it became apparent that the role of a foreign element occupying an Fe site, for example, Ni, or an element from table 1, in determining the hyperfine field at atoms on other Fe sites is not clear. In work on single crystals of composition near  $\text{Ni}_3\text{Fe}$  (Cranshaw 1987a), evidence was presented indicating that Ni atoms on Fe sites substantially increased the field at other Fe sites which were its second neighbours, in contrast to the very successful model of Drijver *et al* (1977a, b), according to which it caused a small decrease. We have attempted to address this question in the present paper, but the results are far from conclusive.

## 2. Experimental

Four specimens are examined. The compositions of the first three are given by  $\text{Ni}_3\text{Fe}_{1-x}\text{Sn}_x$ , with  $x = 0.008, 0.04, \text{ and } 0.1$ . The composition of the fourth is given by  $\text{Ni}_3\text{Fe}_{0.942}\text{Al}_{0.05}\text{Sn}_{0.008}$ . All the specimens were prepared by melting together the components in the correct proportions in an argon arc furnace. The resulting bead was annealed for one day at  $1300 \text{ K}$ , and then rolled down to a thickness of  $125 \mu\text{m}$  for the  $^{119}\text{Sn}$  spectra, and  $25 \mu\text{m}$  for the  $^{57}\text{Fe}$  spectra. The foils were ordered by annealing at  $753 \text{ K}$  for 12 days. Spectra were taken with the specimens in a nitrogen cryostat using a conventional constant acceleration spectrometer.

## 3. Results

### 3.1. $^{119}\text{Sn}$ spectra

The  $^{119}\text{Sn}$  spectra of the three Sn specimens are shown in figure 2. Looking at these spectra one sees that they show similar features. They all have a high-field component

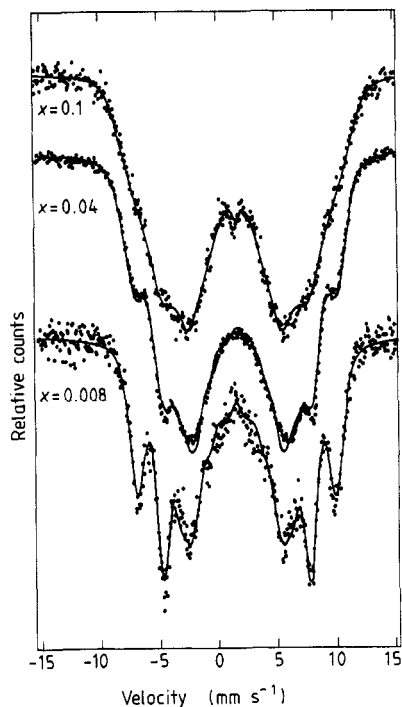


Figure 2. Spectra of  $^{119}\text{Sn}$  dissolved in  $Ni_3Fe_{1-x}Sn_x$ , with  $x = 0.008, 0.04,$  and  $0.1$ .

with a total splitting of about  $17 \text{ mm s}^{-1}$  ( $12.4 \text{ T}$ ), and rather broad low-field components which tend to fill in the middle of the spectrum. The main difference between the spectra lies in the line widths, and the degree to which the low-field part of the spectrum is filled in.

Let us first consider the possibility that Sn atoms are distributed over Fe and Ni sites. In a perfectly ordered alloy, there could be only two possible environments for a Sn atom, one for an atom on an Fe site, where it has 12 Ni first neighbours, and one for an atom on a Ni site, where it has 8 Ni and 4 Fe neighbours. A departure from perfect order permits departures from these numbers of Fe and Ni atoms in the two environments. Let us make the assumption that the field is determined by the occupation of the first-neighbour shell. Then we can write for  $H_i$ , the field at a Sn nucleus with  $i$  Fe neighbours

$$H_i = H_0 + i \Delta H \quad (3.1)$$

where  $\Delta H$  is a constant, and the intensity of the component  $H_i$  is determined by the value of  $\eta$ , the disorder parameter, and the relative occupation of Fe and Ni sites by Sn atoms. With this model we found it impossible to obtain a good fit to the spectra, and we regard this as evidence in favour of our contention that Sn occupies only Fe sites. Accordingly we modify equation (3.1) to read

$$H_{ij} = H_{00} + i \Delta H_1 + j \Delta H_2. \quad (3.2)$$

In this expression,  $\Delta H_1$  is the change of field produced by the presence of an Fe atom in the first-neighbour shell, and  $\Delta H_2$  the change produced by a Ni atom in the second-neighbour shell.

**Table 2.** The values of the parameters found by the program in fitting the  $^{119}\text{Sn}$  spectra of the specimens described in the text.

$x$	$H_{00}$ (T)	$\Delta H_1$ (T)	$\Delta H_2$ (T)	$IS_{00}$ (mm s $^{-1}$ )	$\sigma$ (T)	$\eta$
(i)						
0.008	12.3	-2.9	-5.3	1.560	0.64	0.90
0.04	12.6	-2.9	-5.5	1.571	1.01	0.86
0.1	12.4	-2.7	-5.6	1.621	1.65	0.88
Al $_{0.04}$	12.7	-3.0	-5.1	1.570	1.15	0.88
(ii)						
0.008	12.3	-3.7	-5.4	1.560	0.66	0.92
0.04	12.6	-2.8	-5.3	1.571	1.12	0.90
0.1	12.1	-2.5	-5.3	1.632	1.94	0.99
Al $_{0.04}$	12.7	-2.9	-4.9	1.573	1.30	0.90

Let  $c$  be the concentration of Fe atoms on Ni sites. Then

$$p_i = {}^{12}C_i c^i (1 - c)^{12-i}$$

and

$$p_j = {}^6C_j (3c)^j (1 - 3c)^{6-j}$$

and

$$p_{ij} = p_i p_j \quad (3.3)$$

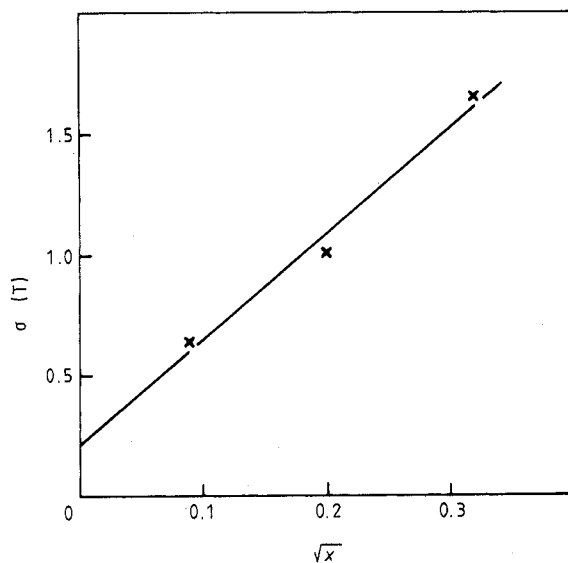
where  $p_{ij}$  gives the intensity of the component  $H_{ij}$ . In the fitting program we allowed  $i, j \leq 3$ , and included a variable,  $\sigma$ , to permit a Gaussian broadening of the field components.

When  $x$  is negligible compared with  $c$ , we are in a position to fit the spectra with  $H_{00}$ ,  $\sigma$ ,  $c$ ,  $\Delta H_1$ , and  $\Delta H_2$  as variables. If  $x$  is not negligible, we can make two alternative simplifying assumptions: Sn atoms on Fe sites are to be regarded as (i) Fe atoms, making no change in hyperfine field at other Sn atoms, or (ii) Ni atoms, and so adding to the concentration,  $3c$ , of Ni atoms on Fe sites. Both permit almost equally good fits. As may be expected from the symmetry of the spectra, no significant improvement could be obtained by including changes of isomer shift.

The results of the fits to the three spectra with assumption (i) are shown in figure 2 as full curves, and the values of the variables for each specimen are given in table 2(i). Table 2(ii) gives the same information for assumption (ii). The fourth line of each table gives the values for the specimen containing Al. This spectrum is, to the eye, indistinguishable from that of the specimen with  $x = 0.04$ .

The sixth column, heading  $\sigma$ , gives the Gaussian broadening of the lines. If this broadening is due to the fluctuation of numbers of Sn atoms in the environment of the Sn atom in question, we would expect that  $\sigma$  would be proportional to  $\sqrt{x}$ . Figure 3 shows that this expectation is borne out reasonably well.

It may be noticed that the specimen with  $x = 0.1$  shows a small absorption peak close to  $H = 0$ . It is possible to find values of  $\Delta H_1$  and  $\Delta H_2$  which yield a component with  $H$  small, and at these values there may obviously be a local minimum in the sum of squares in the fitting program. We have preferred to suppose that the small peak is produced by



**Figure 3.** The standard deviation of the width of the field distributions of table 2 plotted against  $\sqrt{x}$ .

a small quantity of Sn in a non-magnetic state, arising from the high concentration of Sn, and have permitted a single-line component in the fitting program to allow for it.

### 3.2. $^{57}\text{Fe}$ spectra

The  $^{57}\text{Fe}$  spectra of the specimens with  $x = 0.04$  and  $0.1$  are shown in figure 4. They are obviously very similar to each other, and to the specimen with composition  $\text{Ni}_3\text{Fe}_{0.96}\text{Al}_{0.04}$ , shown in Cranshaw (1987a). The lack of any marked dependence of the spectra on concentration of the element substituting for Fe undermines the argument given in that paper that elements with a low or zero moment on Fe sites produce a marked increase in the hyperfine field at Fe atoms which are their second neighbours. Rather it supports the earlier model due to Drijver *et al* (1977a), according to which the field at Fe atoms is almost independent of moments in their second-neighbour shell.

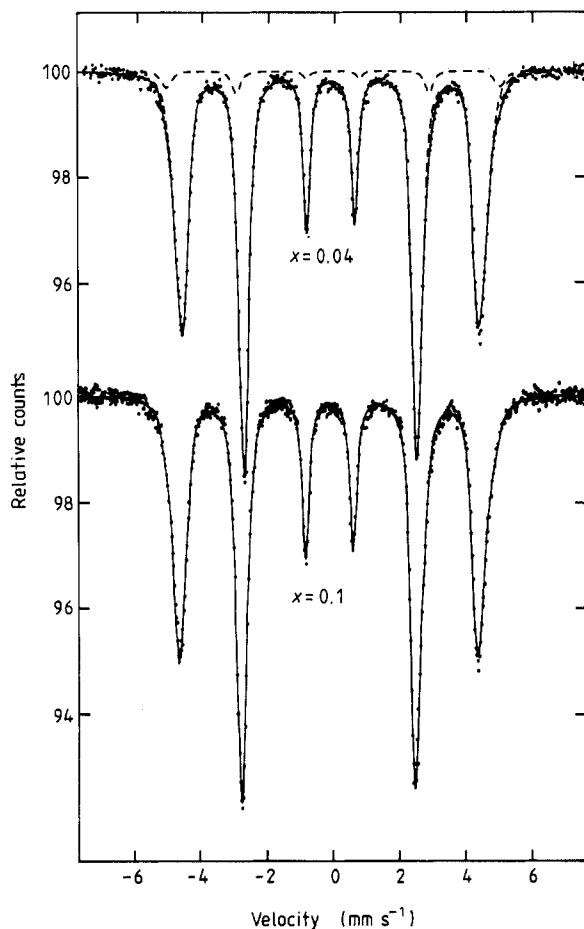
Accordingly we have fitted the two spectra with two models: (i) the model given by Drijver *et al*, (ii) the model given in Cranshaw, assuming that Sn atoms on Fe sites behave as Fe atoms. This is obviously the same as the simplifying assumption (i) in equation (3.1), used there to fit the Sn spectra. Both models give satisfactory fits.

## 4. Discussion

### 4.1. Hyperfine field strengths

4.1.1.  $^{119}\text{Sn}$ . Previous workers have tended to suppose that the presence of an Fe atom in the first-neighbour shell of a Sn atom would increase the magnitude of the hyperfine field. Although we have no reliable theory for predicting these effects, and no experimental information about tin in FCC iron, we believe that the values for the hyperfine field at  $^{119}\text{Sn}$  in Ni and Fe metals, and the predictions of equation (1.2) make it highly





**Figure 4.** Spectra of  $^{57}\text{Fe}$  in the specimens with tin concentration given by  $x = 0.04$  and  $0.1$ . The broken curve in the upper spectrum indicates the component due to Fe atoms on Ni sites with 4 Fe neighbours, using the model of Drijver *et al* (1977a, b). The relative area of the high-field components is 18% in both spectra.

plausible that an Fe atom in the first-neighbour shell of an Sn atom, and an Ni atom in the second-neighbour shell should cause a negative shift of hyperfine field, as shown in table 2.

The actual values of  $\Delta H_1$  and  $\Delta H_2$  predicted by equation (1.2), using the values of  $\mu_{\text{Fe}}$  and  $\mu_{\text{Ni}}$  given earlier are  $-2.7$  and  $-3.9$  T respectively, in satisfactory agreement with experiment. However, it should be pointed out that equally good fits can be obtained by exchanging the two values of  $\Delta H$  between first and second neighbours.

**4.1.2.  $^{57}\text{Fe}$ .** Inspection of figure 4 shows that we are here dealing with the rather small asymmetries of the hyperfine field distribution, and we find that the experimental data are insufficient to distinguish between different models. The higher-field components seem best regarded as due to iron atoms on Ni sites.

#### 4.2. Width of field distributions, $^{119}Sn$

We have shown in figure 3 that the widths of the field distributions (column 6 in table 2) are proportional to  $\sqrt{x}$ , and that when  $x = 0.1$  the width is about 1.6 T. This value is not likely to be an overestimate, and is large enough to give some difficulty in interpreting it. If it were attributed to fluctuations in the number of Fe atoms on the 24 Ni sites which are third neighbours to Sn atoms on Fe sites, or to fluctuations in the number of Sn atoms in the 12 fourth-neighbour sites, we would conclude that  $\Delta H_3 \approx \Delta H_4 \approx 1.2$  T. This value seems rather large. It is more probable that the width is caused by fluctuations in the environment up to the fifth- or sixth-neighbour shell, a region containing 60–70 atoms.

#### 4.3. Order parameter

In an ordered two-component alloy consisting of atoms A and B on  $\alpha$  and  $\beta$  sites, the degree of order can be defined by

$$\eta = W_{A\alpha} - W_{A\beta} \quad (4.1)$$

where  $W_{A\alpha}$  is the proportion of  $\alpha$ -sites occupied by A atoms, and  $W_{A\beta}$  the proportion of  $\beta$ -sites occupied by A atoms. The fitting program gave the concentration of Fe atoms on Ni sites, and, if we confine our attention to Ni sites, we can deduce values for  $\eta$ , which are given in column 7 of table 2. It will be seen that rather high values of  $\eta$  are given by taking assumption (ii) of (3.1). This may add weight to the suggestion that Sn atoms on Fe sites do not much affect the field at Sn atoms which are their second neighbours, or the high value may be the result of our definition of  $\eta$  in the ternary alloy, and the high concentration of tin.

### 5. Conclusions

We have presented evidence that

- (i) in solution in  $Ni_3Fe$ , Sn atoms lie almost exclusively on Fe sites;
- (ii) the spectra of  $^{119}Sn$  can be explained as the sum of components whose fields are given by a linear function of the moments in the first- and second-neighbour shells of the tin atom;
- (iii) the coefficients in the function are in good agreement with those found in other magnetic materials.

We are unable to reach a firm conclusion about the role played by Sn atoms in determining the hyperfine field at other Sn or Fe atoms in their second-neighbour shell.

#### Acknowledgment

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