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**Abstract.** Spectra are presented of four alloys of composition $Ni_3Fe_{1-x}Al_x$ with $x = 0.04$, 0.10, 0.25, and 0.5, and of one alloy with composition $Ni_3Fe_{0.96}Mn_{0.04}$. For the Al substituted alloy with $x = 0.25$, and for the Mn alloy, the temperature dependences of the hyperfine fields at Fe atoms are investigated. It is found that over the range of compositions of Al alloys considered, the low-temperature hyperfine field is almost independent of x, and the Curie temperature falls by 4% and 20% for $x = 0.25$ and 0.50 respectively. The hyperfine field at Fe atoms on Ni sites falls more rapidly with temperature than the field at Fe atoms on Fe sites. A strong magnetic anisotropy is found in the alloy with $x = 0.25$, which is attributed to ordering among the Al and Fe atoms on the cubic Fe sublattice.

1. Introduction

In a paper on the ^{57}Fe Mössbauer spectra of single-crystal specimens with composition near Ni_3Fe (Cranshaw 1987) a prediction was made of the spectrum of $Ni_3Fe_{1-x}Al_x$ with $x = 0.04$, based on a model designed to account for the Ni_3Fe spectra. The fact that the experimental spectrum of a specimen with this composition closely resembled the prediction was regarded as confirmation of the validity of the model. To extend the investigation further, we have taken spectra of specimens with $x = 0.1, 0.25$, and 0.50. We find that the spectra are almost independent of x, an observation that obviously undermines the evidence of the spectrum with $x = 0.04$, and calls into question the model used to interpret the spectra of Ni_3Fe. In this paper, we describe the Al substituted spectra in detail, and present some results on their variation with temperature.

The Al–Fe–Ni alloy system has been reviewed by Rivlin and Raynor (1980), and figure 1, showing the Ni-rich corner of the ternary phase diagram is copied from their paper. This figure (note that the figures are in weight per cent) is not an equilibrium diagram, but represents the state reached by cooling from a high temperature at a rate of $10~K~h^{-1}$. On it we have drawn the Ni_3Fe–Ni_3Al (atomic) section, and the specimens with $x = 0.25$ and 0.50 are marked by an open and a full circle respectively. It will be seen that Ni_3Fe and Ni_3Al are not miscible in all proportions, and the specimen with $x = 0.50$ lies within the miscibility gap. At the Al-rich end of the section, the occurrence of giant moments in Ni_3Al has attracted much interest, and several Mössbauer experiments
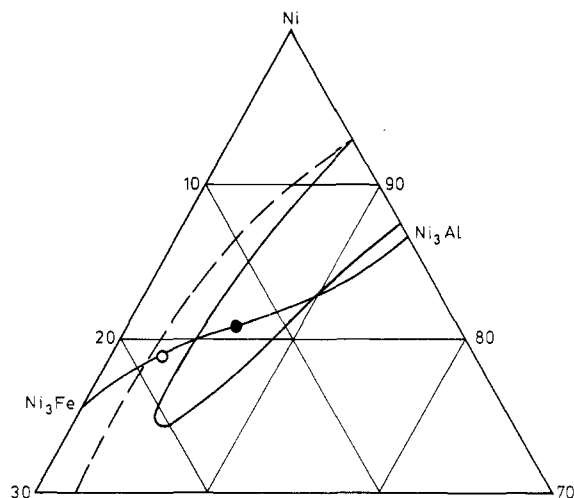
Figure 1. The ternary phase diagram of the Ni–Al–Fe system, from Rivlin and Raynor (1980), plotted in weight per cent. The full curve shows the Ni_3Fe–Ni_3Al section, and the points on the line indicate the composition of the samples under investigation. The broken curve marks the boundary between ordered and disordered states.

have been carried out to investigate the phenomenon (Drijver and van der Woude 1973, van Deen *et al* 1978).

The question of the site occupation of Sn atoms introduced into Ni_3Fe has been discussed in an earlier paper (Cranshaw 1989). Arguments based on the magnitudes of the heats of solution of the metals were presented there that indicated that Sn atoms would go on Fe sites, and the case for Al atoms is even stronger. At the aluminium end of the section, the main conclusion of the work on Ni_3Al, which is relevant to the present work, is that for alloys dilute in Fe ($x \simeq 0.97$), the iron atoms occupy Al sites. (It is interesting to note that Co atoms occupy both Ni and Fe sites (Drijver and van der Woude 1973), in qualitative agreement with the fact that according to the semi-empirical theories of Miedema and de Boer (1977) and Krolas (1981), in solution in nickel the Al–Fe interaction is repulsive with a strength of 63 meV, whereas the Al–Co interaction strength is only 33 meV.) The Curie temperature, T_N of the dilute iron alloy is about 80 K, and the hyperfine field is about 23 T (Drijver and van der Woude 1973). There does not appear to be any earlier Mössbauer investigation of alloys with intermediate Fe concentrations.

The arguments regarding the site occupation of Al and Sn apply also to Mn. It is notable that Mn dissolved in Ni carries a moment of between 3 and 4 μ_B (Cable and Child 1974, Kajzar and Parette 1980), a relatively large moment which has been attributed to its first-neighbour environment. This environment is probably nearly the same in Ni_3Fe and in pure Ni, and so we may expect Mn to carry a large moment when dissolved in Ni_3Fe. Accordingly we have also examined a specimen of composition $Ni_3Fe_{0.96}Mn_{0.04}$. The implications of the results of the present investigations for the interpretation of Ni_3Fe spectra will be presented in another paper.

2. Experimental details

The composition of the first four specimens under investigation is given by $Ni_3Fe_{1-x}Al_x$, with $x = 0.04, 0.1, 0.25$ and 0.5, where subscripts always refer to atomic concentrations. The composition of the fifth is given by $Ni_3Fe_{0.96}Mn_{0.04}$. All the specimens were prepared

by wrapping the minor elements in the powdered form (and in the correct proportions) in nickel foil of the correct weight. The packet was then melted in an argon arc furnace. The weight loss was never greater than 0.1%, and no subsequent chemical analyses were made. The resulting beads were annealed for one day at 1300 K, and then rolled down to a thickness of 25 μm. An exception was the Al substituted specimen with $x = 0.5$, which was too hard to be rolled, and this bead was powdered with an emery wheel. The foils and the powder were ordered by annealing at 753 K for 12 days. Spectra were taken with the specimens in a nitrogen cryostat, at room temperature, or in a temperature controlled oven using a conventional constant acceleration spectrometer.

3. Results

Figure 2 shows the ^{57}Fe spectra of the Al substituted alloys taken at 77 K. It can be seen that despite the large changes in composition, the spectra are very similar to each other, only the spectrum of the specimen with $x = 0.5$ showing perceptible broadening. This spectrum also shows a small paramagnetic peak close to zero velocity, suggesting that insufficient time may have been allowed at the ordering temperature to permit the separation into the iron-rich and aluminium-rich phases indicated by the phase diagram. The specimen with $x = 0.25$ shows somewhat narrower lines than the others.

We analyse the results according to a model based on that of Drijver *et al* (1977a, b). The hyperfine field at an iron nucleus is assumed to be a linear function of the number, i, of iron atoms in its first-neighbour shell, and the numbers of Fe atoms with i Fe neighbours, $0 < i < 12$, can be calculated from the value of c, the concentration of Fe atoms on Ni sites. Drijver and co-workers found only a small effect from the number of Fe second-neighbour atoms, and we regard second-neighbour effects as negligible. Thus the structure in the spectrum depends on only two variables, c and $\delta H_{\leqslant 1}$, where δH_1 is the change of field brought about by increasing the number of Fe atoms in the first-neighbour shell by one. Incorporated in an iterative least squares fitting program, this is a very robust model, in that the program always converges rapidly. The value of δH_1 is the quantity of interest in much of what follows. We find no need to consider the possibility of the occurrence of Fe atoms with Al atoms in their first-neighbour shell, which by analogy with Al in an iron host would be expected to produce a strong reduction in the Fe hyperfine field. Figures 3 and 4 summarise the results obtained. In figure 3 we have plotted the Curie temperature, T_N, and the strength of the hyperfine field at iron nuclei on iron sites against the value of x. The value of T_N for ordered Ni_3Fe is plotted at 940 K, found by Kollie and Brooks (1973). It must be admitted that the value of T_N is an estimate based on a rather inadequate number of observations but the qualitative conclusion is clear. For the Al substituted alloys with $0 < x < 0.25$ the Curie temperature is almost constant and for greater values of x it falls to the value of about 80 K found by Drijver and van der Woude (1973). The iron hyperfine field is likewise almost constant in the region $0 < x < 0.5$ and then falls to the value 23 T observed in the same work. For the specimen with Mn substitution, we have found a slightly higher value of the Curie point, but a value independent of Mn concentration, as for the Al alloys, would be within the experimental uncertainty. The hyperfine field is almost unchanged from the value for pure Ni_3Fe.

In figure 4 the upper full curve represents the magnetisation curve for a spin-$\frac{1}{2}$ magnet plotted against the reduced temperature. Running slightly below this curve are the experimental points for the reduced hyperfine field of the specimens with $x = 0.25$ and
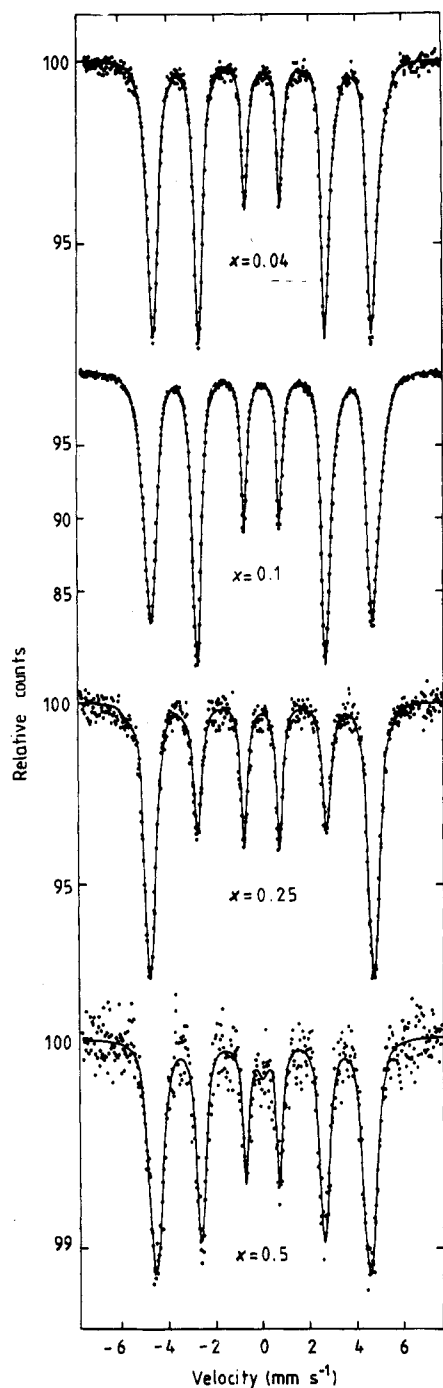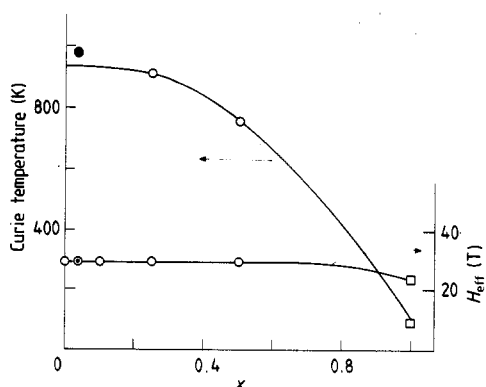
Figure 2. The ^{57}Fe spectra of the Al substituted alloys at 77 K.

0.5, and the specimen with Mn substitution. We have used the requirement of consistency in this diagram to estimate the Curie temperatures. To display the temperature dependence of δH_1 on the same diagram, we have plotted the reduced value of δH_1, i.e.

Figure 3. The Curie points of the alloys plotted against x. The open circles are for Al substituted alloys, and the full circles for Mn alloy. The points at $x \simeq 1.0$ are taken from van Deen *et al* (1978).
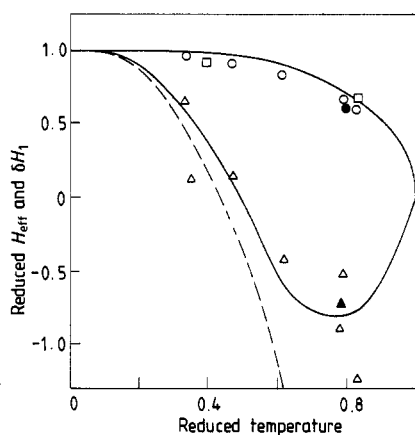

Figure 4. The reduced values of hyperfine field (upper curve), and of δH_1 (lower curve), plotted against reduced temperature. δH_1 is defined in the text. In the upper plot, open circles represent the Al alloy with $x = 0.25$, squares represent the Al alloy with $x = 0.5$, and the full circles represents the Mn alloy. In the lower plot, triangles represent the results on the Al alloy with $x = 0.25$, and the full triangle represents the Mn alloy. The broken curve shows the expected course of δH_1 if the exchange field at Fe atoms on Ni sites were 0.8 times the field at Fe atoms on Fe sites. The full curve is to guide the eye; both δH_1 and H_{eff} are zero at the Curie point by definition.

$\delta H_1(T)/\delta H_1(0)$, derived from the spectra of the Al specimen with $x = 0.25$, and one point from the Mn specimen. The full curve has been drawn to guide the eye. It will be seen that the values fall to zero near the reduced temperature of 0.5, and then become negative. The effect can be seen in figure 5 which shows spectra of the Mn substituted specimen at 77 K and 773 K. Below the spectra are shown histograms of the hyperfine field distribution obtained using the method of Le Caer and Dubois (1979). The reversal of the sign of the asymmetry of the hyperfine field distribution can be clearly seen.

4. Discussion

4.1. Disordering temperature

In pure Ni₃Fe, the chemical order–disorder phenomenon is clearly signalled by a marked change of hyperfine field at the critical temperature (Drijver and van der Woude 1977b). In our alloy with $x = 0.25$ no such sharp change has been observed, indicating that the substitution of some of the iron atoms by Al at our concentration raises the disordering temperature, T_c, above the Curie point. It is interesting to note that Ibragimov *et al*
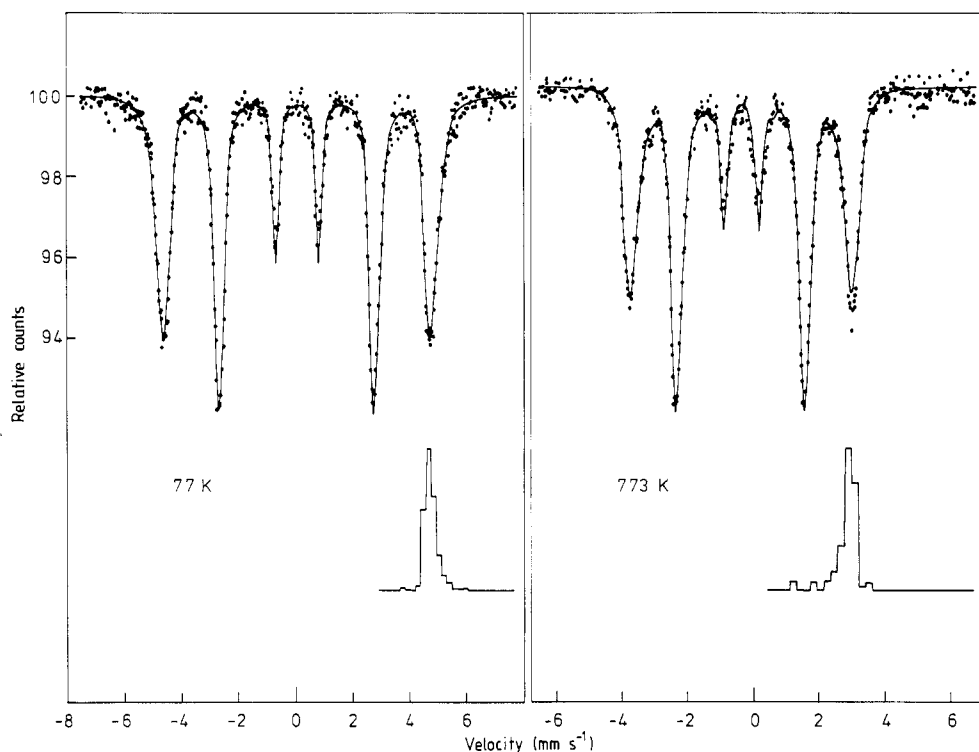
Figure 5. The ^{57}Fe spectra of the Mn alloy at 77 K and 773 K. Below the spectra are distributions of the hyperfine field calculated by the method of Le Caer and Dubois (1979), showing reversal of the sign of the asymmetry of the field distribution.

(1966) found that T_c for $Ni_3Fe_{1-x}Mn_x$ alloys was raised from 778 K to 796 K as x goes from 0 to 0.5, although for $x = 1.0$ the value of T_c is only 748 K.

4.2. Magnetic anisotropy

Ni_3Fe is a soft magnet, and in fact forms the basis of permalloy, a widely used transformer iron for certain applications. It is to be expected that the intensities of the lines in the spectra of Ni_3Fe, and also the Al substituted alloys should be in the ratio $3:z:1:1:z:3$ with z approximately equal to 4, corresponding to a magnetisation vector lying in the plane of the foil, the direction that minimises the magnetisation energy. As is well known, random directions of the local magnetisation vector would give $z = 2$. It can be seen in figure 2 that the value $z = 4$ applies only for values of x less than 0.1. When $x = 0.25$, we find a value of z markedly less than 2, indicating tht the specimen is magnetised nearly normal to the foil. For the specimen with $x = 0.5$, we find $z = 2$, as expected for a powder specimen.

The low value of z for $x = 0.25$ shows that the lattice of this alloy must contain a preferred direction of magnetisation, and that the method of preparation of the specimen has arranged that this direction is normal to the foil. Bearing in mind the existence of the miscibility gap, we may speculate that the preferred direction is due to an attraction between Al atoms on the cubic Fe sublattice, so that they tend to fall either along [100]

lines, or on (100) planes. In the first case the number of Al–Al pairs could be 2, and in the second 4, compared with the mean number 1.5 for a random distribution of Fe and Al atoms on the cubic Fe sublattice. In both cases the unique axis, and presumably the easy axis of magnetisation would be the [100] direction. When $x = 0.5$, we might have Al atoms occupying alternate planes in the Fe sublattice, probably also producing a strong magnetic anisotropy, which of course cannot be observed in the powder specimen. The magnetic anisotropy of the specimen with $x = 0.25$ survives heating to about 800 K, but presumably there exists a range of critical temperatures that are dependent on x.

Ibragimov *et al* (1966) have proposed the ordering of Mn atoms on the Fe cubic sublattice to explain certain physical properties of $Ni_3Fe_{0.5}Mn_{0.5}$, although the ordering that they suggest possesses cubic symmetry and would not account for the magnetic anisotropy noticed here.

4.3. The temperature dependence of the hyperfine field distribution

In describing their work on Ni_3Fe, Drijver *et al* (1977b) remarked that the temperature dependence of the hyperfine field at Fe atoms occupying Ni sites might be expected to be different from that at Fe atoms on Fe sites. They looked for such a difference by examining the temperature dependence of the width of the outer lines of the six-line magnetic spectrum, but found a width that was almost a constant fraction of the hyperfine field. The temperature dependence of δH_1 has been described in section 3, and is shown in figure 4. A simple model to account for this effect assumes an exchange field, H_{ex}^{Ni} at iron atoms on nickel sites that is smaller than that at iron atoms on iron sites. The result of such a reduction in the exchange field may have been observed in the spectra of single-crystal specimens with composition near Ni_3Fe (Cranshaw 1988), and the lowering of the exchange field was there attributed to antiferromagnetic coupling between Fe atoms which are first neighbours to each other on an FCC lattice. The apparent contradiction between the present results and the observation by Drijver and co-workers may be explained by the fact that the line width is not very sensitive to the changes in δH_1. The two spectra of figure 5 would have similar line widths, although there has been a change in the sign of δH_1. The exact form of the temperature dependence, however, is not easily accounted for. The broken curve in figure 4 shows the expected course of δH_1 if $H_{ex}^{Ni} = 0.8 H_{Ex}^{Fe}$. This curve crosses the zero line at about the right value of reduced temperature, but predicts much larger effects at high temperatures than are observed. Moreover, experiments with an effective-field model show that even a zero contribution to the exchange field at Fe atoms on Ni sites from neighbouring Fe atoms would give a larger reduction in the total than 20%, and an antiferromagnetic contribution would make the fall even greater.

5. Conclusions

We have shown that:

(i) the substitution of the iron atoms in Ni_3Fe by aluminium atoms raises the critical temperature for the order–disorder transformation;

(ii) the Curie temperature of alloys with composition $Ni_3Fe_{1-x}Al_x$ is almost independent of x for $0 < x < 0.25$, falling from 940 K for ordered Ni_3Fe to about 910 K for $x = 0.25$. For $x = 0.5$, the Curie temperature is about 750 K;

(iii) at values of x in the region of 0.25, interactions between Al atoms bring about an anisotropy in the spatial distribution. The same interactions may cause the miscibility gap in the $Ni_3Fe–Ni_3Al$ section;

(iv) the hyperfine field at Fe atoms on Ni sites in an Al substituted specimen with $x = 0.25$, and a Mn substituted specimen with $x = 0.04$ falls much more rapidly with temperature than the field at Fe atoms on Fe sites, but the form of the dependence does not seem to be adequately described by a simple reduction of the exchange field.

Acknowledgment

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