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# On the Magnetic Moments and the Degree of Order in Iron-Nickel Alloys

M. F. COLLINS, R. V. JONES* AND R. D. LOWDE
*Atomic Energy Research Establishment*
*Harwell, England*

A study of the background scattering of neutrons by iron-nickel alloys has shown extremely marked indications of short-range order in supposedly disordered specimens as far removed from the stoichiometric ratio for $Ni_3Fe$ as 60Fe40Ni, despite anneals at temperatures as high as 650 and 1000°C. A comparison of the nuclear and magnetic scattering distributions shows that the magnetic moments display a degree of ordering closely similar to that of the chemical constituents, and this demonstrates that within the accuracy of the measurements there must exist two magnetic moments in the crystal, one characteristic of an iron site and one of a nickel site. The values of these moments are determined at four alloy compositions, and are consistent with the earlier results of Shull and Wilkinson.

## Introduction

The problem of describing the magnetic electrons in transition metal alloys has recently been very considerably illuminated by the results of NMR, Mössbauer effect, specific heat and neutron scattering techniques. A central question is whether an individual atom in such an alloy can be said to be in a particular atomic state, having a characteristic magnetic moment, and if so how far

* On attachment from Harvard University, Cambridge, Massachusetts, U.S.A.

that moment depends on the environment of the atom and the composition of the alloy.

An early contribution to this study was made by Shull and Wilkinson[1], who remarked in 1955 that if the moments in a disordered transition metal alloy are not all the same, there will be a background of magnetic disorder scattering in the neutron diffraction pattern of the material. By measuring the magnetic disorder scattering from FeCr, FeNi and CoCr, they showed that such scattering did indeed exist, so that there must be different moments on different atoms. As the start of a programme of such measurements, we have re-examined the system FeNi, and report the results herein.

*Disorder scattering*

Turning for the moment to the *nuclear* scattering, the background intensity due to random disorder in a binary alloy of components $a$ and $b$ is due to a differential cross-section

$$\frac{\partial\sigma}{\partial\Omega}=c_a c_b(b_a e^{-W_a}-b_b e^{-W_b})^2 , \qquad (1)$$

where the $b$'s are coherent nuclear-scattering lengths and the $c$'s concentrations. This intensity is isotropic except for the influence of the Debye-Waller factors $e^{-W}$. If there are two characteristic magnetic moments $\mu_a$ and $\mu_b$ associated with the two types of constituent, then there will also be a magnetic cross-section

$$\frac{\partial\sigma}{\partial\Omega}=\frac{2}{3}c_a c_b(p_a e^{-W_a}-p_b e^{-W_b})^2 , \qquad (2)$$

in which the magnetic scattering length

$$p=0.27\mu f\times 10^{-12}\ \text{cm} ,$$

$f$ being the appropriate form factor. $\mu$ is expressed in Bohr magnetons, and the factor 2/3 is required for the case of unpolarised neutrons incident on an unmagnetised, polycrystalline sample. For unpolarised neutrons the cross-sections (1) and (2) are additive; (2) is again isotropic except for the effects of $e^{-W}$ and $f$.

With FeCr alloys, Shull and Wilkinson (hereafter referred to as SW) found a magnetic cross-section described by (2). Writing for simplicity $f_a=f_b$, they were able to deduce $|\mu_a-\mu_b|$, and thus in conjunction with the saturation magnetisation $\bar{\mu}=c_a\mu_a+c_b\mu_b$ they deduced two alternative sets of moments for $\mu_a$ and $\mu_b$ individually. A concealed assumption in their argument is, of course, the assumption that the system contains just two moments $\mu_a$ and $\mu_b$; in fact, a random distribution of any number of different moments would give a background intensity that was isotropic except for form factor and Debye-Waller effects, and which could, therefore, be confused with the cross-section (2). To examine this question, alloys having short-range order must be used.

If an atom $a$ be imagined at an origin of co-ordinates, and the probability of finding an atom $b$ at $r$ be $P_{ab}$, then the nuclear background scattering cross-section per atom is[2]

$$\frac{\partial\sigma}{\partial\Omega}=\frac{1}{2}(b_a e^{-W_a}-b_b e^{-W_b})^2\sum_r e^{iK.r}[2c_a b_b-P_{ab}(r)] . \qquad (3)$$

If only two magnetic moments existed, associated with the two constituents, the magnetic scattering pattern would have the same shape and would be described by an equation similar to (3) with $p$ in place of $b$. If, therefore, in an alloy with short-range order, the magnetic disorder scattering has the same angular dependence as the nuclear disorder scattering, this is a strong indication that the atoms have magnetic moments close to certain characteristic values $\mu_a$ and $\mu_b$; for any other moment distribution could simulate the nuclear pair distribution function $P_{ab}(r)$ only fortuitously.

Having noticed that SW commented on the magnetic short-range order in their FeNi specimens, we studied the FeNi system from this viewpoint especially, and do indeed find that within experimental error the angular dependences of the magnetic and nuclear intensities are the same. Assuming then that they are identical, and that within the accuracy of our experiment we may say there are effectively only two moments $\mu_a$ and $\mu_b$ present, then if $e^{-W_a}=e^{-W_b}$ we find from eq. (3) that the ratio of magnetic to nuclear background intensities is

$$R=\frac{2}{3}(p_a-p_b)^2/(b_a-b_b)^2 . \qquad (4)$$

Thus $|p_a-p_b|$ may be obtained from a knowledge of $b_a$ and $b_b$.

*Atomic order in iron-nickel alloys*

There is much evidence for the presence of short-range order in the fcc iron-nickel

alloys from measurements of the saturation magnetisation[3], magnetic anisotropy[4], specific heat[5], electrical resistance[6], and total neutron cross-section[7]. Near $Ni_3Fe$ the published data indicate a very sluggish order-disorder transition at a temperature of about 495°C. Direct measurements to confirm the existence of an ordered state using X-rays or neutrons are difficult, because natural iron and nickel have very similar scattering amplitudes for both types of radiation. X-ray superlattice lines have, however, been observed[8),9),6)] after long heat treatments, and magnetic superlattice lines have been detected with neutrons[1),10)]. There is also evidence in the resistivity and saturation magnetisation to suggest at least some short-range ordering over the whole range of compositions from 40 to 80% nickel[6),8)].

**Experimental method**

We have isolated both the magnetic and nuclear background intensities from a series of alloys chosen at 10% intervals of the composition range. The specimens were of purity at least 99.9%, and took the form of plates having dimension $1.59\times1.59\times0.250$ cm³; these plates were examined in transmission, and the grain size was kept in the range 0.001—0.005 in. to avoid "spottiness" in the diffraction pattern. The incident beam delivered $1.1\times10^5$ neutrons $cm^{-2}$ $sec^{-1}$ at wavelength 1.13Å.

The magnetic background intensity was determined from the difference between the diffraction patterns obtained with the specimen unmagnetised and magnetised in a direction externally bisecting the scattering angle; the technique is discussed in a companion paper[11].

To study the degree of atomic order we used 60Fe40Ni and 30Fe70Ni samples in which the nickel was enriched to 99.8% in $Ni^{60}$; this isotope has a coherent nuclear scattering length of only $0.30\times10^{-12}$ cm, much smaller than the value $0.95\times10^{-12}$ cm for natural iron. With the isotopically enriched alloy the factor $(b_a-b_b)^2$ in (3) is large enough to give striking effects in the diffraction pattern. We have isolated them by subtracting from the total nuclear scattering an estimate of the multiple scattering and nuclear inelastic scattering present. This last-mentioned estimate was obtained by appropriately scaling the intensity measured with copper, which has a face-centred lattice of dimension closely similar to that of the nickel-iron alloys. The inelastic and multiply-scattered intensities from copper were separated from one another by taking measurements at several sample thicknesses.

**Results**

Fig. 1 shows the magnetic cross-section at 10, 40, 50, 60, 70, 80 and 90% nickel. The system is fcc for all these compositions except 10% nickel, for which it is bcc. No data have been taken at angles between 28° and 42°, because with our instrumental resolution, scattering from the 111 and 200 Bragg peaks is present in this range.

The alloys were annealed at 700°C and quenched in oil, which according to the data of Wakelin and Yates[6),5)] should produce disordering; yet just as in the data of SW, all cross-sections in the fcc region have a pronounced undulating shape that suggests a short-range order in the magnetic moments. Exactly similar results have been obtained with samples from another source, so that it is highly unlikely that impurity effects are responsible.

As the superlattice lines 100 and 110 for $Ni_3Fe$ fall at 18°15′ and 25°55′, it is clear that the alloys having compositions near the stoichiometric ratio for this compound are showing a pronounced tendency to take on the $Ni_3Fe$ superlattice. More remarkable is the fact that the 60Fe40Ni alloy, with more than twice as much iron as the superlattice requires, should show a similar pattern. In case the explanation might be merely that our disordering treatments were unsatisfactory, we repeated the measurements at 30Fe70Ni and 60Fe40Ni with specimens that had been quenched from 1000°C. The scattering from the former of these alloys was unchanged, though there was a slight diminution in the short-range ordering effects from the latter.

Detailed comparison of the magnetic and nuclear scattering from the same specimen has been made at compositions 30Fe70Ni and 60Fe40Ni using the 99.8% $Ni^{60}$, and the results are presented at Fig. 2. The 30Fe70Ni alloy was annealed for 100 hrs at 480°C, just be-

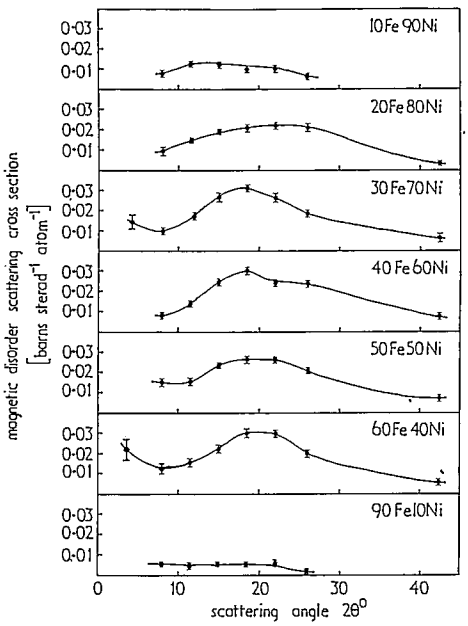


Fig. 1. The background distribution of magnetic scattering from a series of Fe-Ni alloys, showing the presence of short range magnetic order. For perfectly disordered alloys this scattering would decrease monotonically from a maximum value at $2\theta=0$, showing a dependence on angle characteristic of the form factor.

low the ordering temperature, to develop the ordered condition, and the two superlattice lines 100 and 110 of $Ni_3Fe$ appear in both the nuclear and magnetic scattering with a halfwidth at halfheight indistinguishable from the instrumental width, 3.5°. On oil-quenching the same sample from 650°C, curves were obtained that still show a definite trace of the two superlattice peaks. The data in this case are in adequate agreement with the corresponding curves of Fig. 1 and with the results of SW, small differences being reasonably attributable to different sample histories.

For 60Fe40Ni the sample oil-quenched from 650°C again shows distinct short-range order, seemingly based on the $Ni_3Fe$ superlattice pattern. However, the same heat treatment that produced a considerable degree of ordering in 30Fe70Ni had little or no effect on this specimen.

## Discussion

### *The degree of order*

Although the presence of short-range order

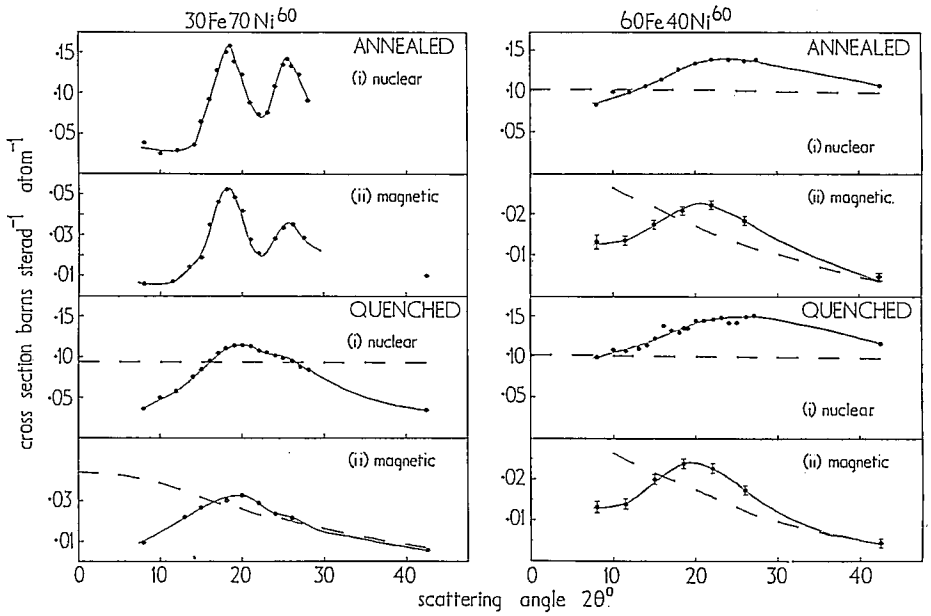


Fig. 2. Measured distribution of background intensity in the scattering pattern of 30% and 60% Fe-Ni[60] alloys, converted to cross-section data. The nuclear and magnetic contributions have been isolated and are shown separately. The annealed 30% alloy shows 100 and 110 superlattice peaks for both the nuclear and magnetic scattering which are sharp to within experimental resolution. Both quenched alloys show diffuse scattering peaks indicative of short range order; in the 60% iron alloy, the different heat treatments have had virtually no effect on the ordering. Dotted lines indicate the scattering predicted for random alloys. For all cases the angular dependence of the magnetic scattering follows that of the nuclear scattering, showing that the magnetic moments are similarly arranged to the atoms in the alloy.

in this alloy has long been appreciated, the amount of it now observed in specimens quenched from 650°C and 1000°C is impressive. Considering first the alloys near to $Ni_3Fe$, the superstructure is one in which the iron atoms place themselves at the cube corners. To form this structure it would be sufficient to imagine some mechanism that effectively caused the iron atoms to repel one another.

For quantitative purposes, imagine that a 25Fe75Ni alloy would give exactly the same nuclear intensity distribution as our 30Fe70Ni one. Then on applying the theory of Wilchinsky[12] it is found that an iron atom has in practice $1.9\pm0.2$ iron nearest neighbours on average instead of the 3 expected for complete disorder; the iron-iron repulsion is therefore effective to the extent of expelling about a third of the atoms from the co-ordination shell in a typical case. The second-nearest-neighbour position is one of the other cube corners of the ordered structure; and here we find that the average population of iron atoms is in practice $2.1\pm0.2$, where 1.5 would represent complete disorder and 6 complete order.

With 60Fe40Ni, the apparent tendency to order on the basis of $Ni_3Fe$ is at first sight extraordinary. However, if 25 out of every 60 iron atoms were to be placed at cube corners and the remaining 35 distributed at random over the face-centring sites, the diffraction pattern of this alloy would show sharp Bragg peaks at the superlattice positions; this arrangement would be as near to perfect order as the constitution allows. The existing situation must be regarded as showing some tendency to order in approximately this manner[13]. It is interesting to reflect that because the scattering length of $Ni^{60}$ is so small, the nuclear diffraction patterns of Fig. 2 can be regarded in rough approximation as arising from the iron atoms alone. The appearance of an intensity maximum near the positions for 100 and 110 does therefore directly imply that the iron atoms tend to seek out the cube corner sites.

According to Guttman[2], a minimum in the scattering at angles below the first superlattice line indicates that each atom has a larger number of unlike atoms as nearest neighbours than obtains in a random alloy, and this is consistent with our conclusions.

*The localisation of the magnetic moments*

The broken lines in Fig. 2 indicate the intensity distributions that would have been obtained with perfectly random binary alloys, and the actual deviation from these lines is a consequence of the term containing $P_{ab}$ in eq. (3). Detailed study of Fig. 2 shows that our results are consistent with the assumption that the magnetic and nuclear scatterings have the same angular dependence, apart from what is introduced by the form factors $f_a$ and $f_b$.

A question arises whether it is physically reasonable to imagine the spin system as a simple binary combination of a given $\mu_a$ and $\mu_b$. The iron atoms, for instance, have a statistical distribution of neighbourhoods ranging from all-iron to all-nickel, and it is scarcely to be imagined that the iron moment is rigorously independent of its surroundings. Indeed, the saturation magnetisation of $Ni_3Fe$ changes by some 5% between the ordered and disordered states, which would suggest an environment-sensitive effect of about that proportion. In one of the papers at this Conference[14], La Force, Ravitz and Day show by NMR that the effective field at a cobalt nucleus in CoFe alloys is altered from the pure-cobalt value by about 1.2% for every iron neighbour; if this measurement reflects the dependence of the atomic moment itself on its surroundings, we may conclude that characteristic moments $\mu_a$ and $\mu_b$ can meaningfully be defined in the CoFe system to within an error of roughly about 5%. A similar situation may be imagined to exist in the FeNi system.

Thus we may interpret our magnetic intensities in terms of localised moments to this order of accuracy, which it so happens is just about equal to the accuracy of the moment figures deduced below.

*Magnitudes of the localised moments*

To determine the magnetic moments from $|p_a-p_b|$ one must make still further assumptions, about the values of $f_a$ and $f_b$. We have taken them to be the same as for the pure metals[15),16], and have deduced two alternative sets of moment values for four disordered alloy systems, with the results listed in Table 1. At iron concentrations of 30 and 60% we have used Fig. 2 and eq (3), measuring $R$ at

Table I.

| %Fe | $\bar{\mu}$ | $\lvert \mu_{Fe} f_{Fe} - \mu_{Ni} f_{Ni} \rvert$ | | $\mu_{Fe}$ | $\mu_{Ni}$ |
|---|---|---|---|---|---|
| | | 100 | 110 | | |
| 10 | 0.83 | — | — | (a) 2.58±0.14<br>(b)−0.78±0.14 | 0.64±0.05<br>1.01±0.05 |
| 30 (annealed) | 1.33 | 1.80±0.08 | 1.58±0.08 | (a) 3.02±0.12<br>(b)−0.06±0.11 | 0.63±0.09<br>1.94±0.09 |
| 30 (quenched) | 1.25 | 1.55±0.08 | 1.35±0.08 | (a) 2.66±0.09<br>(b) 0.06±0.09 | 0.63±0.08<br>1.75±0.08 |
| 60 | 1.80 | 1.20±0.10 | 1.03±0.12 | (a) 2.44±0.08<br>(b) 1.34±0.08 | 0.83±0.06<br>2.48±0.06 |
| 90 | 2.26 | — | — | (a) 2.41±0.04<br>(b) 2.14±0.06 | 0.93±0.10<br>3.26±0.10 |

Magnetic moment data for Fe-Ni alloys as obtained from neutron scattering and magnetisation experiments, together with the two possible sets, (a) and (b), of magnetic moments that satisfy the results. Moments are quoted in Bohr magnetons.

the superlattice line positions. We have also given figures for the ordered 30Fe70Ni alloy, in which case the ratio of integrated intensities in the magnetic and nuclear superlattice lines was used. Noticing that in Fig. 1 the data at 10 and 90% iron do not show excessive amounts of order, we have further made a best fit of these data to eq. (2) and deduced moment values on the assumption of complete disorder. The standard deviations listed in the table are directly due to experimental uncertainties; our assumptions about $P_{ab}$ and $f$ introduce another source of error of essentially the same magnitude (0.1 $\mu_B$). As implied above, the upshot is a happy one insofar as the larger moments at least have been determined to just the accuracy to which they have a physical meaning.

Individual magnetic moments are plotted in Fig. 3 as a function of alloy composition. The values are in general agreement with those of SW, despite the fact that those authors made no allowance for short-range order. The moment set (b) of Table 1 would indicate that iron dissolves dilutely in nickel with a negative moment and has virtually no moment in $Ni_3Fe$; these conclusions are so difficult to believe that in Fig. 3 we have plotted solution (b) with faint crosses only. We have preferred to draw attention to solution (a) by the use of large black circles. It would of course be very desirable to have the correct solutions identified by polarised neutron experiments.

According to solution (a), the overall picture is that in coarse approximation the moments on both types of atom remain broadly unaffected by alloying. When either atom is present in dilute concentration only, it

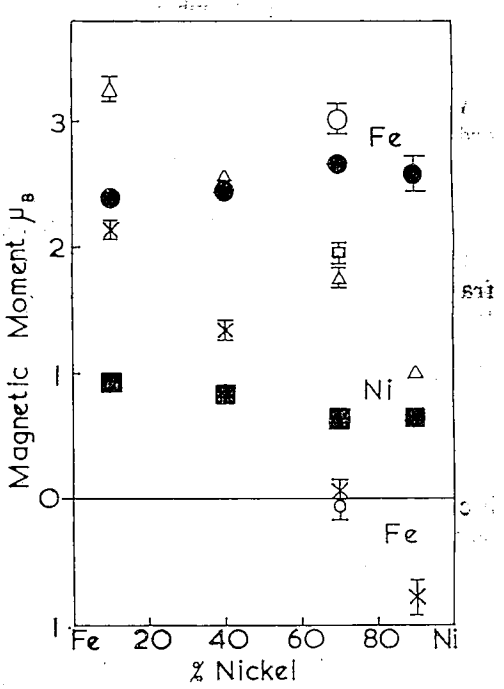


Fig. 3. Moments attributable to 3$d$ electrons in Fe-Ni alloys, as a function of composition. ● iron, solution (a) of Table I; ○ iron, from highly ordered specimens; × iron, solution (b); ■ nickel, solution (a); □ nickel, solution (b), from highly ordered specimens; △ nickel, solution (b).

would appear that its moment is some $0.3\mu_B$ higher than when it is the predominant constituent.

The shape of the saturation magnetisation curve, of course, imposes conditions on the behaviour of $\mu_{Fe}$ and $\mu_{Ni}$ as a function of concentration. For instance, if $\mu_{Ni}$ is constant at $\sim 0.9\mu_3$ towards the extreme left of the diagram, as the set of moments (a) superficially implies, then $\mu_{Fe}$ must be of the form $\mu_{Fe}=2.2+2c_{Ni}$. If, on the other hand, $\mu_{Fe}$ is constant in iron-rich alloys, then $\mu_{Ni}$ must rise above $\mu_{Fe}$ towards the iron-rich end of the series. In 1958, Lomer and Marshall[17] discussed the effects of such restrictions for a wide series of transition metal alloys. Fig. 2 of their original paper gives a prediction of our Fig. 3, and suggests that at 10% nickel the nickel moment of $3.2\mu_B$ is the correct one. Lomer and Marshall's argument ultimately rests on the view that with dilute nickel concentrations it is more reasonable to imagine a large nickel moment than to suppose that a small one has the effect of increasing the moments on a large number of iron atoms. The possibility of severe conduction-electron magnetisation would nowadays make a more sophisticated argument necessary, but the successes of their theory serve as a reminder that one must not too hastily choose between the alternative solutions (a) and (b).

It must be realised that the moment values in Fig. 3 have been derived by a procedure that in effect fits a $3d$ form factor to the angular dependence of the scattering from a given atom, so that they represent only the $3d$ contribution to the total magnetism. If there is in reality a strong conduction-electron polarisation, it would be inexact to say that the moments of Fig. 3 correctly indicate the total contribution at the appropriate atomic site. Moreover, in the presence of appreciable conduction-electron polarisation our method of calculating the moments is inaccurate, because we have assumed $c_a\mu_a+c_b\mu_b=\bar{\mu}$, which is no longer true if $\mu_a$ and $\mu_b$ refer only to the $3d$ contribution in such a situation.

It is interesting to see that in their paper at this Conference, Shull and Yamada[16] conclude that the conduction electron polarisation in iron is about as much as $-0.2\mu_B$, and that $\mu_{Fe}(3d)=2.4$. This would require the $3d$ moments we have given for 90Fe10Ni each to be increased by about $0.2\mu_B$. A similar effect might equally well cause the $3d$ moment of nickel to deviate from $0.6\mu_B$, but the discrepancy would be smaller than for iron.

**Acknowledgments**

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## DISCUSSION

R. NATHANS: In obtaining the magnetic moment values of the iron and nickel atoms in these alloys, the assumption has been made that all the atoms of each kind have the same moment. Since the net moment on an individual iron or nickel moment will depend on its nearest neighbor environment, we can expect that the iron and nickel moments will take on a spectrum of values.

R. D. LOWDE: This matter is discussed in the written version of the paper. I may add that we have tried fitting our $3d$ moments $\mu_{Fe}$ into the formula

$$H_{eff}(Fe)=a\mu_{Fe}+b\bar{\mu}\ ,$$

where the $H_{eff}$'s are taken from Johnson *et al.*[18] Within experimental error this equation can be roughly satisfied with $a=82$ and $b=66\,\text{koe}\mu_B^{-1}$. According to Dr. C. E. Johnson, however, the data for Fe, $Fe_3Al$, FeTi and FeZr all fit the equation within 5% using $a=120$ and $b=30\,\text{koe}\mu_B^{-1}$. If this latter pair of constants is used for iron-nickel, a comparable fit can be achieved only for the 90Fe10Ni alloy. The reason is that with increasing addition of nickel, the field at the iron nucleus falls off while the magnetic moment of the iron atom remains roughly constant; it is therefore not possible to fit the simple formula right across the iron-nickel diagram without a rather substantial coefficient $b$.

J. M. HASTINGS: May I ask Dr. Lowde if he can supply a value for the moment difference for the Fe-Ni system in the permalloy region. Some six years ago, simultaneously with the work of Shull and Wilkinson, Corliss and I also attempted to measure this moment difference. Our experiments were done on a single crystal in which we were able to measure both the nuclear and magnetic superlattice intensities, the object being the elimination of the degree of order as a parameter. The value we obtained was approximately $1.6\mu_B$. This differed significantly from the Shull and Wilkinson value.

R. D. LOWDE: Our value, choosing solution (a), is $2.39\pm0.15\,\mu_B$, in agreement with Shull and Wilkinson's $2.35\pm0.20\mu_B$.