

Neutron Diffraction Studies of the Magnetic Structure of Alloys of Transition Elements

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Neutron diffraction results are presented for a series of alloys of transition elements as an investigation of their magnetic structure. Ferromagnetic disorder scattering has been found for alloys in the disordered state and magnetic superstructure scattering is observed for ordered alloys. Such magnetic scattering when combined with magnetization data offers information on the individual atomic magnetic moments present in the alloy. In general the atomic magnetic moments deviate from their pure elemental values as a function of alloy composition. Scattering data and magnetic moment information are given for members of the Fe—Cr, Ni—Fe, Co—Cr, and Ni—Mn series of alloys.

INTRODUCTION

THE electronic structure existing in alloys of the transition elements has been the subject of considerable discussion, not always without controversy, in the literature of the last decade. Various viewpoints of the structure of the transition elements themselves have been presented and their proponents have in many cases extended the different treatments into the alloy field. Among the more recent review articles of work in this field are those of Goldman¹ and Hume-Rothery and Coles² wherein extensive references to earlier research publications will be found.

Experimentation in this field has centered primarily about magnetic measurements, since for many atomic systems, this type of information can lead to an unambiguous picture of the electronic structure. Such measurements are, however, invariably representative of the macroscopic average over the whole component system and offer no information whatsoever about details from one atom to another. In principal, neutron scattering can distinguish between the different electronic configurations of different atoms via a magnetic interaction and thus offer some guidance in the selection or rejection of particular theoretical viewpoints.

A number of different alloys systems have been studied in this fashion over the past several years, and although the studies are by no means complete since other equally interesting systems remain for investigation, it was thought desirable to summarize the present results. The alloys to be discussed in the present report are those shown superimposed on the Slater-Pauling curve of Fig. 1. It was noticed some fifteen years ago³ that the ferromagnetic moments of the pure elements and many alloys tended to follow such a general curve with respect to average outer electron concentration. Some exceptions were noted, however, and typical of these is the Co—Cr system which possesses magnetic moments that vary as shown in the

figure. In addition to the Co—Cr, Fe—Cr, and Ni—Fe systems, data have been obtained on two alloys of definite composition, Ni₃Fe and Ni₃Mn. These two alloys are known to form ordered superstructures, and the investigation gives information concerning the effect of atomic ordering on the magnetic structure.

NEUTRON SCATTERING CONSIDERATIONS

It is well known that elements of the transition group form alloys possessing solid solubility over extended regions of composition. Such alloys exist usually in the *disordered* form in which the solute atoms reside at random on solvent atom sites. For certain compositions, however, the alloy may take on an *ordered* form wherein the atoms of one species become located at specific crystallographic positions. An arrangement of the latter type is usually brought about by suitable thermal treatment of the alloy, and its existence can be detected by the appearance of superstructure line intensity in the x-ray or neutron diffraction pattern. Both disordered and ordered alloys are included in the present study and it will be desirable to give expressions for the scattered intensity or cross section appropriate to the two cases.

Ferromagnetic Disorder Scattering

When neutrons are scattered from a ferromagnetic alloy of disordered form, there should exist a ferromagnetic disorder scattering whose cross section or intensity will depend upon the difference in the magnetic scattering amplitudes of the two species of atoms. If the incident neutron beam is unpolarized, it can be shown that this cross section for an unmagnetized sample in which the ferromagnetic domains are oriented at random is given by

$$d\sigma = \frac{2}{3}n(1-n)(p_1 - p_2)^2, \quad (1)$$

wherein n and $(1-n)$ are the fractional abundances of the two species and p_1 and p_2 are the magnetic scattering amplitudes. The factor $\frac{2}{3}$ arises because of the randomness of the magnetization vector relative to the scattering vector for the unmagnetized sample. Furthermore

¹ J. E. Goldman, Revs. Modern Phys. **25**, 108 (1953).

² W. Hume-Rothery and B. R. Coles, Advances in Physics **3**, 149 (1954).

³ J. C. Slater, J. Appl. Phys. **8**, 385 (1937); L. Pauling, Phys. Rev. **54**, 899 (1938).

the magnetic scattering amplitude will depend upon the atomic magnetic moment μ according to

$$\begin{aligned} p &= \frac{1}{2}(e^2/mc^2)\gamma\mu f \\ &= 0.270 \times 10^{-12} \mu f, \end{aligned} \quad (2)$$

where γ is the neutron magnetic moment and f is the magnetic form factor descriptive of the spatial origin of the atomic magnetic moment. Thus it is seen that a determination of the ferromagnetic disorder scattering can yield the difference between the magnetic moments of the two types of atoms present in the alloy. If at the same time the average magnetic moment of all the atoms is known from magnetic saturation data, *viz.*,

$$\bar{\mu} = n\mu_1 + (1-n)\mu_2, \quad (3)$$

then expressions (1) and (3) may be combined to permit solution of μ_1 and μ_2 within an algebraic sign ambiguity. Unfortunately the intensity of scattering represented by Eq. (1) does not give information on the sign of the moment difference; hence alternative sets of solutions for the individual moments are obtained. There do exist experimental techniques for removing this ambiguity which involve the use of polarized neutron beams or a study of the paramagnetic scattering at high temperatures, but as yet these experiments have not been performed. Throughout the data presentation, both sets will be given, and it is necessary to use independent arguments in assigning the correct solution.

The ferromagnetic disorder scattering will appear in the diffuse background of the neutron diffraction pattern and its extraction from the various other diffuse scattering components such as multiple scattering, thermal disorder scattering, and isotopic or nuclear spin disorder scattering offers considerable difficulty. In the most favorable case it amounts to only about 5 percent of the total diffuse scattering level so that its evaluation by recognition of the form factor angular dependence is at most uncertain if not impossible. On the other hand, the ferromagnetic disorder scattering is sensitive to the application of an external magnetic field. Therefore, a determination of the diffuse level when the scattering sample is magnetized in different directions with respect to the scattering vector can yield the magnetic disorder scattering. None of the other diffuse scattering components mentioned above will vary with sample magnetization. In practice it has been found most convenient to compare the diffuse level with the sample unmagnetized, for which expression (1) is applicable, to that obtained when the sample is magnetized parallel to the scattering vector, in which case the magnetic scattering amplitudes go to zero and there is no magnetic disorder scattering. A correction must be applied to this change in intensity because of the altered transparency of a scattering sample when magnetized, an effect commonly known as the single transmission effect. This correction is determined for

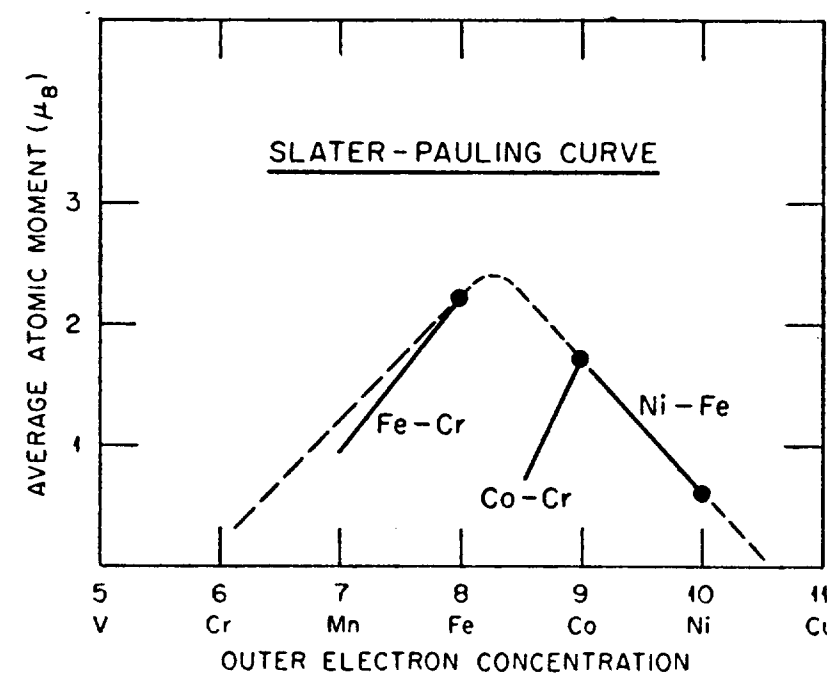


FIG. 1. Slater-Pauling curve relating the average magnetic moment to the outer electron concentration. The particular alloy systems indicated here are discussed in the text.

each sample and is generally small for the substances reported here.

Ferromagnetic Superstructure Scattering

For the ordered ferromagnetic alloys, the magnetic scattering effects will be concentrated in the coherent reflections both for the normal lattice reflections and for the superstructure reflections. Again it is necessary to separate the magnetic component of the scattering from the nuclear component, and this can be done either by recognition of the magnetic form-factor portion or by determining the effect of an external magnetic field on the coherent reflections. The cross section for magnetic scattering in the superstructure reflections will be of the same form as Eq. (1) and hence the same analysis of data is possible as was performed for the disordered state.

In treating the magnetic superstructure data it is necessary to know the degree of long-range order present in the ordered sample. Usually, the long-range order parameter can be evaluated from the nuclear scattering components of the reflections and, if necessary, a suitable correction can then be applied to the magnetic intensity. This procedure is not feasible in the case of ordered Ni₃Fe since the nuclear superstructure effects are very weak. Therefore, other evidence for the degree of long-range order must be invoked.

EXPERIMENTAL RESULTS

Fe—Cr Series

Three members in this series which possessed 15.2, 29.1, and 46.4 atomic percent Cr were prepared and examined along with pure iron. Electrolytic iron bar and electrolytic chromium chips were melted inductively in a vacuum furnace and cast into bar form. Following this the sample stock was given an homogenizing heat treatment at 1300°C in a 95 percent He—5 percent H₂ atmosphere for three hours after which the sample was filed with a tungsten carbide file in a filing machine. The resulting filings sieved through 100-mesh screen were used in the study to insure randomness of crystal-

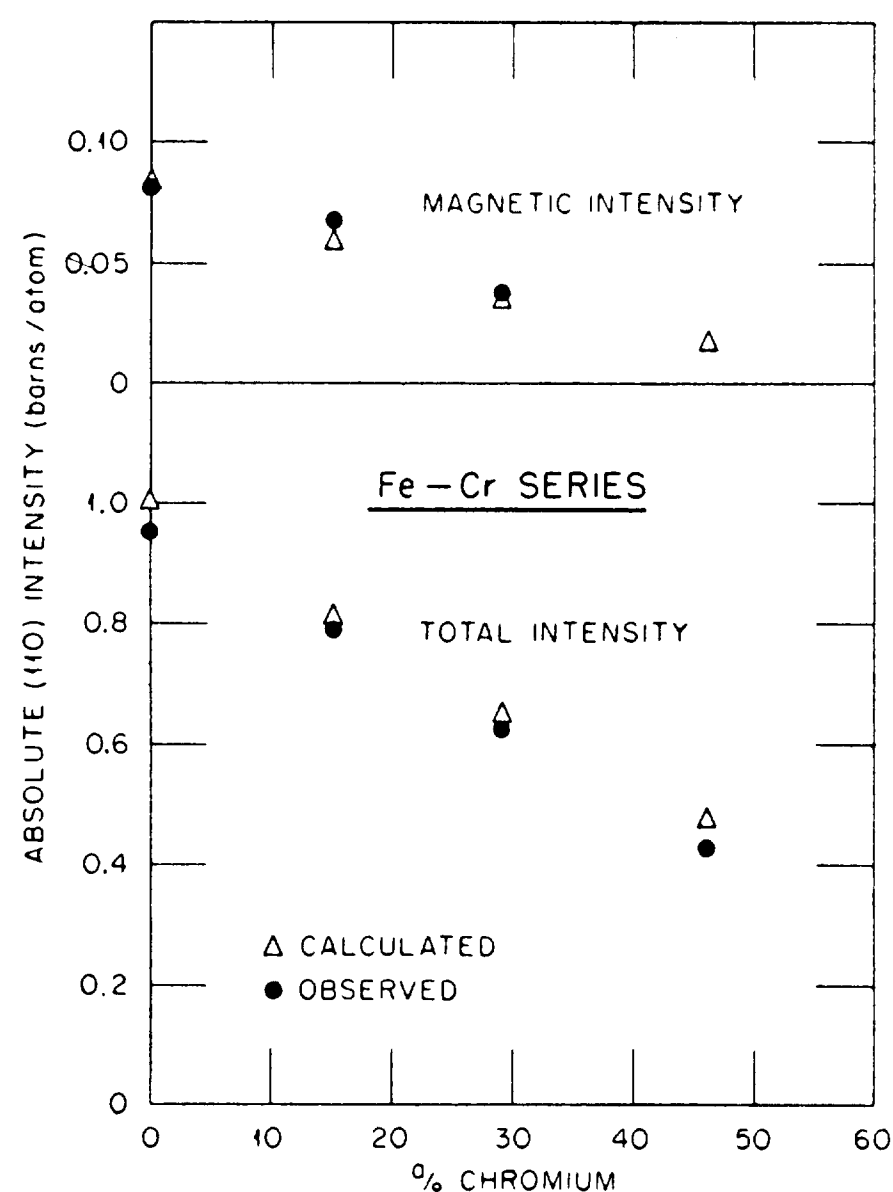


FIG. 2. Comparison between the observed and calculated values of the total intensity and the magnetic intensity in the (110) reflection for the Fe—Cr series of alloys.

lite orientation in the diffraction specimen. Chemical and spectrographic analysis were obtained on the final product of filings.

The diffraction patterns for all of these samples showed only characteristic body-centered cubic reflections with no evidence for either short-range or long-range order. Since the nuclear scattering amplitudes

of Fe and Cr are rather favorable for exhibiting residual order, this can be considered good evidence of the disordered state of these preparations. In the lower portion of Fig. 2 is shown the variation of the integrated intensity of the (110) reflection, expressed in absolute units of differential scattering cross section, for the four members of the series. Along with the observed values are shown those calculated using accepted values for the nuclear scattering cross sections and the agreement can be considered satisfactory.

In the upper portion of Fig. 2 is shown the variation of the magnetic scattering cross section as seen in the (110) reflection for the different alloys. This was determined by measurement of the (110) intensity change upon magnetization of the sample in a direction parallel to the scattering vector. Also shown are the values calculated using expression (2) with average magnetic moment values obtained from magnetization studies.⁴ Agreement between the observed and calculated values indicate merely that the average magnetic moment as seen by neutron scattering is consistent with that obtained in the purely magnetic type of investigation, namely the measurement of saturation magnetization.

TABLE I. Magnetic moment data for Fe—Cr disordered alloys as obtained from neutron scattering and magnetization experiments.

	$\mu_1 - \mu_2$ (μ_B)	$\bar{\mu}$ (μ_B)
Fe	0	2.22
84.8 Fe—15.2 Cr	2.85 ± 0.10	1.81
70.9 Fe—29.1 Cr	2.38 ± 0.07	1.44
53.6 Fe—46.4 Cr	1.62 ± 0.11	1.00

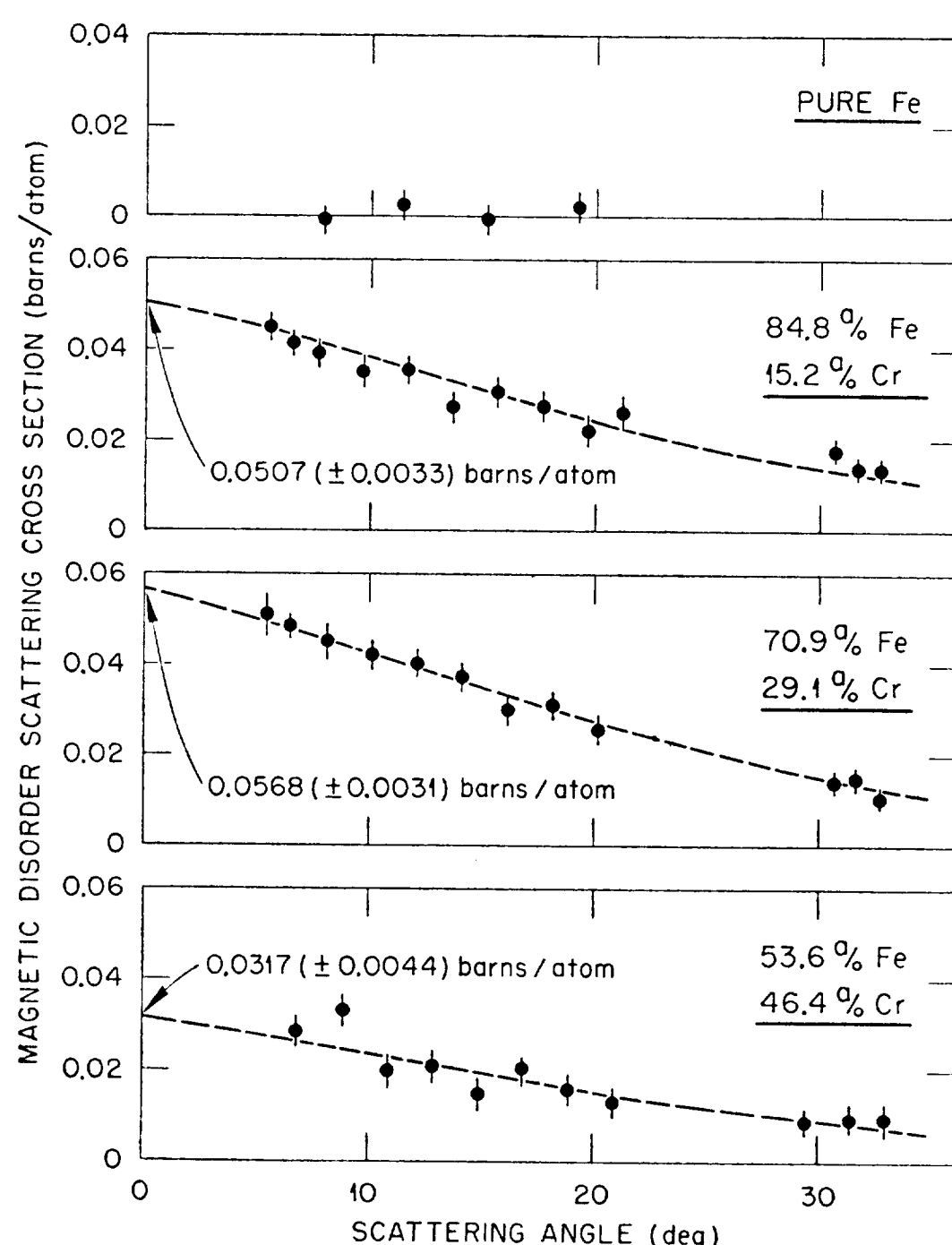


FIG. 3. Ferromagnetic disorder scattering obtained for a series of disordered Fe—Cr alloys.

Of principal interest in the diffraction patterns for these alloys is the appearance of ferromagnetic disorder scattering as detected by the change in diffuse scattering intensity when the sample is magnetized parallel to the scattering vector. The observed change in intensity has been corrected for the magnetic transparency effect and placed on an absolute cross section scale with the results shown in Fig. 3. The magnetic disorder scattering for pure iron is seen to be very much smaller than that encountered in the alloys. Drawn through the various sets of data is the magnetic form factor calculated by Steinberger and Wick⁵ for metallic iron and the close agreement with the observations suggest not only the applicability of this form factor but the presence of complete disorder in the alloy. The intercept of the matched form factor curves at zero scattering angle can then be used to evaluate the difference in the magnetic moments of the iron and chromium atoms and these values for the different alloys are summarized in Table

⁴ The average magnetic moments for all of the alloys to be discussed in this report can be found in R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951).

⁵ J. Steinberger and G. C. Wick, *Phys. Rev.* **76**, 994 (1949).

I. Also shown in the table are values for the average magnetic moment $\bar{\mu}$ determined from magnetization experiments.

Since the algebraic sign associated with the difference values in Table I is undetermined in the present experiment, alternative sets of solutions of the individual moments are possible and these are shown graphically in Fig. 4. The size of the experimental points as shown in the figure is a measure of their accuracy. It is to be noticed that the iron moment falls as chromium is added with either of the two solutions. On the other hand, the possible chromium moment values are widely different, one being large and positive and the other small and negative in the initial concentration region. At the 50-50 concentration the solutions converge and it is impossible to distinguish chromium values from iron values.

Ni-Fe Series

Three members of this series containing 49.9, 60.1, and 74.3 atomic percent nickel were prepared and studied. These were cast from inductively heated melts of the electrolytically pure elements, homogenized

TABLE II. Magnetic moment data for Ni-Fe disordered alloys as obtained from neutron scattering and magnetization experiments.

	$\mu_1 - \mu_2$ (μ_B)	$\bar{\mu}$ (μ_B)
74.3 Ni-25.7 Fe	2.31 ± 0.22	1.19
60.1 Ni-39.9 Fe	2.06 ± 0.21	1.47
49.9 Ni-50.1 Fe	1.93 ± 0.20	1.64

at 1300°C in a 95 percent helium—5 percent hydrogen atmosphere and then filed into a 100-mesh sample preparation. In this state all of the alloys showed the face-centered cubic (f.c.c.) structure with precision lattice constant values and neutron intensities characteristic of a disordered solid solution. Additionally, a portion of the 74.3 percent nickel alloy was given a long-time heat treatment to invoke the Ni_3Fe ordered structure and this will be discussed in the following section.

The ferromagnetic disorder scattering for these alloys is shown in Fig. 5 and again the Steinberger-Wick form factor has been matched to the various groups of data with intercept values as given in the figure. Table II summarizes the magnetic moment differences as calculated from the disorder scattering and also the average magnetic moments taken from magnetization data. The alternative sets of solutions for the individual moments have been evaluated and these are shown in graphical form in Fig. 6 with the size of the points representing their accuracy. Either set of solutions indicates that the nickel moment increases when iron is added, but the possible iron moments differ widely in the two solutions.

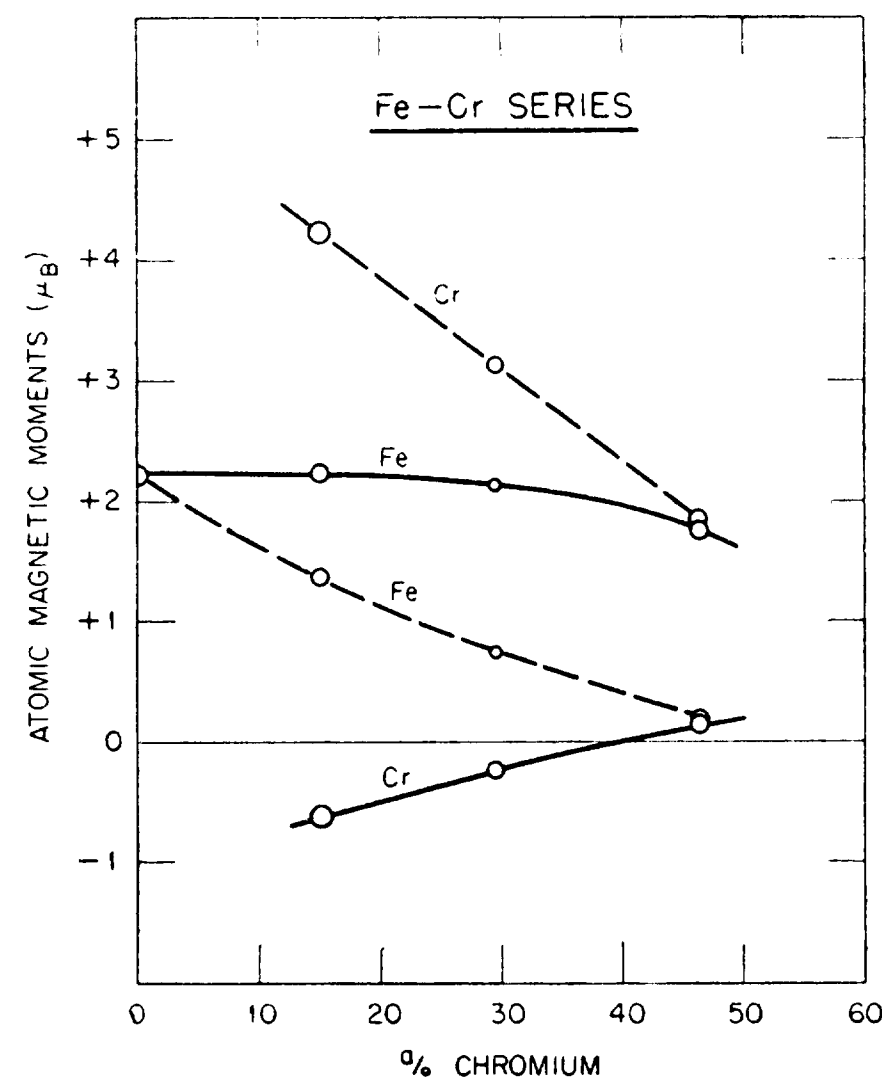


FIG. 4. Variation of the Fe and Cr atomic magnetic moments with atomic composition in Fe-Cr alloys. Alternative solutions are represented by the points connected either by the solid lines or by the dashed lines. The size of the experimental points is a measure of their accuracy.

Ordered Ni_3Fe

It has been well established that an alloy of this composition can be ordered with a structure similar to that of Cu_3Au in which the nickel atoms are located at the face-centered positions and the iron atoms at the

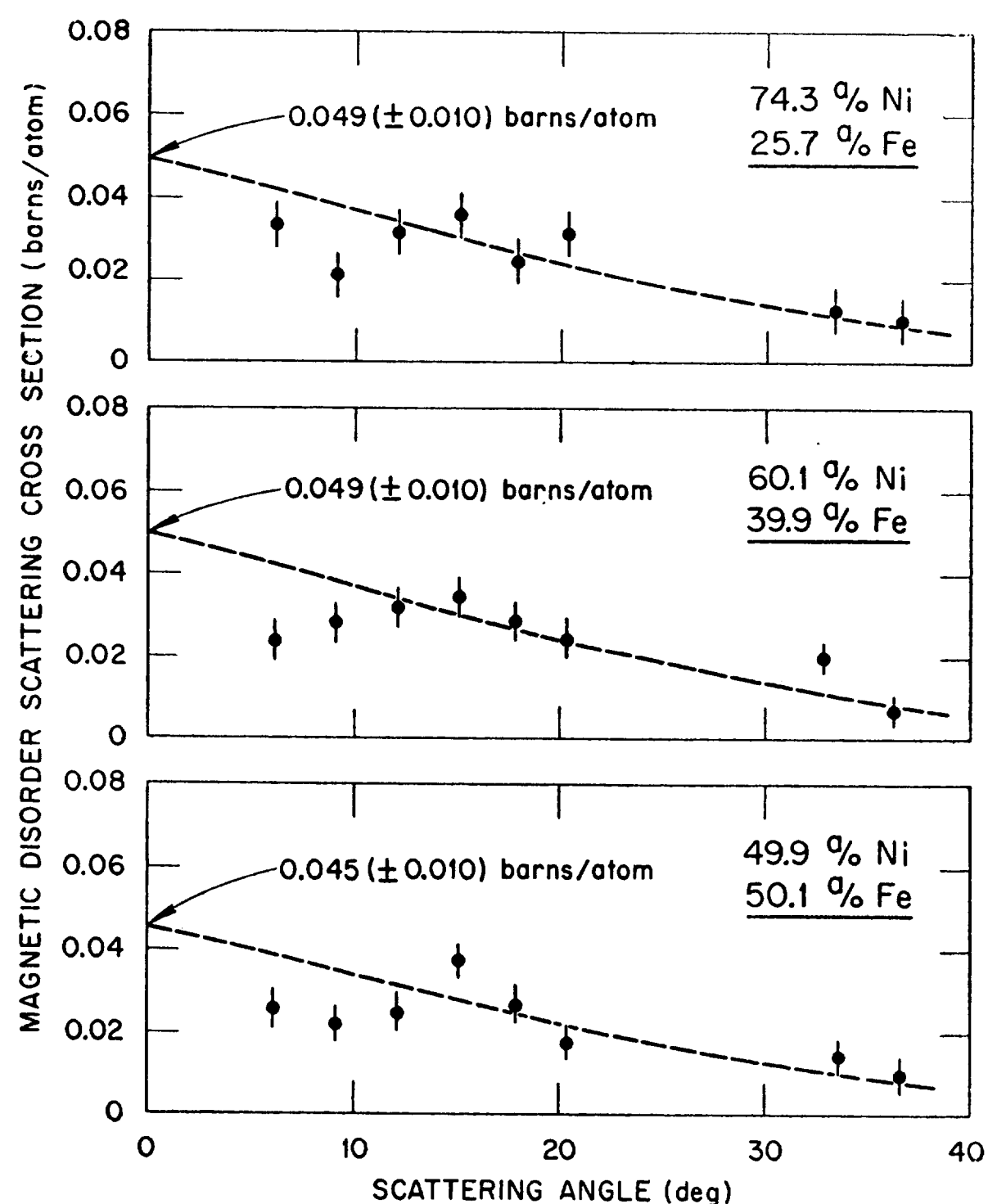


FIG. 5. Ferromagnetic disorder scattering obtained for a series of disordered Ni-Fe alloys. The decrease in scattering at small angles may indicate the presence of short-range magnetic order in the samples.

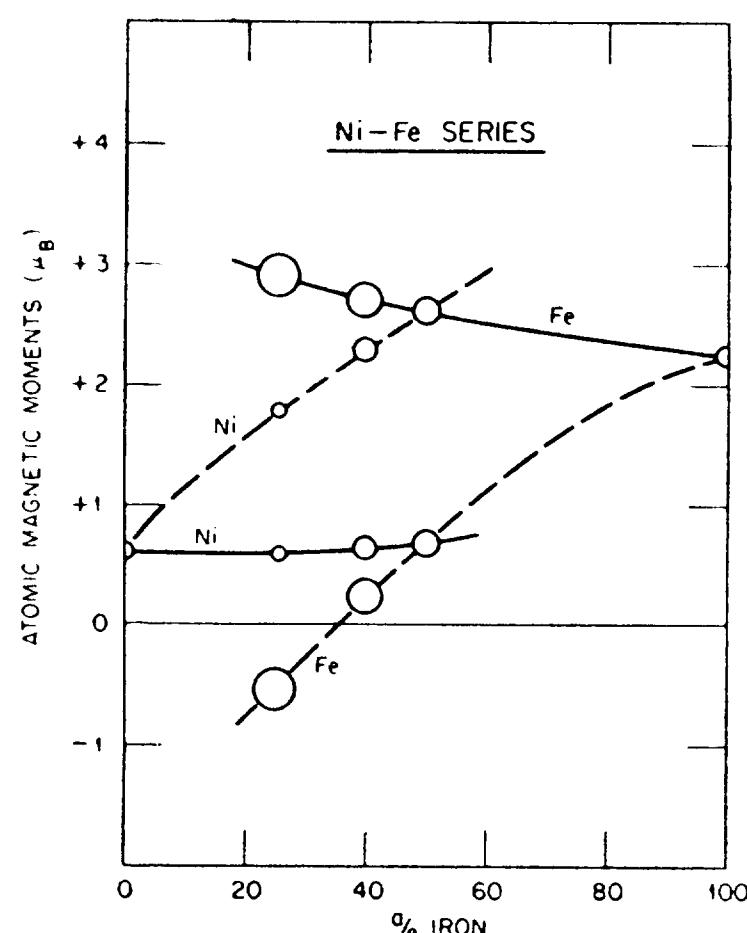


FIG. 6. Variation of the Ni and Fe atomic magnetic moments with atomic composition in disordered Ni-Fe alloys. Alternative solutions are represented by the points connected either by the solid lines or by the dashed lines. The size of the experimental points is a measure of their accuracy.

cube corners. Pronounced differences in magnetic anisotropy, permeability, and other properties have been found for the ordered and disordered preparations, and these have been used to establish an ordering temperature of 490°C. The usual diffraction technique for determining the state of long range order is not too successfully applied for this case because of the equivalence of the scattering amplitudes of Fe and Ni both for x-rays and neutrons.

Two different samples, (A) and (B), from different melts and with different ordering heat treatments have been studied. Sample (A), which contained 74.0 percent Ni, was heated in vacuum at 484°C for 200 hours after which it was cooled at the average rate of 2° every five hours to 350°C before the final cooling. Sample (B)

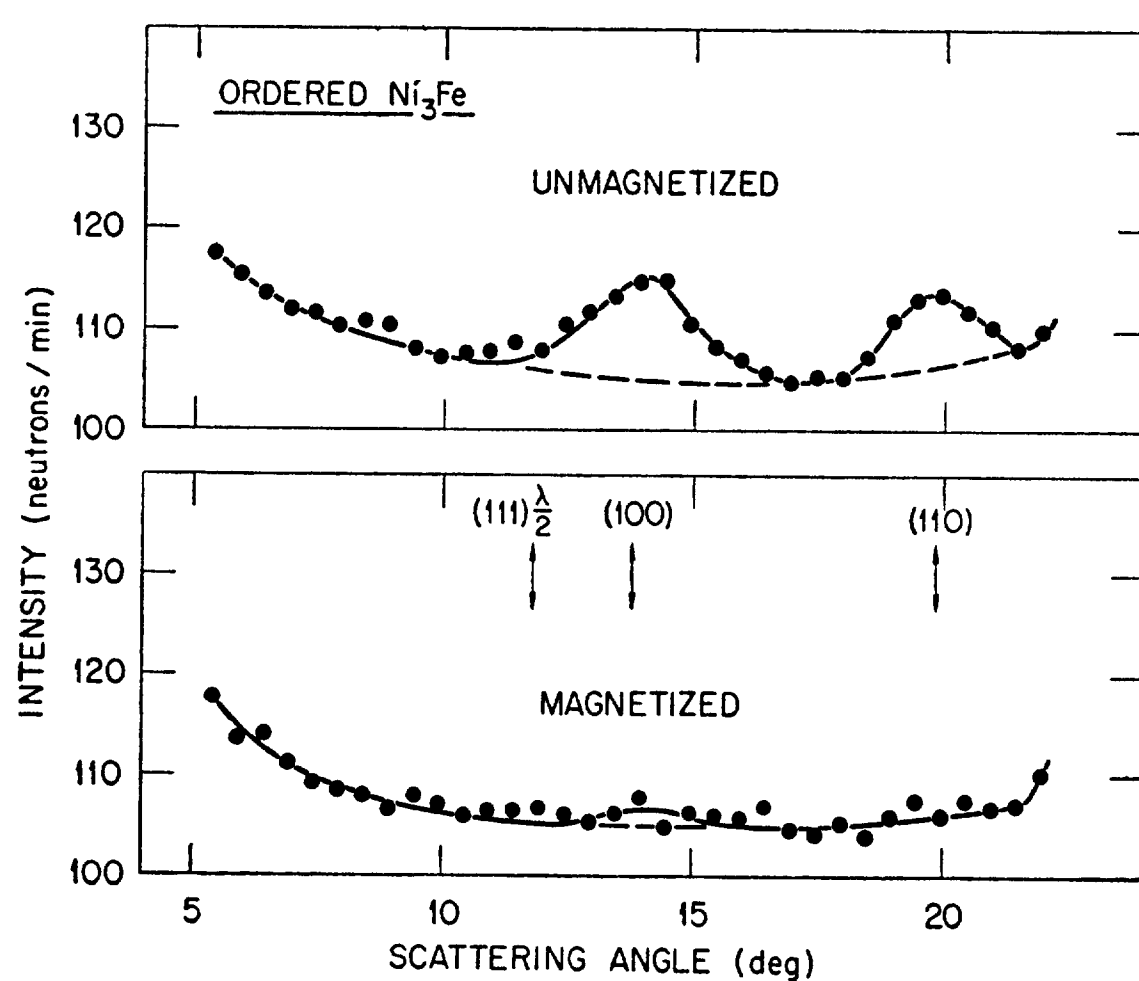


FIG. 7. Portions of the diffraction pattern for ordered Ni_3Fe showing the (100) and (110) superlattice reflections. The top pattern contains both nuclear and magnetic scattering whereas the bottom pattern contains only nuclear scattering.

which was part of the sample containing 74.3 percent Ni mentioned in the previous section, was given a much more elaborate vacuum heat treatment. The sample was first heated through the ordering temperature to 600°C for about an hour before the start of the ordering treatment. The temperature was then lowered to 500°C for 24 hours, after which it was decreased in steps of 25°, and each temperature step was held for about twice the time of the previous temperature. This procedure was followed through 375°C and required about ten weeks to complete. The superstructure lines in the diffraction pattern indicative of ordering were very weak relative to the normal f.c.c. lines. Typical portions of the patterns are shown in Fig. 7, which illustrates the (100) and (110) superstructure lines as obtained with an unmagnetized and a magnetized sample. As seen in the figure, most of the superstructure intensity is field sensitive, and this implies a *magnetic superlattice* as well as a chemical superlattice. From such studies the absolute intensity of the magnetic superstructure lines has been determined for several reflections and these results are illustrated in Fig. 8. Quite good agreement is to be noted in the data for the two samples, and the curve represents the best match of the Steinberger-Wick form factor to the data.

Before using the intercept value of 0.221 barns per Ni_3Fe molecule as the magnetic scattering cross section for the superstructure lines, it is necessary to establish the long-range order parameter. Since the nuclear scattering amplitudes are so similar for this case, it is impossible to make this determination in a direct manner by using the nuclear superstructure intensity and, therefore, indirect evidence must be invoked. It is known that the degree of order must be high, particularly for Sample (B), because of the absence of ferromagnetic disorder scattering in the diffraction pattern in contrast to that found in the disordered sample. In studies of other physical properties which are sensitive to the state of order, equivalent thermal ordering treatment has produced saturation in these properties. The agreement in the scattering data for our Samples (A) and (B) also supports a high saturation value for the degree of order. Moreover, in similar studies on Ni_3Mn (to be discussed in a later section) which orders in an equivalent manner and with closely the same ordering temperature, a long-time ordering treatment similar to that given Sample (B) resulted in a long-range order parameter of 0.905 as measured easily in the diffraction pattern. Accordingly, in the interpretation of the Ni_3Fe magnetic reflections, a long-range order parameter of 0.9 was assumed and this was considered significant to within 10 percent.

After correcting the magnetic superstructure intensity for this lack of complete order, the difference between the iron and nickel moments was evaluated as

$$\mu_{\text{Fe}} - \mu_{\text{Ni}} = \pm 2.35(\pm 0.20)\mu_B.$$

Combining this with the magnetization moment of $1.21\mu_B$ leads to the individual moments:

$$\begin{aligned} \mu_{Fe} &= +2.97(\pm 0.15)\mu_B, & \mu_{Ni} &= +0.62(\pm 0.05)\mu_B, \\ \text{or} \\ \mu_{Fe} &= -0.55(\pm 0.15)\mu_B, & \mu_{Ni} &= +1.79(\pm 0.05)\mu_B, \end{aligned}$$

as the alternative sets of solutions. The largest part of the above values of uncertainty arises from the lack of precise information about the state of order. Very interestingly the moment difference and the individual moments for ordered Ni_3Fe agree very closely to the equivalent moments as obtained for the disordered sample of the same composition.

Co—Cr Series

Two alloys in this series were prepared containing 9.0 and 13.6 atomic percent chromium. Cobalt rondels of purity 99.3 percent and electrolytic chromium were used as starting materials and subsequent spectroscopic and chemical analysis showed about 0.5 percent nickel impurity. In the filed condition the diffraction patterns showed only the hexagonal structure lines. The ferromagnetic disorder scattering was very small for both samples amounting to only $0.0037(\pm 0.0012) \times 10^{-24}$

TABLE III. Magnetic moment data for Co—Cr disordered alloys as obtained from neutron scattering and magnetization experiments

	$\mu_1 - \mu_2$ (μ_B)	$\bar{\mu}$ (μ_B)
91.0 Co— 9.0 Cr	0.96 ± 0.15	1.18
86.4 Co— 13.6 Cr	0.91 ± 0.15	0.77

$cm^2/atom$ and $0.0047(\pm 0.0016) \times 10^{-24} cm^2/atom$ for the 9.0 and 13.6 percent chromium alloys, respectively.

Table III summarizes the moment difference and average moment for the alloys and Fig. 9 illustrates the alternative sets of individual moments as calculated from the data. Of most interest here is the fact that the cobalt magnetic moment falls quite rapidly with chromium addition and that the chromium moments are all positive relative to the cobalt moments. The precipitous drop in saturation magnetization for Co—Cr as illustrated in Fig. 1 has been frequently ascribed by various authors to an antiparallel alignment of a large chromium moment in the alloy. It is seen that this is not the distinguishing feature of the magnetic structure but rather the rapid fall in the cobalt moment itself is responsible for the observed magnetic properties. If a negative chromium moment of $5\mu_B$ were present in the alloy, the disorder scattering should have been about forty times larger than was observed.

Ordered Ni_3Mn

This alloy exhibits magnetic properties which are very sensitive to the state of long range order present in the alloy. The ordered alloy is ferromagnetic with an

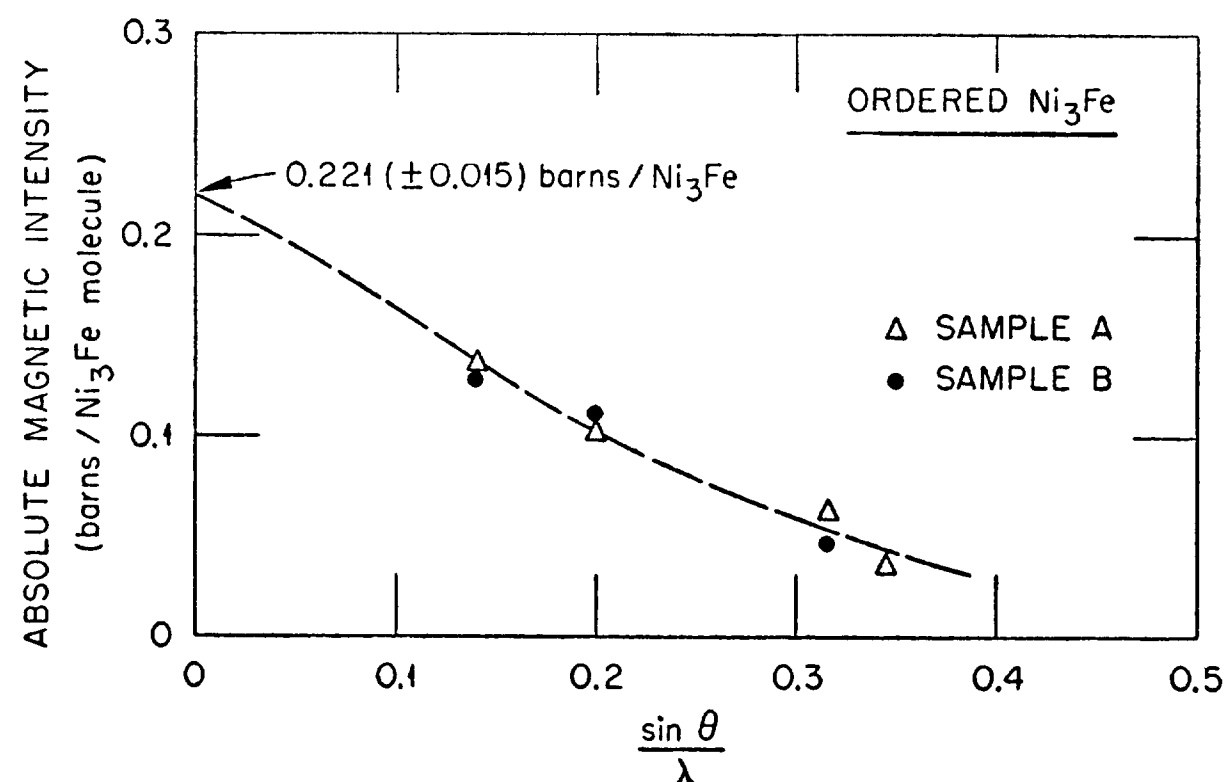


FIG. 8. Ferromagnetic scattering observed in the superlattice reflections for two samples of ordered Ni_3Fe .

average magnetic moment approaching $1.02\mu_B$ whereas the disordered alloy is essentially paramagnetic at room temperature with possible residual traces of weak ferromagnetism dependent upon the state of disorder. Several samples of both ordered and disordered preparations have been studied with most emphasis on a sample⁶ (74.0 atomic percent nickel) which was given an ordering vacuum heat treatment identical to that given Sample (B) of Ni_3Fe which was described in a previous section. Figure 10 shows the diffraction patterns obtained for this highly ordered sample and a disordered sample of unheated filings. Pronounced superstructure intensity is to be seen in the ordered sample pattern and some residual short-range order is seen in the diffuse scattering in the disordered sample pattern. The nuclear scattering amplitudes for nickel and manganese are quite favorable for exhibiting the effects of order, and from the nuclear scattering com-

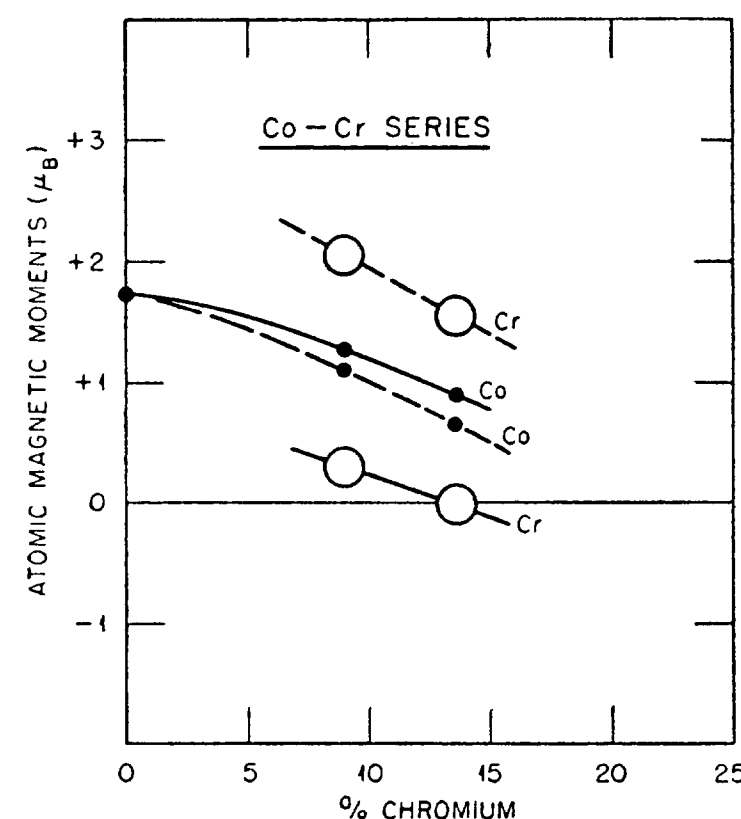


FIG. 9. Variation of the Co and Cr atomic magnetic moments with atomic composition in disordered Co—Cr alloys. Alternative solutions are represented by the points connected either by the solid lines or by the dashed lines. The size of the experimental points is a measure of their accuracy.

⁶ We are indebted to Dr. Lewis R. Aronin of the Massachusetts Institute of Technology Metallurgical Project for sending us this sample of Ni_3Mn .

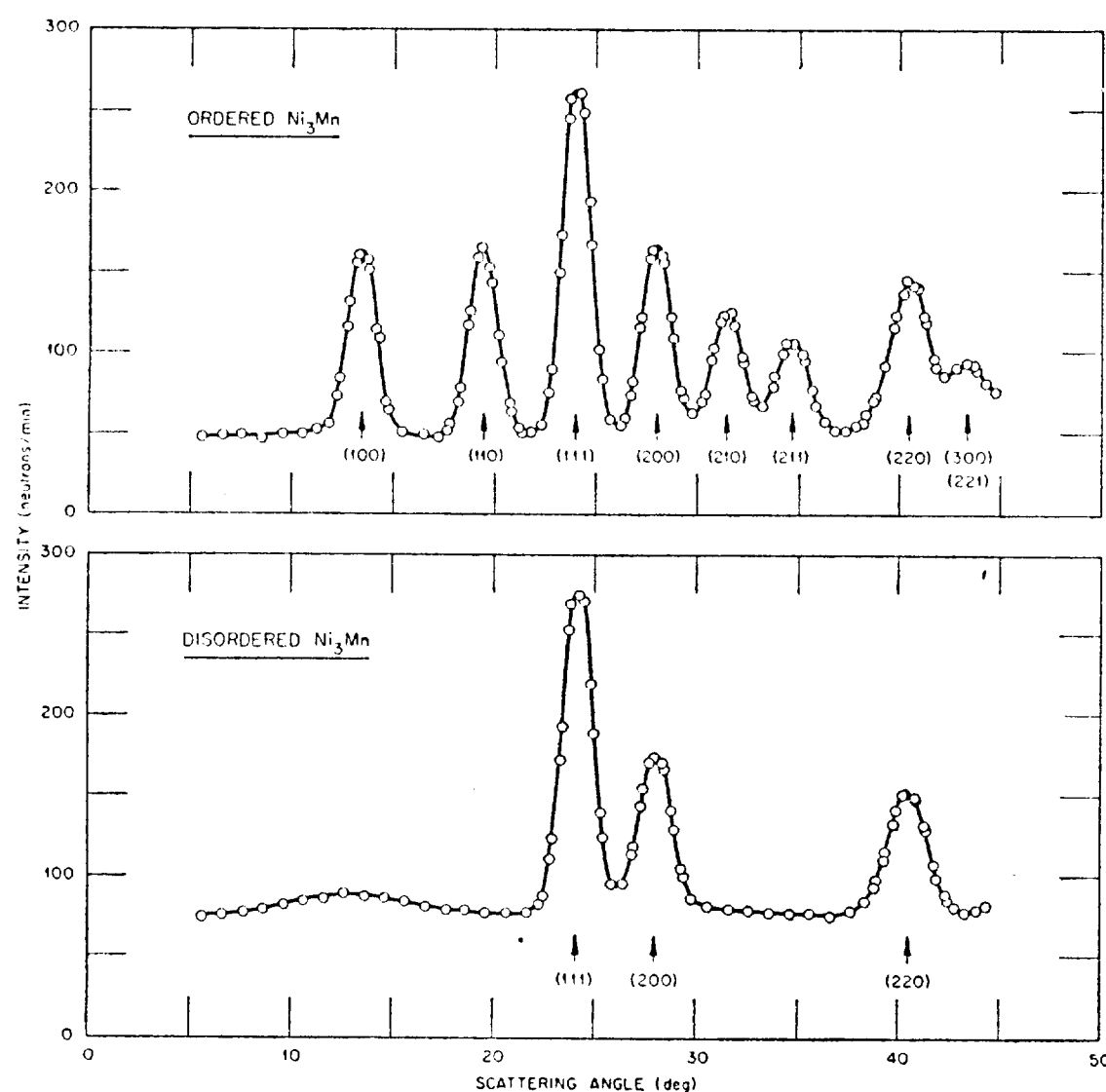


FIG. 10. Neutron diffraction patterns obtained for ordered and disordered Ni_3Mn . Residual short-range order is to be seen in the lower pattern.

ponent in the superstructure lines, the long-range order parameter is evaluated as 0.905.

The ferromagnetic components in the superstructure lines were evaluated by observing the change in intensity upon magnetization and these are shown in Fig. 11. The best magnetic form factor fit to the data yields a superstructure magnetic cross section of $0.400 (\pm 0.061) \times 10^{-24} \text{ cm}^2$ per Ni_3Mn molecule after correction for the lack of complete order. In turn this gives $2.88 \pm 0.20 \mu_B$ as the difference between the magnetic moments of manganese and nickel in the ordered alloy. Combining this with the average ferromagnetic moment of $1.02 \mu_B$ yields the alternate sets of individual moments:

$$\mu_{\text{Mn}} = +3.18 (\pm 0.25) \mu_B, \quad \mu_{\text{Ni}} = +0.30 (\pm 0.05) \mu_B,$$

or

$$\mu_{\text{Mn}} = -1.15 (\pm 0.25) \mu_B, \quad \mu_{\text{Ni}} = +1.73 (\pm 0.05) \mu_B.$$

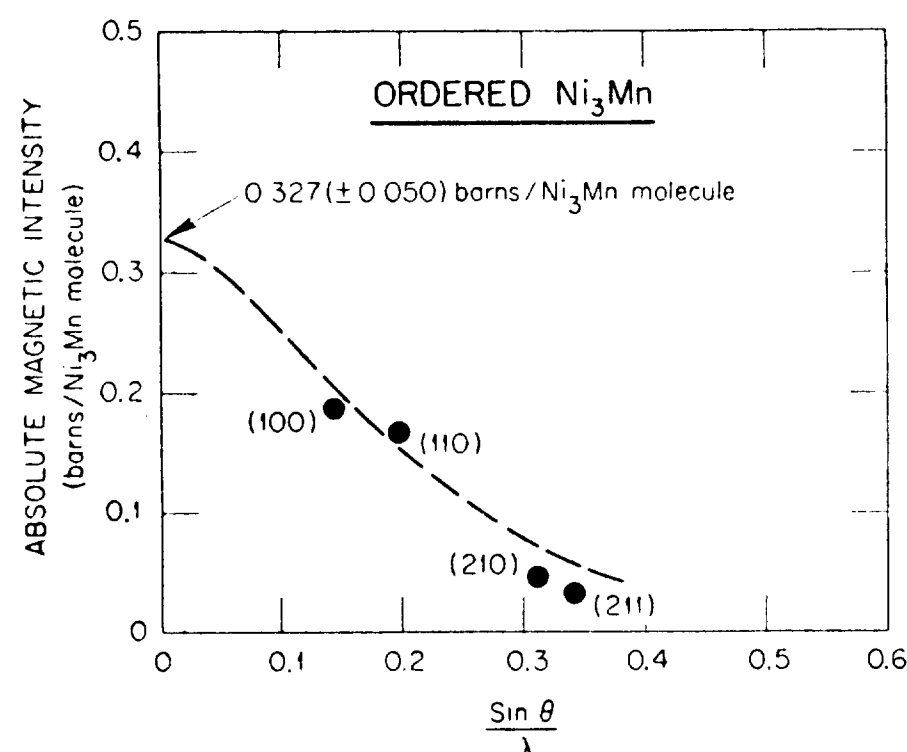


FIG. 11. Ferromagnetic scattering observed in the superlattice reflections of ordered Ni_3Mn .

Probably the first set is the correct one although the experimental data do not distinguish between the two.

A pronounced difference is to be noted in the diffuse scattering level of the patterns of Fig. 10 and this results because of the additional disorder scattering in the pattern for the disordered sample. The average nuclear disorder scattering can be calculated (this should be isotropic if no residual short-range order were present) and this accounts for most of the observed difference. Some magnetic disorder scattering modified by short-range order may very well exist in the diffuse scattering but at the present time this has not been evaluated. However, on the basis of the Ni_3Fe data, it seems unlikely that the individual moments should differ much from those in the ordered state. It can be said definitely that the disordered sample is not antiferromagnetic at room temperature.

SUMMARY

From the results presented on the above illustrative systems of alloys certain general conclusions are available. First of all, it has been shown for these alloy systems that a heterogeneous magnetic structure exists; that is, different magnetic moments are present either in a disordered or in an ordered distribution which depend upon the type of atomic distribution. Moreover, these moments are to be associated with localized atomic moments whose magnetic form factors differ little among themselves or from the theoretical calculations of the $3d$ -shell form factor as performed by Steinberger and Wick. Both the disordered and ordered magnetic scattering as seen in the diffuse scattering and superstructure lines are representative of magnetic form factor differences and the fact that this difference for Ni and Mn or Ni and Fe is significantly the same as that for Fe alone implies a closely similar d -shell for elements in this group.

In the case of Ni_3Fe , ordering of the lattice has been shown to have little or no effect on the component magnetic moments. This suggests that the local electron concentration of surrounding atoms has little effect on the magnetic moment and hence on the electron configuration of a central atom. Rather the over-all lattice composition seems to determine the individual moments. Changing the composition is seen to change the local moments although the significance of this is obscured because of the alternative sets of moment values consistent with the experimental data. In spite of this ambiguity it is established that the addition of Cr into either Fe or Co results in lowered moments for the solvent atoms whereas the addition of Fe into Ni elevates the Ni moment. The marked departure of the Co—Cr magnetization data from the general sequence as shown in Fig. 1 is found to result from a lowered value of the Co moment rather than an antiparallel orientation of the Cr moment.