where

$$J_\alpha^{nn'}(k)=\frac{1}{\omega_c}\int_c w_{nk}^*\frac{\partial w_{n'k}}{\partial k_\alpha}dr. \quad \text{(B.24)}$$

APPENDIX C. EFFECTIVE-MASS APPROXIMATION TO MATRIX ELEMENTS $\varphi_{ll'}$

The matrix elements $\varphi_{ll'}$ are given by (2.25) or

$$\varphi_{ll'}=\frac{1}{\Omega}\int e^{-i(k-k')\cdot r}\varphi w_l^* w_{l'}dr. \quad \text{(C.1)}$$

The assumption that φ has no Fourier components of the order of a reciprocal lattice vector means that only the constant part of the periodic function $w_l^* w_{l'}$ can contribute. Therefore

$$\varphi_{ll'}=\varphi_{kk'}W_{ll'}, \quad \text{(C.2)}$$

where

$$\varphi_{kk'}=\frac{1}{\Omega}\int e^{-i(k-k')\cdot r}\varphi dr, \quad \text{(C.3)}$$

$$W_{ll'}=\frac{1}{\omega_c}\int_{\omega_c} w_l^* w_{l'}dr. \quad \text{(C.4)}$$

The quantity $\phi_{kk'}$ is just the plane-wave matrix element of the potential. Since the latter is assumed to have no Fourier components of the order of a reciprocal lattice vector, k' must be close to k and we may expand $W_{ll'}$ as

$$W_{ll'}=\frac{1}{\omega_c}\int w_{nk}^*\left[w_{n'k}+(k_\mu'-k_\mu)\frac{\partial w_{n'k}}{\partial k_\mu}+\cdots\right]dr$$
$$=\delta_{nn'}+(k_\mu'-k_\mu)J_\mu^{nn'}(k)+\tfrac{1}{2}(k_\mu'-k_\mu)(k_\nu'-k_\nu)\times J_{\mu\nu}^{nn'}(k)+\cdots, \quad \text{(C.5)}$$

where $J_\alpha^{nn'}(k)$ is given by (B.24) and

$$J_{\mu\nu}^{nn'}(k)=\frac{1}{\omega_c}\int_{\omega_c} w_{nk}^*\frac{\partial^2 w_{n'k}}{\partial k_\mu \partial k_\nu}dr. \quad \text{(C.6)}$$

The $J_{\mu\nu}^{nn'}(k)$ satisfy the identity

$$J_{\mu\nu}^{nn'}(k)-(J_{\mu\nu}^{n'n}(k))^*=\frac{\partial J_\mu^{nn'}(k)}{\partial k_\nu}+\frac{\partial J_\nu^{nn'}(k)}{\partial k_\mu}, \quad \text{(C.7)}$$

which follows at once the orthonormality of the w_l's.

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Magnetic Structure of Fe_4N†

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The magnetic structure of Fe_4N has been examined in a neutron diffraction study. The results are in agreement with a model proposed by Wiener and Berger on the basis of magnetic measurements on a series of related compounds. Ferromagnetically aligned moments of 3 μ_B and 2 μ_B are found for the corner and face-center Fe atoms (respectively) in the cubic unit cell. The difference in moments is apparently due to bonding interaction between nitrogen, at the body-center position, and the face-center Fe's.

INTRODUCTION

THE nitride Fe_4N is a magnetic compound with a Curie point at 488°C and a net moment per formula unit of about 9 Bohr magnetons (extrapolated measurement: 8.86 μ_B at 0°K).[1] The average moment per iron atom is thus almost identical with that observed in body-centered α-iron (2.22 μ_B). The crystal structure is most closely related to nonmagnetic face-centered γ-iron, however. It may be considered as simply an expanded γ-iron lattice with nitrogen placed at the body-center of the unit cell.[2] The magnetic

† Work performed under auspices of the U. S. Atomic Energy Commission.
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[1] C. Guillaud and H. Creveaux, Compt. rend. **222**, 1170 (1946.)
[2] K. H. Jack, Proc. Roy. Soc. (London) **A195**, 34 (1948).

TABLE I. Wiener-Berger model for Fe_4N.

Fe coordinates	Outer electrons	μ_B
0, 0, 0	$3d^74s$	3
$\frac{1}{2}, \frac{1}{2}, 0$	$3d^84s$	2
$\frac{1}{2}, 0, \frac{1}{2}$	$3d^84s$	2
$0, \frac{1}{2}, \frac{1}{2}$	$3d^84s$	2

structure of this compound is therefore of some interest. It is also of interest with regard to the information one might obtain on the nature of nitrogen-metal bonding in a metallic compound of this sort. Hence, it was considered worthwhile to examine this structure with neutrons.

SOME MODELS CONSIDERED

In a recent paper by Wiener and Berger,[3] magnetic studies were made on two transition metal nitrides closely related to Fe_4N: Fe_3NiN and Fe_3PtN. These were shown to be completely ordered alloys with the same structure as Fe_4N, except that the corner Fe of the face-centered cell is replaced by Ni or Pt. On the basis of their measurements, and also using the published data on Fe_4N and Mn_4N,[1,4] Wiener and Berger proposed that nitrogen acts as a "donor" of electrons in structures of this type. That is to say, the nitrogen gives up one electron to the incomplete d shell of each of the three transition metal atoms on face-center positions, and accordingly the moment for each of these atoms is diminished by $1\,\mu_B$. In this way it was possible to account for the observed net moments for Fe_3NiN, Fe_3PtN, Fe_4N, and Mn_4N. A very similar idea had been suggested previously for Fe_4N by Guillaud,[5] who based his assumptions on the observed temperature variation of magnetization for Fe_4N (as compared to pure iron), although he did not propose a particular structure. The structure proposed by Wiener and Berger is given in Table I.

Although it is reasonable to suppose that nitrogen will behave in a consistent manner in similar compounds, Wiener and Berger pointed out that the cases of Fe_4N and Mn_4N are ambiguous. For these compounds one can obtain equally good agreement with observed magnetic data by assuming that nitrogen acts as an "acceptor" of electrons (from face-center Fe $3d$ shells). The electron acceptor role of nitrogen had been proposed for Fe_4N by Zener in an earlier paper,[6] and as can be seen in Table II, the resulting structure is ferrimagnetic. The negative sign for the first Fe moment is to indicate opposite spin alignment relative to that of the other three Fe's. While indistinguishable by the usual magnetic measurements, the Wiener-Berger and Zener models for Fe_4N would yield quite different neutron diffraction patterns.

TABLE II. Zener model for Fe_4N.

Fe coordinates	Outer electrons	μ_B
0, 0, 0	$3d^74s$	-3
$\frac{1}{2}, \frac{1}{2}, 0$	$3d^64s$	4
$\frac{1}{2}, 0, \frac{1}{2}$	$3d^64s$	4
$0, \frac{1}{2}, \frac{1}{2}$	$3d^64s$	4

[3] G. W. Wiener and J. A. Berger, J. Metals **7**, 360 (1955).
[4] C. Guillaud and J. Wyart, Compt. rend. **222**, 71 (1946).
[5] C. Guillaud, Compt. rend. **223**, 1110 (1946).

These were not the only models one might expect, however. Another logical structure to consider was one with all equal ferromagnetically-aligned moments. This would give a pattern differing greatly from that expected for the Zener model, but very nearly the same as that for the Wiener-Berger model. The equal moments model predicts zero magnetic scattering for those Bragg peaks whose indices are neither all even or all odd. The nuclear scattering for these peaks is due only to nitrogen. The Wiener-Berger model predicts some magnetic scattering for these peaks, but it is so small that it could easily be lost in small errors in the absolute scale factor and the Debye-Waller factor (the magnetic scattering for the other peaks is identical for all three models). The two models can be distinguished, however, by applying a magnetic field to the sample in a direction parallel to the scattering vector. A saturation field in this direction eliminates the magnetic scattering of neutrons, and hence if any intensity change at all is observed for the peaks with odd and even indices, then equal moments must obviously be ruled out.

EXPERIMENTAL DETAILS

The sample of Fe_4N used in the present study was prepared by G. W. Wiener, of the Westinghouse Research Laboratories, by nitriding thin iron strips with a stream of NH_3 and H_2 in a quartz tube furnace. An x-ray powder photograph revealed the presence of some unreacted α-iron, but no contamination due to other iron nitrides. The lattice constant was found to be 3.797 A, as compared to the reported[2] value of 3.795 A.

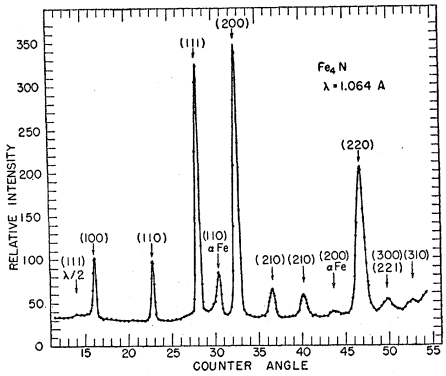

FIG. 1. Preliminary neutron diffraction pattern for Fe_4N. $\lambda = 1.064$ A.

[6] C. Zener, Phys. Rev. **85**, 324 (1952).

After grinding to 300 mesh, approximately 50 grams of sample were available for neutron diffraction measurements. A cylindrical fused-silica sample holder was used in the collection of all diffraction data except those recorded during the magnetic field studies. For the magnetic studies, in which diffracted intensities were compared with and without a saturation field parallel to the scattering vector, the sample was contained in a rectangular holder with thin vanadium windows on the transmission faces.

A preliminary diffraction pattern and all of the magnetic field data were observed on the double-crystal spectrometer of Corliss and Hastings at a mean neutron wavelength of 1.064 A. Additional data were collected using high-resolution slits on the double-crystal spectrometer of Nathans at a mean neutron wavelength of 1.040 A. These patterns are shown in Figs. 1 and 2. For the final set of intensities the 1.064 A data were adjusted to 1.040 A and averaged in with the observations made at that wavelength. The details of the magnetic field data will be discussed in the next section.

Two possible sources of error appear in the diffraction patterns. The most noticeable occurs in the case of α-Fe contamination. Using the resolved (110) and (200) peaks to establish scale, overlapping peaks at higher angles were subtracted out by calculation. The second case arises from background "swells" due to the sample holder. Here a separate fused-silica pattern was used to estimate the proper background. Any error resulting from these procedures should be quite small.

From measurements of the effective absorption coefficient it was found that the absorption factor would vary less than 2% over the entire angular range of observation. Absorption corrections were therefore neglected. The observed intensities were corrected for half-wavelength contamination, however. These corrections were quite small in most cases, but approached as much as 6% for some of the weaker peaks. The half-wavelength component of the primary beam was determined directly by measuring the intensities of the (410) reflection from a Rochelle salt single crystal at the λ and $\lambda/2$ positions.

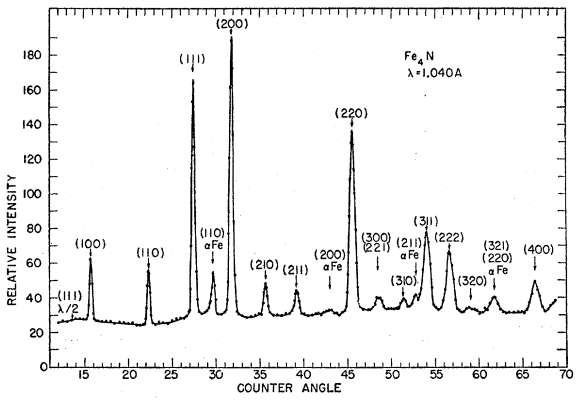

FIG. 2. Neutron diffraction pattern for Fe_4N at $\lambda=1.040$ A.

TABLE III. Magnetic structure factors for trial models (in units of 10^{-12} cm).

	Wiener-Berger	Zener	Equal moments
Indices all even or all odd	$-2.207f$	$-2.207f$	$-2.207f$
Mixed even and odd	$-0.245f$	$1.717f$	0

ANALYSIS

Before collecting diffraction data, preliminary intensity calculations had been made for the three magnetic structure models discussed earlier. The nuclear neutron scattering lengths used in these and subsequent calculations were taken from the compilation of Shull and Wollan,[7] and had the following values:

$$b_{Fe}=0.96\times10^{-12}\text{ cm},\quad b_N=0.94\times10^{-12}\text{ cm}.$$

In computing the magnetic contributions to the intensities, the assumed moments for the various models were reduced to room temperature values using $\sigma/\sigma_0=0.91$ from the magnetization data of Guillaud and Creveaux.[1] The magnetic form factor used was that measured recently by Nathans and Shull[8] in polarized beam experiments on metallic iron. This seemed a logical choice since the average number of magnetic electrons for Fe_4N is the same as that for α-Fe.

The nuclear structure factors take the following forms:

(1) $F_{nuc}=4b_{Fe}+b_N$ for h, k, and l indices all even.
(2) $F_{nuc}=4b_{Fe}-b_N$ for all indices all odd.
(3) $F_{nuc}=b_N$ for one even index and two odd.
(4) $F_{nuc}=-b_N$ for one odd index and two even.

The magnetic structure factors are given in Table III for the three trial models. The symbol f represents the magnetic form factor.

Intensities were calculated by using the standard formula for a cylindrical sample,

$$I_c=\left(\frac{Kj}{\sin\theta\sin2\theta}\right)(F_{nuc}^2+q^2F_{mag}^2)\exp\left(-2B\frac{\sin^2\theta}{\lambda^2}\right),$$

where K is the instrument constant, j is the crystallographic multiplicity, B is the Debye-Waller temperature parameter, and q^2 is the average value of the square of the magnetic interaction vector (equal to $\frac{2}{3}$ in the present case).

Upon obtaining the preliminary diffraction data at 1.064 A it was immediately evident that the Zener model could not be correct, but fairly good agreement was found for both of the other trial structures. This can be seen in Table IV. The observed data were scaled by using the (111), (200), and (220) planes, since these yield the same intensities for all three models. The

[7] C. G. Shull and E. O. Wollan, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2.
[8] R. Nathans and C. G. Shull (unpublished data, 1957).

TABLE IV. Comparison of preliminary intensity data for the trial models ($\lambda=1.064$ A).

hkl	Wiener-Berger	Zener	Equal moments	I_{obs}
100	138	343	134	139
110	136	292	132	130
111	646	646	646	660
200	880	880	880	868
210	104	164	103	112
211	86	125	85	101
220	826	826	826	824
{300} {221}	70	85	69	82

Debye-Waller parameter was $B/\lambda^2=0.50$, so that the exponential factor had the convenient form $\exp(-\sin^2\theta)$.

In order to test the equal moments model, magnetic field studies were then conducted on the (100) peak. The (111) peak was also examined in order to check for magnetic saturation of the sample. The (100) measurements were made by setting the counter at the top of the peak and alternating field-on and field-off observations at equal time intervals. The field direction was reversed at each successive field-on measurement. Back ground was measured on both sides of the peak with field on and off for a combined observation time equal to that of each of the peak measurements. The following results were obtained

(1) Field off, peak+background: 58 960 counts.
(2) Field on, peak+background: 58 003 counts.
(3) Background: 26 886 counts.

The (1) and (2) percent change is 1.6 ± 0.4, and thus the case of equal moments must be ruled out. For the change in the actual peak intensity one must subtract out the background. One finds that this change is $3.0\pm0.9\%$. In the case of the (111) peak, the measured change was $13.9\pm2.4\%$, as compared to a calculated 14.1%.

The magnetic contribution to the (100) intensity arises from the difference in the corner and face-center moments. Since the sum of the moments (over the complete cell) is known from the published magnetic data, and also can be derived from the (111) peak, it is possible to solve for the individual moments. From the observed (100) intensity change of 3% the calculated moments are $\mu_c=2.98\ \mu_B$ and $\mu_{fc}=2.01\ \mu_B$ for the corner and face-center sites, respectively. These results agree very well with the values $3\ \mu_B$ and $2\ \mu_B$ assumed by Wiener and Berger. Even at the probable error limits the agreement is also quite good. At the lower limit one obtains $\mu_c=2.86\ \mu_B$ and $\mu_{fc}=2.05\ \mu_B$, and at the upper limit $\mu_c=3.09\ \mu_B$ and $\mu_{fc}=1.97\ \mu_B$.

Taking the Wiener-Berger model as the proper magnetic structure, intensity calculations were made for comparison with the final set of observed intensities. The optimum values for the scale factor and the crystal

TABLE V. Comparison of final intensity data ($\lambda=1.040$ A).

hkl	I_{calc}	I_{obs}
100	145	141
110	144	134
111	691	707
200	948	945
210	113	119
211	94	107
220	917	907
{300} {221}	78	86
310	56	60
311	493	480
222	402	403
320	43	42
321	80	87
400	226	212

Debye-Waller parameter were determined by the usual procedure of plotting $\ln(I_{obs}/I_{calc})$ against $\sin^2\theta$. The Debye-Waller parameter so obtained was 0.345×10^{-16} cm^2. The observed and calculated intensities are compared in Table V.

DISCUSSION OF RESULTS

While the spin system proposed for Fe_4N by Wiener and Berger has been confirmed in the present study, it should be pointed out that their complete model cannot be verified by neutrons alone. The electron configurations shown in Table I can be checked only to the extent of determining the number of unpaired d electrons at the two different Fe sites. The remarkable results reported recently by Weiss and DeMarco[9] for α-Fe suggest that a general re-examination of earlier views on atomic $3d$ states may be in order. The unexpected results of these authors were confined to the body-centered metals (Fe and Cr) among those examined, but it is not clear what one might expect to find in alloys and interstitial structures. This may prove to be particularly interesting in the case of Fe_4N, since the neutron results can be interpreted only in terms of a direct bonding interaction between between N and the face-center Fe's. As Wiener and Berger suggest, the bonding can be either ionic or covalent, although the covalent interaction would seem to be more reasonable. In the latter case the bond would be formed using p electrons from nitrogen and d electrons from the face-center Fe's.

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[9] R. J. Weiss and J. J. DeMarco, Revs. Modern Phys. **30**, 59 (1958).