

Neutron Diffraction Determination of Antiferromagnetism in Face-Centered Cubic (γ) Iron

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Microcrystalline particles of γ iron of nearly identical orientation in a single-crystal copper matrix give a neutron diffraction pattern, in the liquid helium temperature range, consistent with the development of antiferromagnetism. The spin structure resembles that of γ manganese, but with the spin vectors inclined at about 19° from the normal to the ferromagnetic sheets. The spin directions in alternate sheets are antiparallel. The moment per iron atom is about $0.7 \mu_B$ and the Néel temperature, estimated from the Brillouin function temperature dependence of the magnetic intensities, is about 8°K .

INTRODUCTION

INVESTIGATION of the magnetic properties of face-centered cubic (γ) iron has been hampered by the temperature range in which it is normally stable and by the inability to retain this phase by quenching without large additions of alloying elements. There has been evidence for antiferromagnetism in some of the alloys, for example, stainless steel,¹ but a definitive knowledge of the magnetic state of pure γ iron has been lacking. Recently, it has been found possible to retain γ iron in the form of small particles that precipitate from solid solution in copper at 700°C and lower temperatures.² Unless cold-worked, these particles do not transform to α iron at a measurable rate at temperatures from 300°K to as low as 1.43°K . It occurred to one of us (L. G.) that such specimens were satisfactory for an investigation of the magnetic structure by neutron diffraction. Such a study, made at room temperature and at 77°K by L. G. and J. S. K., gave no evidence of an ordered magnetic state at those temperatures. The subsequent investigations at lower temperatures by S. C. A. show that the atomic magnetic moments become antiferromagnetically ordered below about 8°K .

EXPERIMENTAL

Two samples of copper-iron alloys were prepared. Sample 1 was a cylinder 0.50 cm diam and 0.64 cm long, machined from a large grain found in a slowly solidified casting; it contained 2.8 atom percent iron. Sample 2 was a cylinder 0.66 cm diam and 1.00 cm long, machined from a grain grown at a temperature just below the melting point of the alloy; it contained 3.3 atom percent iron. The total iron content was de-

termined in both cases by chemical analysis. In both samples, $[110]$ lay along the cylinder axis. Both samples were annealed in argon for 24 hours at 1050°C , rapidly cooled to room temperature, and then annealed at 700°C for 48 hours. With this heat treatment, the iron was primarily present as equidimensional particles about 1 micron in diameter, having the same orientation as the parent copper crystal matrix. In effect, the γ iron, although polycrystalline, was a dispersed single crystal with respect to its diffraction properties. The lattice constants of copper ($a=3.616 \text{ \AA}$) and gamma iron ($a=3.588 \text{ \AA}$)² at room temperature are sufficiently similar for coincidence of the x-ray diffraction peaks, except in the back-reflection region. At room temperature, the neutron diffraction pattern is simply that of the copper nuclear scattering of 1.032 \AA neutrons, except for the weak nuclear scattering of $\lambda/2$ and $\lambda/3$ components in the incident beam. These components were completely removed in the single-crystal work by the use of plutonium (for $\lambda/2$) and iridium (for $\lambda/3$) filters for sample 2, and a plutonium filter alone for sample 1.

A preliminary neutron diffraction examination was made of sample 1 mounted on a goniometer in air, at room temperature, and at 78°K by allowing a slow stream of liquid nitrogen to flow directly on to it. The patterns obtained at these temperatures did not differ significantly from that given by pure copper.

The measurements at liquid-helium temperatures made on the two single crystals used the goniometer-mounted cryostat,³ and the single-crystal automatic neutron diffractometer⁴ previously described. With both single crystals, the $[110]$ axis was accurately aligned parallel with the rotation axis, allowing measurement of reflections of the type (hhl) . The intensities of the reciprocal lattice points were recorded at 0.05° intervals over a range of several degrees of Bragg angle on each side of these points, along central lattice directions. In addition to the nuclear reflections, all possible

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¹ E. I. Kondorskii and V. L. Sedov, Soviet Phys.—JETP **8**, 1104 (1959).

² J. B. Newkirk, Trans. Am. Inst. Mining, Met. Petrol. Engrs. **209**, 1214 (1957).

³ S. C. Abrahams, Rev. Sci. Instr. **31**, 174 (1960).

⁴ E. Prince and S. C. Abrahams, Rev. Sci. Instr. **30**, 581 (1959).

TABLE I. Temperature dependence of the (110) structure amplitude (sample 1).

Temperature (°K)	$F^2(110)^a$ (10^{-26} cm ² /unit cell)	$F^2(001)$ (10^{-26} cm ² /unit cell)	Averaged $F^2(\text{nuclear})^b$ (10^{-24} cm ² /unit cell)
1.43	0.26 ± 0.05	...	
4.21	0.38 ± 0.04	$<0.06 \pm 0.03$	9.144
4.63	0.22 ± 0.05	...	

^a After subtraction of the zirconium-titanium sample holder scattering.^b Based on the composition Fe_{0.928}Cu_{0.972}.

magnetic superlattice reflections in the (hhl) zone were examined.

With sample 1 at 4.2°K, one additional peak at (110) was found. In particular, no intensity significantly greater than background was found at $(\frac{1}{2}00)$, $(\frac{1}{2}\frac{1}{2}0)$, $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, (100), or (112). The intensity of (110) appeared strongly temperature dependent, as shown in Table I. The precision of these structure amplitudes was low, in part because the small sample (about 20 mg Fe) gave very low counting rates, and in part because of a temperature-independent component in the intensity at (110). It was later discovered that this component was caused by nuclear scattering from the zirconium-titanium sample holder.

With sample 2, an initial exhaustive survey of the (hhl) layer at room temperature showed no signs of any reflections at reciprocal lattice points forbidden by the copper nuclear scattering. The scattering previously observed from the sample holder was eliminated by modifying this assembly. At 4.2°K, all equivalent forms of the 13 independent nuclear reflections with $\sin(\theta)/\lambda \leq 0.8$ in the (hhl) layer were measured, to provide an absolute scale. A smooth increase in structure factor with increasing $\sin(\theta)/\lambda$ was observed, indicating the presence of extinction in the larger spacing planes. The structure factors reached a steady value at $\sin(\theta)/\lambda \geq 0.63$, above which extinction was regarded as negligible. Absorption is also negligible, with $\mu R = 0.06$.

In addition to the nuclear reflections at 4.2°K, (001) and (110) were also clearly observed in sample 2. To check the possibility that these reflections might be caused by simultaneous or "unweganregung" reflection, the complete cryostat assembly was rotated $\pm 15^\circ$ about the (001) and (110) scattering vectors. The intensities of these reflections were unaffected by these rotations, thus eliminating this possibility. The temperature of the helium reservoir, and hence the sample,

TABLE II. Temperature dependence of the (001) and (110) structure amplitudes (sample 2).

Temperature (°K)	$F^2(110)$ (10^{-26} cm ² /unit cell)	$F^2(001)$ (10^{-26} cm ² /unit cell)	Averaged $F^2(\text{nuclear})^a$ (10^{-24} cm ² /unit cell)
1.43	0.276 ± 0.021	0.044 ± 0.008	
4.21	0.254 ± 0.023	0.041 ± 0.010	9.169
4.63	0.252 ± 0.022	0.039 ± 0.010	

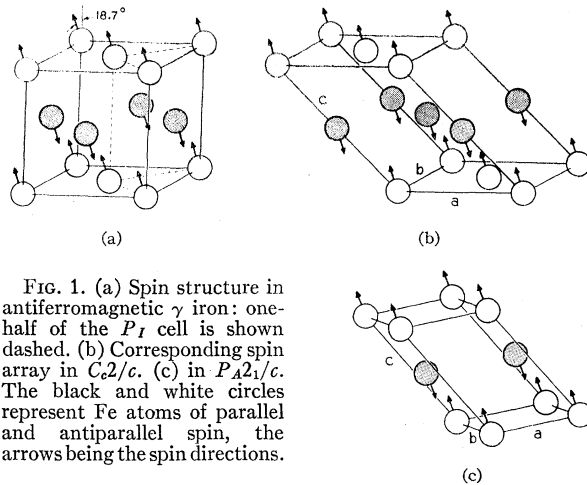
^a Based on the composition Fe_{0.928}Cu_{0.972}.

FIG. 1. (a) Spin structure in antiferromagnetic γ iron: one-half of the P_1 cell is shown dashed. (b) Corresponding spin array in C_{c2}/c . (c) in P_{A21}/c . The black and white circles represent Fe atoms of parallel and antiparallel spin, the arrows being the spin directions.

was varied by changing the pressure to 2.5 mm (corresponding to 1.43°K) and to 1115 mm (4.63°K). The intensities of (001) and (110) at the three temperatures of this experiment are given in Table II, on an absolute scale.

THE MAGNETIC STRUCTURE

The absence of fractional order reflections in the liquid-helium temperature diffraction patterns indicates no integral change in the unit cell dimensions. The F^2 values in Table I suggest an antiferromagnetic structure of the γ -manganese type,⁵ in which the magnetic moments of atoms in alternate (001) planes are parallel or antiparallel to $[001]$. The more reliable F^2 values from sample 2 (Table II) show a small but clear contribution from (001), however, It may be observed that the amplitude of $F^2(001)$ in Table II is consistent with our inability to observe it from sample 1; the larger crystal, and an improvement in technique, led to increased sensitivity. The simplest model is a variant of the γ -manganese structure, in which the spin vectors are inclined to a former cube axis, normal to the ferromagnetic sheets. Figure 1(a) illustrates this structure.

The structure amplitudes in Tables I and II were measured without use of an external magnetic field. It must therefore be assumed, by virtue of the original cubic symmetry, that the normal to a ferromagnetic sheet has an equal chance of coinciding with any of the original cube axes. The structure factor expressions for (001) and (110), averaged over the three distinct sets of domains, have the form $F^2(001) = (4p_{001})^2/3$ and $F^2(110) = (4p_{110})^2/3$; p is the magnetic scattering amplitude with value $0.539 \times S \times f \times 10^{-12}$ cm, where S is the spin quantum number and f is the magnetic form factor.

Under the same assumptions, the magnitude of the magnetic interaction vector, g , for the (001) reflection

⁵ G. E. Bacon, I. W. Dunmur, J. H. Smith, and R. Street, Proc. Roy. Soc. (London) A241, 223 (1957); D. Meneghetti and S. S. Sidhu, Phys. Rev. 105, 130 (1957).

is given by $q^2 = \sin^2 \alpha$ and for the (110) reflection by $q^2 = 1 - \frac{1}{2} \sin^2 \alpha$, where α is the angle between the spin vector and [001]. The result for (110) is obtained assuming equal contributions to the observed intensity from (110) and (1 $\bar{1}$ 0), and is independent of the azimuth of the spin vector in the (001) plane. The angle α may now be evaluated, from the structure amplitudes in Table II, as about 19°. To specify the azimuthal angle experimentally would require measurement of the intensities of reflections with $h \neq k$. The rapid decrease of the magnetic form factor with increasing Bragg angle makes this difficult. With the present experimental information, there is no independent check on the single spin-axis structure⁶ shown in Fig. 1(a). The absence of fine structure in the magnetic reflections does seem to exclude the possibility of spiral arrangements with periods less than a few times the cubic cell edge.

THE MAGNETIC SYMMETRY

It is possible to establish some restrictions on the azimuth of the spin-vector orientations in Fig. 1(a) by a consideration of the magnetic symmetry of this spin collection, under certain assumptions. These are (1) that the symmetry relates to single spin-axis structures only (multispin axes are excluded) and (2) that the highest possible point symmetry of the spin sites is used. The presence of $F^2(001)$ and $F^2(110)$, forbidden by the nuclear space group $Fm\bar{3}m$, can be accounted for only by a change from the single-colored F -Bravais lattice to a black and white lattice. The standard chromatic lattice representation⁷ P_I is obtained by rotating a pair of cube axes through 45° in their own plane, as shown by dotted lines in Fig. 1(a). The maximum lattice symmetry of this array is monoclinic, since the spins (which may be regarded as possessing the symmetry of rotating cylinders) lie neither normal to the ferromagnetic sheets, nor in the sheets; the maximum point symmetry is $2'/m'$. There are no P_I lattices in the monoclinic system, so that a new choice of unit cell orientation is required. Two equivalent choices are shown in Fig. 1(b) and (c). Within C_{2h} , Fig. 1(b) corresponds to C_c2/c : the chromatic centering halfway along the monoclinic c edge also gives rise to the necessary chromatic two-fold axes and mirror planes. In C_c2/c , $a_{\text{monoclinic}} = b_{\text{monoclinic}} = a_{\text{cubic}}$, $c_{\text{monoclinic}} = \sqrt{2} a_{\text{cubic}}$ and $\beta = 135^\circ$. The spins are here required to lie precisely parallel to the monoclinic ac plane (normal to a former cube axis lying in the ferromagnetic sheet). Figure 1(c) corresponds to $PA2_1/c$: again the necessary chromatic symmetry elements for $2'/m'$ point symmetry are generated by the chromatic A -face centering. Now the spins are required to lie normal to a former [110] in the

ferromagnetic sheets. In $PA2_1/c$, $a_{\text{monoclinic}} = b_{\text{monoclinic}} = a_{\text{cubic}}/\sqrt{2}$, $c_{\text{monoclinic}} = (\frac{3}{2})^{\frac{1}{2}} a_{\text{cubic}}$ and $\beta = 144^\circ 44'$.

The magnetic symmetry, under the initial assumptions, thus restricts the spin vectors either to a plane parallel with a former cubic (100) or to a former cubic (110).

NÉEL POINT AND MOMENT OF THE IRON ATOMS

The temperature dependence of $F^2(110)$ and $F^2(001)$ (see Table II) closely follows a Brillouin curve for $S = \frac{1}{2}$, with $T_N = 8^\circ\text{K}$. The predicted values of F_T^2/F_0^2 for $T = 1.43, 4.21, 4.63^\circ\text{K}$ are 1.00, 0.945, 0.915. The erratic temperature dependence of $F^2(110)$ in Table I made estimation of T_N very uncertain for sample 1.

Taking the absolute values of $F^2(110)$ and $F^2(001)$ at 1.43°K as equivalent to the corresponding values at a temperature of 0°K , and with the spin structure given in Fig. 1, the magnitude of the moment per iron atom can be evaluated. The coherent scattering length of Cu is taken as 0.75×10^{-12} cm, of Fe as 0.96×10^{-12} cm, the magnetic form factor⁸ for the (001) reflection as 0.84 and for (110) as 0.70. It is assumed, for both samples, that the 0.3%⁹ of iron dissolved in the Cu matrix at 700°C remains in solution (as a purely paramagnetic contribution). In sample 2, some iron was also present in the ferromagnetic α form. This amount was estimated from the magnetic susceptibility¹⁰ as about 0.02%.

The moment can now be evaluated, based on an angle of 19° between the spin vectors and the normal to the ferromagnetic sheets. For sample 1, the moment is $(0.74 \pm 0.08)\mu_B$ and for Sample 2 it is $(0.72 \pm 0.04)\mu_B$. These errors assume a total composition error of 3%, a 20% error in the total intensity for sample 1 and a 10% intensity error for sample 2. These moment values are lower limits, since no antiferromagnetic scattering would come from any unoriented γ iron or from iron still in solid solution as a result of incomplete attainment of equilibrium.

DISCUSSION

The Néel temperature of 8°K is appreciably lower than that of stainless steel¹ (40°K), and far less than is suggested by the temperature variation of the magnetic susceptibility of γ iron in its normally stable range.¹¹ Although the γ -iron precipitate is probably saturated with copper, this amounts to only 1 atom percent at the annealing temperature¹² and would

⁸ R. Nathans, C. G. Shull, G. Shirane, and A. Andresen, *J. Phys. Chem. Solids* **10**, 138 (1959); R. J. Weiss and A. J. Freeman, *ibid.* **10**, 147 (1959).

⁹ M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).

¹⁰ H. J. Williams and R. C. Sherwood (unpublished results, (1962)).

¹¹ W. Sucksmith and R. R. Pearce, *Proc. Roy. Soc. (London)* **A167**, 189 (1938); E. Schiel, E. Wachtel and A. Kalkuhl, *Ann. Physik* **4**, 58 (1959).

¹² W. Oelsen, *Stahl u. Eisen* **69**, 468 (1949).

⁶ Quite simple multi-axis spin structures could account for the experimental data equally well.

⁷ N. V. Belov, N. N. Neronova and T. S. Smirnova, *Soviet Phys.—Cryst.* **2**, 311 (1957).

affect the magnetic properties very little compared to the large amounts of nickel and chromium in stainless steel. The iron particles in the present experiment have lattice constants that are reasonable for bulk γ iron and hence are probably negligibly strained.

Magnetic susceptibility measurements¹⁰ on both samples indicate a gentle maximum at about 5°K. Extrapolation from the paramagnetic range for both samples to a zero value for $1/\chi$ gave Curie-Weiss constants of -8 to -13°K . The magnetic moment and Néel temperature given in the present investigation are thus regarded as quite close to the properties of pure

γ iron. No explanation is offered at present for the tilted spins.

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K X-Ray Fluorescence Yield of Argon*

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Reported values of the K x-ray fluorescence yield of argon lie in two distinct groups, viz., low values (about 0.07) and high values (about 0.13). A new measurement herein reported gives 0.14 ± 0.014 . This measurement was made from the "escape peak" in the pulse-height distribution of a flow proportional counter with monochromatic x rays. An Fe^{55} radio-isotope was used as the source of primary x rays. Corrections were made for the L and M ionizations in the argon gas, for the reabsorption of the K fluorescent x rays, and for background counts.

I. INTRODUCTION

THE method of measuring the K x-ray fluorescence yield of argon by analysis of the pulse-height distribution (PHD) of a proportional counter has been previously described,¹ and several such measurements²⁻⁵ have been carried out in the last ten or so years. However, these measurements are not satisfactorily consistent—they vary from 0.06 to 0.13. With the exception of the values given by Heintze,⁴ Locher,⁶ and Parratt,⁷ all of the published experimental K yields of argon, regardless of the experimental methods, lie in what may be called a group of low values,⁸ clustering around 0.07.

The exceptions cited are in a group of high values—around 0.13.

The theoretical values are likewise divided into two groups. In the theory of atomic fluorescence, developed by Wentzel,⁹ the application of a simple wave function gave a value of 0.07 for the K fluorescence yield of argon.¹ Rubenstein,^{10,11} using the Hartree wave function, obtained a value of 0.13. Dexter and Beeman,¹² using an experimental value¹³ for the lifetime of the K hole in argon, obtained 0.123.¹⁴ In the Dexter-Beeman calculations, Fock wave functions were used to evaluate the radiative transition probabilities. The latest calculation of the fluorescence yield by Callan¹⁵ gave 0.125, in which the screened hydrogenic wave function was used.

In the experimental determination of the K yield by the proportional counter method, corrections must be made for the L and M ionization by the primary x rays,

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¹ E. H. S. Burhop, *The Auger Effect and Other Radiationless Transitions* (Cambridge University Press, New York, 1952).

² S. C. Curran, J. Angus, and A. L. Cockroft, *Phil. Mag.* **40**, 36 (1949).

³ G. Bertolini, A. Bisi, and L. Zappa, *Nuovo cimento* **10**, 1424 (1953).

⁴ J. Heintze, *Z. Physik* **143**, 153 (1955).

⁵ G. R. Harrison, R. C. Crawford, and J. I. Hopkins, *Phys. Rev.* **100**, 841 (1955).

⁶ G. L. Locher, *Phys. Rev.* **40**, 484 (1932).

⁷ L. G. Parratt, *Rev. Mod. Phys.* **31**, 616 (1959).

⁸ For example, see also C. D. Broyles, D. A. Thomas, and S. K. Haynes, *Phys. Rev.* **89**, 715 (1953); D. West, *Progress in Nuclear Physics* (Butterworths-Springer, London, 1953), Vol. 3, p. 18; and S. C. Curran, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. XLV, pp. 174–221.

⁹ G. Wentzel, *Z. Physik* **43**, 524 (1927).

¹⁰ R. A. Rubenstein and J. N. Snyder, *Phys. Rev.* **97**, 1653 (1955).

¹¹ R. A. Rubenstein and J. N. Snyder, *Phys. Rev.* **99**, 189 (1955).

¹² D. L. Dexter and W. W. Beeman, *Phys. Rev.* **81**, 456 (1951).

¹³ L. G. Parratt, *Phys. Rev.* **56**, 295 (1939).

¹⁴ The width of the argon K state reported by Parratt as 0.58 eV in 1939 (reference 13) was later restated by Parratt in 1959 as 0.5 ± 0.05 eV (reference 7). Had Dexter and Beeman (reference 12) used the later value they would have reported 0.14 for the argon K fluorescence yield.

¹⁵ By private communication; see also E. J. Callan, *Phys. Rev.* **124**, 793 (1961).