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Atomic Magnetic Moments in B2 Transition Alloys

I. Alloy VFe*

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The atomic moments in ordered VFe alloy, have been determined approximately by neutron diffraction. The alloy contained 46.7 atomic % Fe by analysis. After homogenization at 1250°C and quenching, it was annealed at 600°C for 6 hours and was found to be about 77% ordered. The spins of the Fe and V sites were found to be respectively $0.305\pm.040$ and $0.070\pm.040$ based on the Freeman and Watson neutral-atom spherical $3d$ form factors. These correspond to about 0.36 for each Fe atom, and 0.035 for each V, in a completely ordered 1:1 alloy. Indications were obtained from X-ray measurements that there is some electron transfer from Fe to V; taking this into account would result in slightly smaller values of the Fe spin. Further work on VFe at 85% ordering is in progress. A powder spectrum of TiFe at room temperature showed no magnetic effects.

Introduction

A neutron diffraction study of transition metal alloys with the B2 (CsCl) arrangement was undertaken in order to obtain information relevant to the electronic structure of these metals and alloys.

Beck and coworkers[1] have obtained the ordered B2 structure in several transition alloys, including VFe, TiFe, TiCo, and TiNi. Lattice contractions (relative to elemental radius sums), together with the magnetic properties, were taken to indicate a significant degree of electron transfer[2]. VFe is ferromagnetic while the Ti alloys are apparently not. Nevitt[3] found for ordered VFe (1 : 1) a saturation moment of about 0.82 Bohr magnetons per unit cell, while that for TiFe (1 : 1) was found to be at most very small and probably zero. It is possible to postulate electron configurations on the basis of some model such as that of Pauling[4], which will give agreement with these magnetic data, with electron transfer in either direction. If electron transfer is from Fe to V it is of interest to determine whether any moment exists on the vanadium atom. However, electron transfer to Ti from Co or Ni (either of which could easily have zero moment in a model having no electron transfer, due to filling of magnetic levels from valence levels) would be expected to produce ferromagnetism unless the electron transfer is very small, or unless perhaps the alloys should happen to be antiferromagnetic. Electron transfer from Fe to Ti would have to be rather considerable to reduce the Fe moment to zero. We intend very soon to investigate the possibility of antiferromagnetism in TiFe and TiCo; room temperature neutron powder work on TiFe shows no evidence of magnetism of any kind.

The experiments reported here are primarily concerned with atomic moments in VFe, investigated by the method of Shull and Wilkinson[5]. In addition, as an aid to the determination of the direction of electron transfer, quantitative X-ray measurements were carried out with VFe.

Neutron work on VFe

Our principal work on VFe was performed with a rectangular block (2.7×2.0×0.7 cm) cut from a button prepared in an argon arc furnace. Chemical analysis gave the composition as 46.7 atomic percent Fe. After four days of annealing in argon at 1250°—1300°C the button was quenched in cold water, and in this state was found to be ferromagnetic with a Curie temperature well above room temperature. It was annealed at 600°C for 6 hours in order to obtain the ordered structure. This resulted in a fall of

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the Curie temperature to a value between 0° and 25°C. (Nevitt reports about 280°K[3].)

The ordering parameter, expressed as a percentage, may be written

$$100\frac{(x-x_d)}{(x_o-x_d)}$$

where x represents the mole fraction of Fe or V at any given site and x_d and x_o represent the values for maximum disorder and maximum order respectively. For the VFe sample the ordering parameter was determined by neutron diffraction above the Curie temperature, using both powder and single crystal methods. For the powder work the block was rotated to reduce graininess due to the large crystallite size, but considerable scatter was nevertheless obtained. With the intensities for $(h+k+l)=2n$ scaled to the calculated values, those for $(h+k+l)=2n+1$ averaged 0.68 of calculated values for 100 percent ordering; taking the square root of this fraction as the ordering parameter we obtain 82±5 percent. Much more self-consistent results were obtained with a single crystal (about 1.2 mm in size) broken from the block; the data are given in Table I.

Table I. Single Crystal Intensities at Room Temperature

hkl	$I^{\text{obs}*}_{\text{corr}}$	
100	1416	
110		1849
200		1953
210	1340	
220		1879
300	1336	
Mean	1364	1887

*Corrected for background and for Lorentz and temperature factors; $B=0.453\times10^{-16}\,\text{cm}^{-2}$.

The ordering parameter obtained is 76.0 ±1.0 per cent. A weighted mean of 77.0 per cent was assumed in later calculations. With this value the site compositions are:

Site 1: 82.7 atomic %Fe, 17.3 atomic %V

Site 2: 10.7 atomic %Fe, 89.3 atomic %V

Rough values of the atomic moments were obtained from powder measurements made with unpolarized neutrons at 77°K. An electromagnet operating at 4300 gauss was found to be sufficient to saturate the specimen, and was positioned with its field parallel to the scattering vector in order to permit measurements in the absence of magnetic contributions to scattering. Measurements on (100) and (110), interpreted with $3d$ form factors of Watson and Freeman[6] gave for the spins at the two sites

$$S_{\text{Fe}}=+0.59\pm.08$$

$$S_{\text{V}}=-0.05\pm.10$$

on the arbitrary assumption that the larger spin is on the Fe.

Table II. Polarized Neutron Measurements

Reflection	Specimen	No. of meas.	Avg. bkgnd.	$I^{a)}$ off	$I^{a)}$ on	F.R.$^{b)}$	$\left(\frac{b+p}{b-p}\right)$
100	*xtl* 1	15	93	96	62	1.55	1.25
	xtl 2	1$^{c)}$	2354	2784	1453	1.91	1.38
	block	11	49	735	403	1.82	1.35
	block	14	48	1122	633	1.77	1.32
Weighted mean							1.325 ±0.040
110	block	8	47	433	252	1.72	1.31
	block	8	51	792	451	1.76	1.33
	block	8	51	716	404	1.77	1.32
Weighted mean							1.320 ±0.020

a) Average peak height above background, with radiofrequency *on* (to reverse spin) and *off*.

b) F. R. = "flipping ratio" $=I_{\text{off}}/I_{\text{on}}=[(b+p)/(b-p)]^2$.

c) General scan: intensity values are summed over peak; background given is an average value times the peak width.

Better values which required no assumption of this kind were obtained with the polarized beam spectrometer (S3, Professor C.G. Shull, M.I.T.). Again (100) and (110) were studied at 77°K, with the neutron spin parallel and antiparallel to the field. Most measurements were made with the polycrystalline block in various orientations; however some measurements were also made on the 1 mm single crystal (*xtl* 1) and a larger, less perfect on (*xtl* 2). The results are given in Table II.

Interpretation of these data with the $3d$ neutral atom form factors originally calculated by Watson and Freeman[6] give for the spin values

$$\text{Fe site } S=+0.453\pm.037$$

$$\text{V site } S=+0.054\pm.036$$

uncorrected for disorder. A later calculation was performed with $3d$ neutral atom form factors later reported by Freeman and Watson[7], calculated with $3d^{n-2}4s^2$ configuration analytic Hartree-Fock functions.

Form factors for each site were calculated from the known site compositions. The results were

$$\text{Fe site } S=0.305\pm.040$$

$$\text{V site } S=0.070\pm.040$$

If the spin of each kind of atom is assumed to be independent of the site it is in, we may calculate spin values of 0.362 for Fe, 0.035 for V (corresponding to a 100% ordered 1 : 1 alloy). The value for V is within experimental error of zero.

For the present alloy the calculated saturation moment, ignoring orbital contributions, is 0.75 μ_B, in good agreement with 0.71 μ_B interpolated from the data of Nevitt[3] for the ordered alloy at this composition; the value for the disordered alloy would be 0.85 μ_B. Our own saturation magnetization measurements, made on the block sample with no attempt to make demagnetization corrections, gave 0.56 μ_B, which was expected to be low.

X-ray work on VFe

In order to obtain an indication of electron transfer, studies were made on the alloy with X-rays. A powder sample of VFe (1 : 1) kindly furnished by Prof. P. A. Beck, which a neutron powder spectrum showed to be about 65±5 % ordered, was studied with Cr Kα radiation on an XRD-5 spectrometer. The intensity ratio for (100) and (110) planes was only 0.187 of that calculated with Freeman and Watson form factors[7] with Dauben and Templeton anomalous dispersion corrections[8]; this gives an apparent ordering parameter of 43.2%. A small single crystal (0.3 mm) from our block was examined with CrKα, and also with MoKα at low excitation to prevent the (200) white radiation streak from interfering with (100). Absorption corrections were made, and the apparent ordering parameter from the (100) and (200) reflections was 28.4 and 36.4% for Cr and Mo radiation respectively.

Any interpretation of these figures is subject to considerable uncertainty due to the uncertainties in the form factors; in addition, the anomalous dispersion corrections contribute some uncertainty, particularly with CrKα. However, it is probably significant that all three of the X-ray apparent ordering parameters were much lower than the neutron ones. This suggests strongly that if any significant amount of electron transfer takes place, it is in the direction of Fe to V rather than the reverse.

Discussion

The results of the polarized neutron work indicate that in VFe the iron has a moment of about 0.7 μ_B while the vanadium has a very small moment or more probably none at all. The magnitudes of these moments are subject to the present uncertainties in the form factors; in addition, no corrections for non-spherical spin distribution have been made. Finally, electron transfer would require $3d$ form factors for ions, such as V^-, Fe^+, to be used instead of those for the neutral atoms. Taking this into account would have the effect of reducing the iron moment, by about ten percent for one electron assumed to be transferred, and of increasing the vanadium moment slighly.

The alloy has recently been reannealed to an ordering parameter of about 85 per cent, and will be ordered even further if possible; atomic moments obtained from the reannealed specimens will be more meaningful than those given here.

Acknowledgment

Samples of VFe and TiFe were kindly made available by Professor P.A. Beck (University of Illinois) and Dr. M.V. Nevitt (Argonne National Laboratory). We are also indebted to Professor Beck for helpful discussions, and to Dr. Nevitt for advance communication of his magnetic results. An arc fusion furnace for alloy preparation was made available to us through the courtesy of Prof. N. Grant (MIT), and was operated by Mr. R. Cairn. The neutron spectrometers at the MIT reactor were made available to us by Professor C. G. Shull, to whom we are indebted for much valuable assistance and suggestions. Mr. John Mellor and Mr. Leo Feinstein assisted with some of the neutron measurements. This work was sponsored by the Office of Ordnance Research under Contract DA-19-020-ORD-4696.

Note added in proof (by D. P. Shoemaker and L. G. Feinstein): Further measurements have been made on a specimen annealed 60 hours at 625°C and estimated to be 90 percent ordered. From studies of planes (100), (110), (111), and (200), site spins of $S_1=0.350$ and $S_2=0.024$ were obtained, corresponding to $S_{\mathrm{Fe}}=0.394\pm.020$, $S_{\mathrm{V}}=0.006\pm.025$. Neutron powder diagrams of 1 : 1 TiFe and 1 : 1 TiCo at 4°K show no evidence of magnetic superstructure. We acknowledge with thanks the assistance of Dr. R. Ferrier.

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

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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

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