Magnetic-moment distribution in ferromagnetic Fe-Cr alloys*

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The magnetic-moment distribution in disordered ferromagnetic bcc Fe_3Cr has been determined by polarized-neutron diffraction. The measured magnetic structure factors, when compared with those of pure Fe obtained by Shull and co-workers and those for a Fe-Cr alloy of slightly smaller Cr content measured by Lander and Heaton, show an appreciably smaller asphericity. The composition dependence of the asphericity has been compared both with a localized-electron model and with calculations based on the coherent-potential approximation (CPA). The concentration dependences of the total spin magnetic moments, of the difference between the magnetic moments of the constituents, and of the density of states at the Fermi level are also compared with the CPA calculations. It is shown that the theory is able to reproduce the general trend of the experimental data in these alloys.

INTRODUCTION

In recent times there has been an extensive study of disordered ferromagnetic $3d$ alloys by means of polarized-neutron diffraction. Several fcc alloys have been investigated, e.g., Co-Ni,[1] Co-Fe,[2,3] Ni-Fe,[4-6] Cu-Ni,[7] and attention has been given to the detailed concentration dependence of magnetic-moment distribution, and in particular to the negative moment density and to the asphericity of the magnetic moment. As already noted[1] the concentration dependence of asphericity provides information on the behavior of the band structure of the alloy. There is also some evidence that the asphericity of electron distribution is connected with structures of crystals, thus behaving as a phase parameter which provides information on the stability of structures and their phase transitions.[8,9] It has also been shown that the coherent-potential approximation can give the concentration dependence of asphericity as described for Co-Ni[10,11] and Fe-Ni[6] alloys.

It was considered of some interest to extend these studies to bcc alloys. As far as it is known to us, only one other study of a disordered ferromagnetic bcc alloy has been performed up to now, i.e., $Fe_{0.81}Cr_{0.19}$ by Lander and Heaton.[12] That study found that the form factor was very similar to that of pure Fe,[13] which is a result quite different from that found for fcc alloys. Therefore we extended the measurements to an alloy of higher Cr content, and although the single crystal obtained had only 24 at.% Cr, our results show appreciable difference from those of pure Fe.

EXPERIMENTAL

The experiment was carried out at room temperature. The single crystal was obtained from Metals Research Ltd. and the chemical analysis gave a composition of 24 at.% Cr. Several samples were cut from the crystal with thickness ranging from 0.008 to 0.1 cm. No long-range order could be detected by neutron diffraction, though several heat treatments were attempted to establish it. Annealings at temperatures from 470 to 1250 °C followed by slow or rapid quenching did not produce changes in the magnetic properties, contrary to the findings of Dekhtyar,[14] but in agreement with Baerlecken and Fabritius.[15]

Long-range order was not found also in $Fe_{0.79}Cr_{0.21}$ by Lander and Heaton, who could, however, establish the presence of appreciable short-range order in their sample. We did not attempt to measure the short-range-order parameter in our sample. Secondary extinction and multiple scattering were found to be appreciable for all samples used in the present experiment.

However, we could obtain values of the magnetic structure factors free of extinction and multiple scattering for all reflections. In fact, for the innermost reflection (110) we measured the ratio γ of the magnetic structure factor to the nuclear structure factor for several different thickness of the samples and two different neutron wavelengths. We found that γ was increasing with decreasing wavelength and sample thickness. The samples used had thickness ranging from 0.008 to 0.05 cm and the neutron wavelengths were 0.88 and 1.03 Å. We found, by extrapolating to zero wavelength and zero sample thickness, the result that at the lowest thickness and wavelength investigated γ was still 3% lower than the extrapolated value. We assumed the extrapolated value to be free from extinction and multiple scattering. A similar extrapolation was attempted for the following reflections, but it was found that the effects of extinction were smaller than the statistical errors for the smallest thicknesses of the samples; therefore the small

residual extinction was corrected for by calculating its value from the estimated extinction on (110), taking into account the effective reflectivity for each reflection. These γ values were corrected for half-wavelength contamination, which was found to have an effective value of 0.8%. No depolarization of the neutron beam in our samples could be detected. The values of the magnetic structure factors obtained from the corrected γ ratios by using for the nuclear scattering amplitudes $b_{Fe} = 0.951 \times 10^{-12}$ and $b_{Cr} = 0.352 \times 10^{-12}$ cm are given in Table I.

The magnetic moment was measured by means of the ballistic-galvanometer method; we found $\mu_T = 1.57 \pm 0.03$ μ_B/(atom) at room temperature on the same crystal from which the samples used for the neutron diffraction experiment were obtained. This value is consistent with the measures by Fallot.[16]

DISCUSSION

The results were analyzed by least-squares fit with the theoretical magnetic form factors calculated by Watson and Freeman[17] for free ions, which should give reasonable results for the asphericity of the magnetic electron distribution. We used therefore the phenomenological model which we already used for Co-Ni, Co-Fe, and Fe-Ni alloys[1,3,6]; the orbital contribution was calculated by us following the lines of Blume's work[18] on Ni^{++} and using the wave functions obtained by Fourier inversion of the spin form factors together with the experimental g factor of pure Fe, which is 2.075. The experimental magnetic structure factors were fitted with the expression

$$F_M(hkl) = \mu_1[\langle j_0 \rangle + A_{hkl}(\tfrac{5}{2}p - 1)\langle j_4 \rangle]$$

$$+ \mu_T[(g-2)/g]f_{orb} + [\mu_T(2/g) - \mu_1]f_{neg},$$

$$(1)$$

where $F_M(hkl)$ is the magnetic structure factor per atom in units of Bohr magnetons, μ_1 is the $3d$ spin part of the magnetic moment, μ_T is the total magnetic moment, $\langle j_0 \rangle$ and $A_{hkl}\langle j_4 \rangle$ are, respectively, the spherical and aspherical $3d$-spin form factors, A_{hkl} being an angular factor given by Weiss and Freeman,[19] p is the population of the e_g sublevel (which together with the t_{2g} sublevel originate from a splitting of the d level in a cubic crystalline field), the g factor determines the fraction of orbital and spin moment, f_{orb} is the orbital form factor, and f_{neg} is the form factor relative to the negative magnetic moment which is assumed to be already negligible at the first Bragg reflection. The only free parameters in the fit are μ_1 and p.

According to diffuse neutron scattering measurements,[12,20] Cr in Fe-Cr alloys has a magnetic mo-

ment antiferromagnetically aligned to the Fe matrix. In fact, Lander and Heaton found $\mu_{Cr} = -0.46 \pm 0.11$ μ_B, $\mu_{Fe} = 2.36 \pm 0.05$ μ_B, with polarized-neutron diffuse scattering,[12] in agreement with one of the two possible values obtained by Shull and Wilkinson with unpolarized neutrons.[20] However, these values are rather doubtful since no corrections for inelastic incoherent scattering were reported by those authors, and one may expect that a substantial fraction of the incoherent scattering is inelastic; moreover, the corrections for multiple scattering with short wavelengths like those used by Lander and Heaton are rather doubtful if not experimentally substantiated. We think therefore that more accurate experiments are needed to give a precise value to the Cr magnetic moment.

We used expression (1) to fit our data, using for the form factors averages of the double-ionized form factors of Fe and Cr,[17] the averages obtained by weighing the pure-ion form factors with the individual magnetic moments. We found that the best fit could not be obtained with the magnetic moments as given by the diffuse scattering experiments,[12] but instead with a ratio of Fe and Cr magnetic moments of +1.2. This in our opinion is an indication that the pure-ion form factors are not adequate for describing the magnetic electron distribution in this alloy. This fact was also found in Fe$_{0.81}$Cr$_{0.19}$.[12]

The relevant values obtained from the fit are given in Table II, where they are compared with the values obtained by fitting with expression (1)

TABLE I. Magnetic structure factors in units of Bohr magnetons per atom at room temperature.

hkl	Fe [a]	Fe$_{0.81}$Cr$_{0.17}$ [b]	Fe$_{0.76}$Cr$_{0.24}$ [c]
000 [d]	2.177	1.664	1.57 ± 0.03
110	1.367 ± 0.011	1.045 ± 0.018	1.050 ± 0.015
200	0.880 ± 0.006	0.681 ± 0.012	0.636 ± 0.006
211	0.544 ± 0.004	0.399 ± 0.010	0.406 ± 0.009
220	0.379 ± 0.004	0.271 ± 0.007	0.277 ± 0.006
310	0.298 ± 0.004	0.221 ± 0.007	0.195 ± 0.006
222	0.135 ± 0.004	0.095 ± 0.005	0.087 ± 0.006
321	0.100 ± 0.004	0.070 ± 0.005	0.069 ± 0.004
400	0.155 ± 0.004	0.108 ± 0.005	0.086 ± 0.004
330	0.028 ± 0.004	0.023 ± 0.003	0.025 ± 0.004
411	0.081 ± 0.004	0.058 ± 0.003	0.052 ± 0.004
420	0.044 ± 0.004	0.030 ± 0.005	0.039 ± 0.006
332	−0.035 ± 0.004	−0.022 ± 0.005	−0.007 ± 0.003
422	−0.022 ± 0.004	−0.010 ± 0.005	−0.014 ± 0.006
510	0.039 ± 0.004	0.032 ± 0.005	0.015 ± 0.007
431	−0.028 ± 0.004	−0.025 ± 0.005	−0.018 ± 0.008

[a] Reference 13.
[b] Reference 12.
[c] Present work.
[d] This is the total magnetic moment obtained by bulk-magnetization measurements.

TABLE II. Contributions to the magnetic moments as obtained by a fit with expression (1) of the text to the magnetic-structure-factor data of Fe (Ref. 13), Fe$_{0.81}$Cr$_{0.19}$ (Ref. 12), and Fe$_{0.76}$Cr$_{0.24}$ (present work); μ_{e_g} is the e_g part of the spin magnetic moment, i.e., $\mu_{e_g} = \mu_1 p$.

Material	μ_T (μ_B)	μ_1 (μ_B)	μ_{neg} (μ_B)	μ_{orb} (μ_B)	p	μ_{e_g} (μ_B)	χ^2	Number of reflections included
Fe	2.177	2.288±0.014	−0.190±0.014	0.079±0.005	0.528±0.006	1.208±0.015	89	all (26)
Fe	2.177	2.287±0.014	−0.189±0.014	0.079±0.005	0.533±0.007	1.22±0.02	69	15
Fe$_{0.81}$Cr$_{0.19}$	1.664	1.743±0.024	−0.140±0.024	0.060±0.004	0.524±0.009	0.91±0.02	28	all (15)
Fe$_{0.76}$Cr$_{0.24}$	1.57±0.03	1.765±0.017	−0.252±0.026	0.057±0.004	0.479±0.010	0.85±0.02	31	all (15)

and the same free-ion form factors the experimental values for pure Fe[13] and for Fe$_{0.81}$Cr$_{0.19}$.[12] It may be noted that the values obtained by those authors using instead the $3d^{n-2}4s^2$ form factors coincide within experimental errors with those obtained by us with the Fe^{++} and Cr^{++} form factors. In the case of Fe$_{0.81}$Cr$_{0.19}$ we found, for a ratio of Fe to Cr magnetic moments of +2.2, a fit which is better than that obtained by Lander and Heaton with the magnetic moments of diffuse neutron scattering and a Cu form factor.

However, the quality of the fit was definitely worse than that obtained for fcc alloys with the same method[1,3,6]; a difference in behavior between fcc and bcc $3d$ metals has been noted in the scattering factor determinations with x rays, in which case in the reciprocal space the experimental form factors of pure bcc elements appear to be more contracted with respect to the theoretical free-atom ones, though fcc elements are in much better agreement with calculations.[9]

As discussed in Ref. 6, the negative magnetic moment of expression (1) is to be considered only as a parameter of the fit useful, at most, for comparison between different materials.

The experimental and calculated magnetic structure factors are compared in Fig. 1 for Fe$_{0.76}$Cr$_{0.24}$.

The value of the asphericity parameter p was found to be very insensitive to the choice of the form factors used in the fit, in fact its fluctuations in changing the form factors from those of Cr to that of Cu were contained within 1%, and in our opinion p is the most model-independent results obtained by the analysis of the neutron data.

In Fig. 2 the concentration dependence of the e_g population p is given for the available compositions. In Fig. 2 is given also the value obtained for pure Cr,[21] but it is doubtful whether it can be
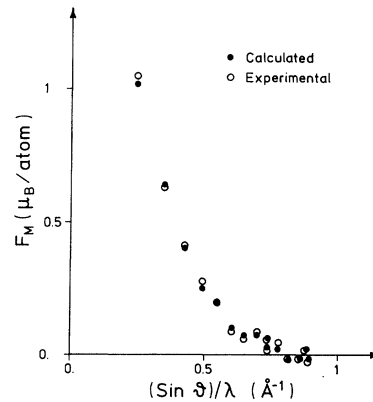

FIG. 1. Comparison of experimental (black dots) and fitted (open circles) values of magnetic structure factors for Fe$_{0.76}$Cr$_{0.24}$.

compared with the other data, Cr being antiferro-magnetic.

We tried to compare these points with the localized-electron model in which each atom is assumed to keep the same asphericity for all compositions. If the asphericities of Cr and Fe in the alloys are assumed to be those of pure metals one gets curve (1) of Fig. 2, assuming the concentration dependence of the Cr and Fe magnetic moment as obtained by Shull and Wilkinson.[20] Curve (2) is obtained as a best fit to the data of Fe and Fe-Cr alloys, assuming the same concentration dependence of Cr and Fe moments, but leaving the Cr and Fe populations as free parameters; the fit gives $p_{Fe} = 0.53 \pm 0.01$, $p_{Cr} = 1.1 \pm 0.2$. As can be seen, curve (1) is inconsistent with the data while curve (2) appears to give a fit of very poor quality. This fact may be considered to be a further indication that the localized-electron model is inadequate to describe the asphericity in the alloys, as already noted.[6,22]

A more sound theoretical interpretation of magnetic properties of $3d$ alloys has proved to be the coherent-potential approximation (CPA). Hasegawa and Kanamori[23] have calculated the concentration dependence of magnetic moments of several $3d$ alloys starting with simplified density-of-state curves for the pure elements. In the case of Fe-Cr alloys they were able to reproduce the experimental concentration dependence of the magnetic moments. In previous studies the method was extended[6,10,11] to treat the concentration dependence of asphericity in Co-Ni and Fe-Ni fcc ferromagnetic alloys, using as a starting point the detailed density of states for the e_g and t_{2g} subbands calculated by Hodges and Ehrenreich.[24] Similarly, CPA was extended also to the study of asphericity in bcc alloys, and interatomic exchange integrals were also included in order to give a more realistic de-

scription of the magnetic system; details of the method will be given in a subsequent work.[25] For Fe-Cr the densities of states for the individual e_g and t_{2g} subbands were derived from the calculations of Duff and Das[26] and Wakoh and Yamashita.[27] The coherent potential is obtained from the equations

$$\Sigma_{\sigma\mu}(z) = x\epsilon_{A\sigma\mu} + (1-x)\epsilon_{B\sigma\mu}$$
$$- [\epsilon_{A\sigma\mu} - \Sigma_{\sigma\mu}(z)] F_{\sigma\mu}(z)[\epsilon_{B\sigma\mu} - \Sigma_{\sigma\mu}(z)] ,$$
$$(2)$$

where $\Sigma_{\sigma\mu}(z)$ is the coherent potential for spin state σ and band μ (e_g or t_{2g}), z is a complex parameter corresponding to energy, x is the atomic composition, i.e., the percentage of the A constituent in the alloy (A and B refer to the constituent, in this case Fe and Cr, respectively),

$$F_{\sigma\mu}(z) = \int_{-\infty}^{\infty} \rho_\mu^{(0)}(\epsilon)[z - \Sigma_{\sigma\mu}(z) - \epsilon]^{-1} d\epsilon , \qquad (3)$$

in the same approximation as used Refs. 28 and 29 and described in Ref. 25 with $\rho_\mu^{(0)}(\epsilon)$ as the starting density of states for μ band,

$$\epsilon_{i\sigma\mu} = \epsilon_{i\mu} + U_i n_{i-\sigma\mu} + \sum_{\sigma'\mu' \neq \mu'} U_i n_{i\sigma'\mu'} - J_i \sum_{\mu \neq \mu'} n_{i\sigma\mu}$$

$$\pm Z \sum_{\mu' \neq \mu} [xJ_{i1}^N(n_{1\uparrow\mu'} - n_{1\downarrow\mu'})$$

$$+ (1-x)J_{i2}^N(n_{2\uparrow\mu'} - n_{2\downarrow\mu'})] , \qquad (4)$$

where i stands for A or B, $\epsilon_{i\mu}$ is the energy level of the band μ of i atom, U is the intratomic Coulomb interaction energy potential, J is the intratomic exchange interaction, $n_{i\sigma\mu}$ is the number of electrons of the spin state σ in the band μ for the atom i, Z is the number of nearest neighbors, J_{ij}^N is the nearest-neighbor interatomic exchange interaction, and the $-$ and $+$ signs refer to the up and down spin state energies, respectively.

By solving numerically and simultaneously the eight complex transcendental equations (2) and (3) we obtain the Σ and F functions. These functions are used to calculate the density of states of the alloy for each band σ and μ, as given by the equation

$$\rho_{i\sigma\mu}(\epsilon) = -\frac{1}{\pi} \text{Im}\left(\frac{F_{\sigma\mu}(z)}{1 - [\epsilon_{i\sigma\mu} - \Sigma_{\sigma\mu}(z)] F_{\sigma\mu}(z)}\right), \qquad (5)$$

where $z = \epsilon + i \times 0$.

These densities of states have been calculated in a self-consistent way, and were used to calculate the concentration dependence of the total spin mag-
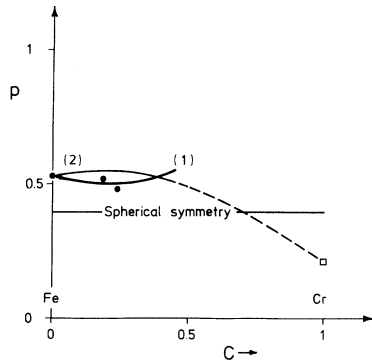

FIG. 2. Concentration dependence of the asphericity parameter, i.e., the population p of the e_g sublevel. The curves represent localized-electron model results as described in the text.
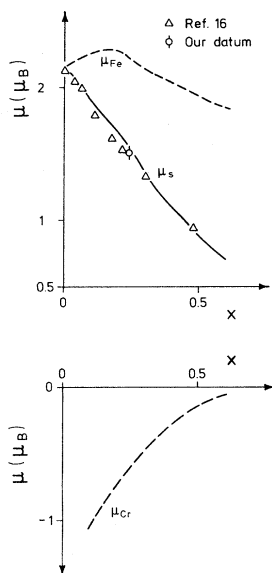
FIG. 3. Comparison of total spin magnetic moment μ_s of the alloy (that is the experimental bulk magnetic moment less the orbital contribution, assuming the same g factor of Fe for all of the compositions) with the CPA values (continuous curve). The dashed curves give the calculated magnetic moments of the constituents in the alloys.

netic moment of Fig. 3, where they are compared with the measurements of Fallot[16] and with the value of our material. In that figure is also given the concentration dependence of the constituent individual moments which have been used to obtain the difference $\mu_{Fe} - \mu_{Cr}$, which is compared in Fig. 4 with the values obtained in Ref. 20 with the implicit hypothesis that the constituent magnetic moments do not depend on the local environment. The concentration dependence of the e_g magnetic mo-

FIG. 5. Concentration dependence of the e_g magnetic moment. CPA (curve) compared with the experimental values of Table II.

ment is compared in Fig. 5 with the data for pure Fe,[13] $Fe_{0.81}Cr_{0.19}$,[12] and $Fe_{0.76}Cr_{0.24}$ of the present work.

The concentration dependence of the density of states at the Fermi level is compared with the data obtained by Chen et al.[30] in a specific-heat experiment in Fig. 6. The parameters used in the calculations are listed in Table III. The values of J_{ii}^N were derived from the spin-wave dispersion relations as determined for Fe by Mook and Nicklow[31] and for Cr by Als-Nielsen et al.[32]

As it can be seen in Fig. 3, the CPA calculations reproduce with fair accuracy the total spin magnetic moments while for the other concentration dependences shown in Figs. 4–6 the calculations account only for the general trend of the experimental data, but there appears to be an increasing discrepancy with increasing Cr content of the alloys. This may be due to the use of a too simple a model Hamiltonian[11] to describe the large itinerancy of the Cr and Fe electrons as compared with the fcc transition
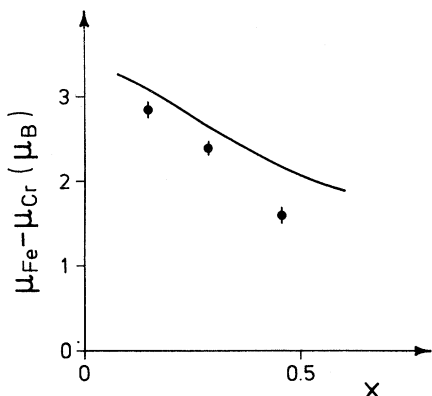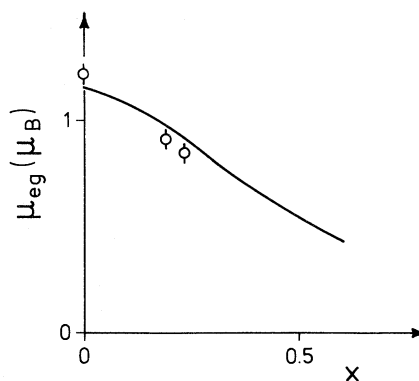

FIG. 4. Difference of the CPA-calculated spin magnetic moments in the alloy (curve) as compared with the experimental data obtained by Shull and Wilkinson (Ref. 20).
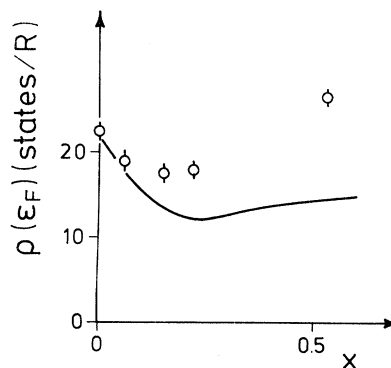

FIG. 6. Density of states at the Fermi level as obtained by CPA (curve) and by the specific-heat measures of Ref. 30. The experimental points have been normalized to the theoretical value for Fe.

TABLE III. Parameters used in the calculations of Eq. (2)−(5). Values are in Ry.

	U	J	J_{ii}^N	J_{ij}^N	ϵ_{e_g}	$\epsilon_{t_{2g}}$
Fe	0.14	0.08	0.0012	0.00	−1.19	−1.21
Cr	0.08	0.06	−0.0030	0.00	−0.73	−0.73

elements and alloys, where this model seems to work very well.[6,10,11] This is evidenced by the fact that the widths of the d bands in Fe and Cr are about twice as large as those of Co and Ni.

As a conclusion we may note that these alloys indicate that in the bcc structure, although the general behavior of the magnetic moment distribution is similar to that found in fcc alloys, it appears that there is an appreciably stronger departure from the free-atom behavior, and this should be connected with the fact that both the spin-up and spin-down bands are unfilled and that electrons further inside the bands are responsible for the magnetic properties.

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