A polarized neutron study of the magnetic form factors in CeFe₂

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Abstract. The magnetization distribution in the ferromagnetic phase of CeFe₂ at 10 K has been determined using a combination of polarized and unpolarized neutron diffraction measurements on a single crystal. The results confirm previous results on powders, and the prediction of band structure calculations, that both the Fe and Ce atoms carry a magnetic moment, and that Ce is magnetized oppositely to Fe. The value of the Fe moment deduced from the measurements is $\mu_{Fe} = 1.174(10)\,\mu_B$, somewhat smaller than that given by the theory. The value obtained for the Ce moment is strongly dependent on the assumption made about the relative numbers of unpaired 5d and 4f electrons. If the ratio of 5d/4f magnetization is taken as the value obtained in the band structure calculations (i.e. 0.75) the total Ce moment is $-0.14(3)\,\mu_B$. The magnetization distribution around the Fe atoms deviates significantly from spherical symmetry; the form of the asymmetry indicates that the electrons occupy orbitals which are a coherent mixture of E_g-like and T_{2g}-like functions.

1. Introduction

The electronic structure of Ce has been the subject of a particularly large number of experimental and theoretical investigations because the element and its compounds exhibit behaviour which sets it apart from the rest of the rare earth series. To explain some of this behaviour it has been suggested that the 4f electrons in Ce, unlike those in the other rare earths, may in some circumstances form energy bands [1–3]. These circumstances are met by the cubic CeT₂ (T = Fe, Co, Ni) Laves-phase compounds which have anomalously small lattice constants compared with the corresponding compounds of these transition metals with other rare earths. Out of this group, CeFe₂ alone is ferromagnetic having a Curie temperature of 230 K, a saturation magnetization of 2.3 μ_B per formula unit and a lattice parameter $a = 7.304$ Å [4]. The structural and magnetic properties of the pseudo-binary alloys Ce(Fe$_{1-x}$M$_x$)₂ with M = Al, Co and Ru have recently been reported [5]. The powder diffraction data suggest that in the pure compound CeFe₂, but not in the alloyed systems, the Ce atom carries a moment of $\simeq 0.3\,\mu_B$ antiferromagnetically aligned with respect to the Fe atoms. These measurements also show that the ferromagnetic alignment of the Fe moments in CeFe₂ is only just stable since 10% substitution of Co for Fe, and even less of Ru, makes the ground state antiferromagnetic.

Eriksson *et al* [6] have recently made detailed band structure calculations for the CeT₂ Laves phases which associate the small lattice constants with 3d–4f hybridization and correctly predict the minimum at CeCo₂. These authors have also made spin-polarized

calculations to obtain the spin densities and spin moments in $CeFe_2$ which is the only one of the three to order magnetically. They predict spin moments on both Fe and Ce with the Ce moment aligned oppositely to that of Fe. The calculated Fe moment (1.43 μ_B) is almost entirely of 3d character, whereas that of Ce is an almost equal mixture of 4f ($-0.4\,\mu_B$) and 5d ($-0.3\,\mu_B$) contributions. The orbital contributions to the moments were calculated to be 0.08 μ_B for Fe and 0.15 μ_B for Ce.

The present experiments were undertaken to obtain a more precise characterization of the magnetic moment on the Ce atom in $CeFe_2$ and to provide an experimental test of the band theory.

2. Material preparation

The intermetallic compound $CeFe_2$ is formed in a peritectic reaction at 940 °C between the compound Ce_2Fe_{17} and a liquid phase containing $\simeq$ 48 at.% Fe [7]. Large grains of $CeFe_2$ were grown in a matrix of eutectic Ce–Fe containing 60 at.% Ce obtained by melting the appropriate proportions of 99.9% pure Ce and 99.99% pure Fe together in an argon arc furnace.

The ingot was placed in an alumina crucible and sealed in a quartz ampoule. It was annealed for two hours at 930 °C before slow cooling to 645 °C over a period of three days. Finally the melt was held at 645 °C for a further two days to enhance grain growth. The resulting ingot contained many grains of $CeFe_2$ ranging in size up to $\simeq 5 \times 5 \times 5$ mm. As attempts to separate the grains from the eutectic by chemical means were unsuccessful, grains were identified using x-ray Laue photography and cut out of the matrix by spark erosion. The crystals used in the experiment measured $\simeq 2 \times 3 \times 3$ mm and weighed $\simeq 70$ mg.

3. Neutron diffraction measurements

The magnetic structure factors of ferromagnetic materials are difficult to measure accurately using unpolarized neutrons, particularly when, as in the present case, the magnetic moments are small. On the other hand, measurement of the polarization dependence of the neutron cross-section is capable of yielding precise magnetic structure factors even when the ratio of magnetic to nuclear scattering is low. To obtain magnetic structure factors from the results of polarized neutron measurements it is necessary to know whether the crystal scatters according to kinematic theory, and if not to find an extinction model which relates the scattered intensity to the structure factors. To establish such a model in the present case, a set of integrated intensity measurements was made using unpolarized neutrons, on the same crystal used to measure polarized neutron flipping ratios.

3.1. Integrated intensity measurements

Integrated intensities were measured on the D15 diffractometer at the Institut Laue–Langevin (ILL) using normal beam geometry. The crystal was mounted with a $\langle 110 \rangle$ axis vertical in a He-vapour-cooled cryostat, at a temperature of 10 K. Reflections in the zero and first layers with $(\sin\theta)/\lambda < 0.7$ Å^{-1} were recorded with neutron wavelengths of 1.07 and 0.85 Å. Data for symmetrically equivalent reflections measured at the same wavelength were averaged together yielding structure amplitudes for 46 unique $hkls$ at 1.07 Å and 40 at 0.85 Å. These structure amplitudes were used as data in a least squares structure refinement.

Since there are no free positional parameters in the cubic Laves-phase structure, the only adjustable parameters are the isotropic temperature factors of the iron and cerium atoms, their magnetic moments, a scale factor for each of the two wavelengths, and the two extinction parameters of the Becker–Coppens extinction model [8]. The ferromagnetism makes only a small contribution to the integrated intensities, except at the lowest angles, and the moment values are strongly correlated with the temperature factors; it was therefore decided to fix the moments at the values obtained from the polarized neutron measurements. With these values very good agreement between the observed and calculated structure amplitudes ($R = 0.8\%$) was obtained with $B_{Fe} = 0.197(7)$ Å^2 and $B_{Ce} = 0.224(9)$ Å^2, a fixed domain radius of 10 μm and a mosaic spread of $2.0(2) \times 10^{-6}$ rad^{-1}. The degree of extinction is rather small; the intensity reduction in the strongest measured reflection (440) is only some 5%. With such a small degree of extinction the two parameters of the Becker–Coppens model cannot be determined independently.

3.2. Polarized neutron measurements

Polarized neutron flipping ratios were measured using the D3 polarized neutron diffractometer, which uses neutrons from the hot source of the ILL high-flux reactor. Measurements were made at two neutron wavelengths: 0.845 and 0.545 Å, for two different values of applied field: 2.0 and 4.6 T, and at two different temperatures: 9 and 175 K.

The most extensive set of data was collected at 9 K with 4.6 T applied field. The crystal was mounted with the [110] axis approximately parallel to the field direction, and measurements were made of all reflections of the forms hhl and $h + 2, h, l$ having $(\sin\theta)/\lambda < 1.0$ Å^{-1} with $\lambda = 0.845$ Å. The lower-angle reflections $(\sin\theta)/\lambda < 0.6$ Å^{-1} were also measured at the shorter wavelength ($\lambda = 0.545$ Å). Magnetic structure factors were calculated from the flipping ratios, making corrections for extinction using the parameters determined from the integrated intensity measurements, and for incomplete polarization of the beam using polarization values measured with a CoFe test crystal. The results obtained in this way for the same reflections measured at different wavelength, and for equivalent reflections measured on different layers at the same wavelength, were not in good agreement. The divergence was most apparent in those reflections for which the flipping ratios were furthest from unity. This observation suggests that depolarization of the incident beam by the crystal had not been adequately taken into account. Such depolarization could result if the crystal were magnetically anisotropic and if $\langle 110 \rangle$ were a 'hard' direction. To check this hypothesis the crystal was reorientated so that a $\langle 001 \rangle$ axis was approximately parallel to the field and some of the flipping ratio measurements were repeated. The results suggested that the depolarization was even greater with this orientation.

Since it is difficult to devise a reliable way to measure the depolarization in a small irregularly shaped crystal, and since measurements, under different experimental conditions, of quite a number of equivalent reflections were available, it was decided to use these measurements to determine the effective polarizations which would give the best consistency between the different data. The basis of this determination was a simple model for the magnetic structure; allowing spherically symmetric moments on the Fe and Ce atoms with 3d and 4f form factors respectively. The data for the least squares refinement were the flipping ratios measured at 9 K in 4.6 T with $\lambda = 0.845$ and $\lambda = 0.545$ Å. The parameters which were refined were the values of the Fe and Ce moments and the effective polarizations at the two wavelengths. The temperature factors and extinction parameters were fixed at the values obtained from the integrated intensity measurements. Successive refinements based on flipping ratios and integrated intensities confirmed that the results of the two least squares procedures were effectively independent. The parameters obtained from the refinement

Table 1. The mean values of the magnetic structure factors measured for CeFe$_2$, compared with those calculated for (column a) the model with spherically symmetrical form factors, and (column b) the model described in the text in which the form factors are expressed as multipole expansions with the parameters given in column A of table 2.

h	k	l	$(\sin\theta)/\lambda$	F_m(obs)	F_m(calc) a	b	h	k	l	$(\sin\theta)/\lambda$	F_m(obs)	F_m(calc) a	b
1	1	1	0.1186	−9.0(2)	−9.02	−9.37	8	6	2	0.6985	0.12(5)	−0.02	0.12
2	2	0	0.1937	0.66(4)	0.62	0.61	7	7	3	0.7085	−0.14(4)	−0.24	−0.09
3	1	1	0.2272	5.7(1)	5.64	5.47	10	2	2	0.7118	0.67(4)	0.48	0.57
2	2	2	0.2373	11.1(2)	11.57	11.07	6	6	6	0.7118	0.27(4)	0.48	0.37
4	0	0	0.2740	10.5(2)	10.36	9.77	10	4	2	0.7503	0.07(7)	−0.01	−0.01
3	3	1	0.2986	4.86(4)	4.71	4.43	11	1	1	0.7596	0.14(5)	0.12	0.15
4	2	2	0.3355	−0.03(1)	−0.34	−0.07	7	7	5	0.7596	0.20(4)	0.12	0.22
5	1	1	0.3559	−3.15(3)	−3.12	−3.12	8	8	0	0.7749	0.06(6)	0.19	0.14
3	3	3	0.3559	−2.93(3)	−3.12	−2.96	9	5	5	0.7839	−0.01(6)	−0.08	0.10
4	4	0	0.3875	5.06(7)	5.38	5.26	8	6	6	0.7988	0.11(4)	0.00	0.20
5	3	1	0.4052	2.59(3)	2.72	2.51	11	3	3	0.8075	−0.13(6)	−0.04	−0.05
6	2	0	0.4332	−0.11(2)	−0.20	−0.16	12	0	0	0.8219	0.51(7)	0.04	0.17
5	3	3	0.4491	1.71(4)	1.85	1.78	8	8	4	0.8219	−0.06(5)	0.04	−0.04
6	2	2	0.4543	3.55(3)	3.84	3.70	7	7	7	0.8304	0.14(5)	−0.01	0.27
4	4	4	0.4745	3.11(4)	3.55	3.24	12	2	2	0.8444	0.05(4)	0.01	0.05
7	1	1	0.4891	1.50(4)	1.65	1.52	10	6	4	0.8444	0.01(6)	−0.01	−0.04
5	5	1	0.4891	−1.49(3)	−1.65	−1.50	9	9	1	0.8745	−0.01(5)	0.04	0.03
6	4	2	0.5126	0.07(2)	0.12	0.12	10	8	2	0.8878	0.03(8)	−0.01	0.06
5	5	3	0.5261	1.08(4)	1.13	1.24	13	1	1	0.8957	−0.16(6)	0.04	−0.02
8	0	0	0.5479	2.03(4)	1.99	2.09	9	9	3	0.8957	0.07(5)	−0.04	0.08
7	3	3	0.5606	−0.85(4)	−1.01	−0.85	11	5	5	0.8957	−0.09(7)	−0.04	−0.16
6	6	0	0.5812	−0.08(7)	0.07	−0.13	10	6	6	0.8983	−0.22(6)	−0.10	−0.19
8	2	2	0.5812	0.08(3)	0.07	0.12	12	4	4	0.9087	−0.04(7)	−0.12	−0.12
5	5	5	0.5932	−0.43(3)	−0.70	−0.43	9	7	7	0.9164	−0.10(8)	−0.07	−0.11
6	6	2	0.5971	1.19(3)	1.44	1.34	13	3	3	0.9366	−0.04(5)	−0.06	−0.13
9	1	1	0.6240	−0.74(3)	−0.61	−0.66	9	9	5	0.9366	0.17(5)	0.06	0.26
6	6	4	0.6425	−0.01(4)	−0.04	0.02	8	8	8	0.9491	−0.23(6)	−0.14	−0.27
8	4	4	0.6711	0.54(4)	0.72	0.68	14	2	0	0.9686	0.05(9)	0.01	−0.04
7	7	1	0.6815	0.44(5)	0.35	0.45	10	10	0	0.9686	−0.06(9)	−0.01	−0.16
9	3	3	0.6815	0.30(3)	0.35	0.24	10	8	6	0.9686	0.00(7)	0.01	0.12
7	5	5	0.6815	0.25(4)	0.35	0.28	9	9	7	0.9949	−0.11(6)	−0.10	−0.04
10	2	0	0.6985	−0.06(5)	0.02	−0.06							

based on flipping ratios were: $\mu_{Fe} = 1.22(2)$ μ_B; $\mu_{Ce} = -0.108(6)$ μ_B, $P_{0.84} = 0.88(1)$; $P_{0.54} = 0.90(1)$. The polarizations measured using the CoFe crystal were 0.975(1) at 0.84 Å and 0.917(2) at 0.54 Å, giving depolarizations of 0.90 and 0.98 respectively for the two wavelengths. The fact that the depolarization is significantly greater at the longer of the two wavelengths suggests that it may be due to small-scale inhomogeneities in the field at the surface of the crystal, through which the shorter-wavelength neutrons pass sufficiently quickly not to be severely depolarized.

The magnetic structure factors for equivalent reflections, recalculated using these effective polarizations were in reasonable agreement with one another and were averaged to give the mean magnetic structure factors for reflections in the asymmetric unit $h \geqslant k \geqslant l \geqslant 0$. These mean magnetic structure factors are listed in table 1; their standard deviations were calculated from the deviations of individual measurements from the mean.

A similar refinement procedure was carried out with the flipping ratios measured at

175 K although in this case data had only been recorded at a single wavelength (0.845 Å). The results of the refinement were $\mu_{Fe} = 1.14(2)$ μ_B, $\mu_{Ce} = -0.08(2)$ μ_B, $P = 0.934$.

The data measured with the lower applied field showed even more depolarization and were not analysed further.

4. Temperature dependence of the moments

To ascertain whether the Fe and Ce moments have the same temperature dependence, the flipping ratios of the 220 and 222 reflections were measured over the range 10 to 235 K. These two reflections were chosen because to a good approximation the former depends only on the Ce moment and the latter only on the Fe moment. The magnetic structure factors deduced from these measurements, normalized to unity at 10 K, are plotted as a function of temperature in figure 1. Although the points at 170 and 200 K might suggest that the Ce moment falls more slowly with temperature than that of Fe below 180 K and more rapidly close to T_c, more data are necessary to confirm this behaviour. In the applied field of 4.6 T there is no dramatic loss of moment at the Curie temperature, and the Ce moment continues to be oppositely polarized to that of Fe in the aligned paramagnetic phase.
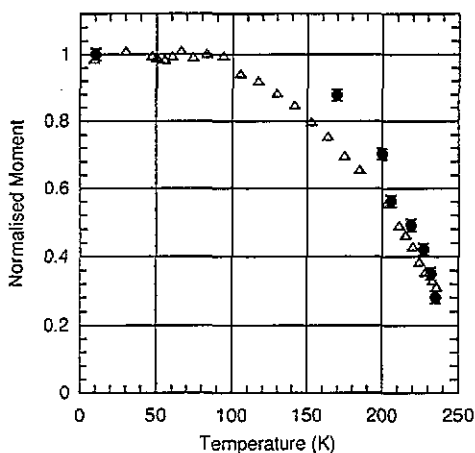

Figure 1. Temperature dependence of the Fe (open triangles) and Ce (filled circles) moments, normalized to their values at 10 K.

5. Determination of the magnetic form factors

The principal motivation for this experiment was to determine whether or not the Ce atom in CeFe₂ carries a moment and if so to determine the form factor associated with it. It was evident from the preliminary analysis of the flipping ratios that there is indeed a moment associated with Ce, and that it is oppositely polarized to the Fe atoms. In this section the model of the magnetization is elaborated to take account of the effect of the crystal field on the magnetization of the Fe atoms and to include a parametrized function to describe the radial distribution of the Ce magnetic moment.
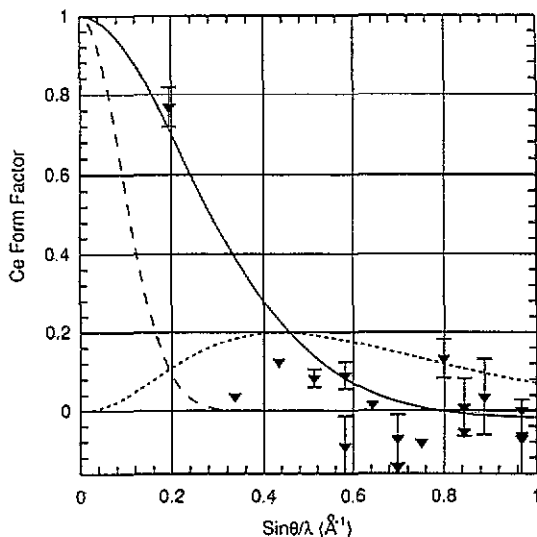
Figure 2. Magnetic scattering from the 'Ce-only' reflections in CeFe$_2$ normalized to -0.108 μ_B/Ce. The full curve shows the Ce 4f (j_0) form factor, the curve with short dashes the Ce 4f (j_2) form factor and the curve drawn with longer dashes the Ce 5d form factor.

If the magnetization around the Fe atoms was spherically symmetric then the magnetic scattering in reflections hkl with h, k, l all even, but with only one of h, k, $l = 4n$, ('Ce only' reflections) would be due to the Ce magnetic moment only. The magnetic structure factors observed for these reflections are plotted in figure 2, where they are compared with the Ce 5d and 4f form factors. It is clear that the magnetic scattering in these reflections cannot simply be due to a spherically symmetric magnetization centred on the Ce sites. This conclusion is strengthened by looking at the other reflections to which a spherical Ce magnetization contributes. If it is assumed that the whole of the difference between the observed magnetic scattering and that due to a spherical iron atom carrying 1.22 μ_B is due to magnetization centred on Ce, then these differences can be used to derive points on the Ce form factor. These points are plotted in figure 3 and again compared with the Ce 5d and 4f form factors. The lack of any kind of monotonic dependence of the plotted points on $(\sin \theta)/\lambda$ confirms that it is necessary to go beyond the spherical approximation in order to fit the data.

The point symmetry of the Fe sites in CeFe$_2$ is $3m$. Under a crystal field of this symmetry the 3d functions of T$_{2g}$ symmetry in the cubic crystal field are split further into a singly and a doubly degenerate set. With the threefold axis as quantization direction the doubly degenerate pair can be written as

$$\phi_{+t} = (\sqrt{2}|2\rangle - |-1\rangle)/\sqrt{3} \qquad \phi_{-t} = (\sqrt{2}|-2\rangle + |1\rangle)/\sqrt{3}$$

and the singly degenerate function as $\phi_{0t} = |0\rangle$.

The E$_g$ functions remain a doubly degenerate pair which transform according to the same irreducible representation as ϕ_{-t} and ϕ_{+t}. With this quantization axis they become

$$\phi_{+e} = (\sqrt{2}|-1\rangle + |2\rangle)/\sqrt{3} \qquad \phi_{-e} = (\sqrt{2}|1\rangle - |-2\rangle)/\sqrt{3}.$$

The angular dependences of the densities due to each of these functions are given by the combination of spherical harmonic functions

$$\rho_{-t} = \rho_{+t} = Y(0, 0) - 0.3194Y(2, 0) - 0.0953Y(4, 0) + 0.3984(Y(4, 3) - Y(4, -3))$$
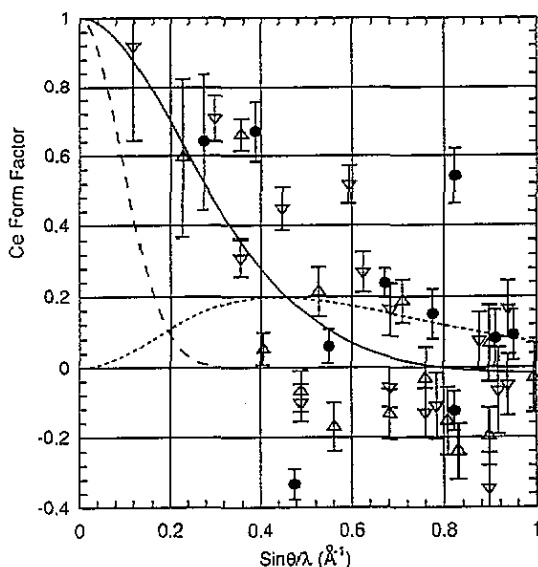
Figure 3. The Ce form factor calculated from the differences between the observed magnetic scattering and that calculated for the structure with spherical moments of 1.22 μ_B on the Fe atoms only. The differences are normalized to a Ce moment of -0.108 μ_B. The filled circles are reflections with $h, k, l = 4n$, triangles with apex up those with $h + k + l = 4n + 1$ and triangles with apex down those with $h + k + l = 4n + 3$. The plotted curves are as in figure 2.

$$\rho_{0t} = Y(0, 0) + 0.6389 Y(2, 0) + 0.8571 Y(4, 0)$$

$$\rho_{-e} = \rho_{+e} = Y(0, 0) - 0.3333 Y(4, 0) - 0.3984(Y(4, 3) - Y(4, -3)).$$

Components of magnetization centred on Fe sites which have the angular dependence of $Y(2, 0)$, $Y(4, 0)$ or $Y(4, 3)$ can contribute to the 'Ce-only' reflections. However, their contributions cancel with one another when they occur in the proportions corresponding to E_g or T_{2g} symmetry. These aspherical functions also augment or diminish the scattering due to Fe in the other reflections and so can be responsible for some of the differences plotted in figure 3.

To determine the importance of these effects a more sophisticated model of the magnetization was set up. In this model the Fe magnetization is modelled by a density of the form

$$\rho_{Fe} = a\langle j_0\rangle Y(0, 0) + b\langle j_2\rangle Y(2, 0) + \langle j_4\rangle[cY(4, 0) + d(Y(4, 3) - Y(4, -3))]$$

where $\langle j_0\rangle$, $\langle j_2\rangle$ and $\langle j_4\rangle$ are the radial integrals calculated by Watson and Freeman [9] and a, b, c and d are parameters to be determined. The band structure calculations suggest that the Ce moment has significant contributions from 5d spin, 4f spin and 4f orbital moment. Its form factor was therefore expressed as

$$f_{Ce} = \mu_{5d}\langle j_0\rangle_{5d} + \mu_{4fs}\langle j_0\rangle_{4f} + \mu_{4fo}(\langle j_0\rangle_{4f} + \langle j_2\rangle_{4f})$$

where $\langle j_0\rangle_{5d}$ is the 5d form factor given by [3], and $\langle j_0\rangle_{4f}$ and $\langle j_2\rangle_{4f}$ are the Ce 4f form factors [10]. The parameters a, b, c, d, μ_{5d}, μ_{4fs} and μ_{4fo} were determined by a least squares fit of the magnetic structure factors calculated from this model to the observed values given in table 1. The values which gave the best fit are shown in table 2 and the corresponding calculated magnetic structure factors in the final column of table 1.

Table 2. Parameters of the multipole model of the magnetization distribution in $CeFe_2$: column A with no constraints on the parameters; column B with μ_{5d}/μ_{4fs} constrained to 0.75.

Atom	Parameter	Refined value	
		A	B
Ce	μ_{5ds}	−0.41(12)	−0.067(16)
	μ_{4fs}	−0.047(13)	−0.099(21)
Fe	a	1.169(10)	1.174(10)
	b	−0.003(10)	−0.008(10)
	c	0.044(17)	0.049(19)
	d	−0.082(11)	−0.083(11)
	χ^2	5.7	6.5

6. Discussion

The total moment per formula unit is given by $2a + \mu_{5d} + \mu_{4fs} + \mu_{4fo} = 1.88(13)$ μ_B which is not consistent with the value of 2.3 μ_B given by the saturation magnetization [4] unless there is some positive magnetization amounting to some 0.2 μ_B per Fe atom which is so diffuse that it does not contribute significantly to the Bragg reflections. It is perhaps more likely that the 5d moment of Ce has been overestimated since its form factor falls so rapidly with $(\sin\theta)/\lambda$ that it contributes significantly to only a very few reflections. To test this possibility a further refinement was carried out in which the ratio of 5d to 4f moments on Ce was constrained to be that obtained in the band structure calculations, i.e. 0.75. This refinement gave virtually the same parameters for the Fe magnetization but the Ce 5d moment dropped to −0.07(2) μ_B with a corresponding increase in the 4f spin and orbital moments to −0.10(3) and 0.03(2) μ_B respectively. The complete set of parameters is given in column B of table 2. The quality of fit with these parameters, as measured by χ^2, was 6.5 compared with 5.7 for the unconstrained refinement. On the other hand the total moment per formula unit is 2.2(3) μ_B, in much better agreement with the saturation magnetization.

No linear combination of $\rho_{\pm t}$, ρ_{0t} and $\rho_{\pm e}$ with positive coefficients can give a density with the coefficients b, c, d of table 2. Only orbital functions which are linear combinations of $\phi_{\pm t}$ with $\phi_{\pm e}$ can give a density which has the ratios between the multipole coefficients which were found, and in particular a negative value for c/d at the same time as a near zero value of b. The observed ratios can be obtained from the orbitals

$$\phi_{+a} = 0.624|-1\rangle + 0.781|2\rangle \qquad \phi_{-a} = 0.781|-2\rangle - 0.624|1\rangle$$

$$\phi_0 = |0\rangle$$

$$\phi_{+b} = 0.781|-1\rangle - 0.624|2\rangle \qquad \phi_{-b} = 0.624|-2\rangle + 0.781|1\rangle.$$

These have probability densities

$$\rho_{\pm a} = Y(0,0) - 0.2653Y(2,0) - 0.1354Y(4,0) - 0.2913[Y(4,3) - Y(4,-3)]$$

$$\rho_{\pm b} = Y(0,0) - 0.0539Y(2,0) - 0.2929Y(4,0) + 0.2913[Y(4,3) - Y(4,-3)].$$

The observed multipole parameters correspond to 51% of the unpaired electrons being in the $\phi_{\pm a}$ orbitals, 27% in ϕ_0, and 22% in $\phi_{\pm b}$; whereas a spherical distribution would have

the proportions 40%, 20%, 40% respectively. In the Laves-phase structure of $CeFe_2$ the Fe atoms are coordinated by six Ce and by six other Fe atoms disposed at the vertices of an icosahedron as illustrated schematically in figure 4(a). The electron density in the ϕ_0 orbitals is maximum in the direction of the threefold axis [111] of the icosahedron which points to the centres of its two opposite triangular faces whose vertices are all Fe atoms. The density associated with the $\phi_{\pm a}$ orbitals is quite similar to that of the E_g functions which have maxima in the directions of the cube axes, inclined at $\pm 54°$ to the triad axis. The directions of the maxima of the $\phi_{\pm a}$ functions are inclined at a greater angle: $\pm 65°$, to this axis which makes them nearly parallel to the Fe–Ce bonds which are inclined at $72°$ to the triad. The disposition of the Fe–Fe and Fe–Ce bonds with respect to the lobes of the ϕ_0 and $\phi_{\pm a}$ functions in the (112) plane is shown schematically in figure 4(b). The observation that the orbitals preferred by the unpaired electrons of iron extend in the directions between, rather than towards, near-neighbour iron atoms is consistent with their behaviour in ferromagnetic BCC iron where the preferentially occupied E_g orbitals also extend in directions away from near-neighbour atoms [11].
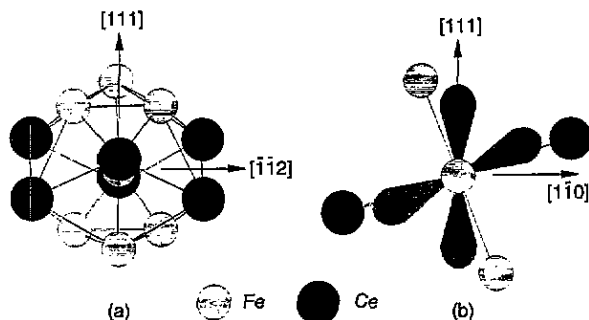

Figure 4. (a) Schematic representation of the icosahedron coordinating the iron atoms in $CeFe_2$. (b) Section through the coordination octahedron of (a) perpendicular to the [1$\bar{1}$2] axis. The directions of the lobes of the ϕ_0 and $\phi_{\pm a}$ functions relative to the Fe–Fe and Fe–Ce bonds are indicated.

7. Conclusions

These polarized neutron scattering results confirm the previous observation [5] and the theoretical prediction [6] that the Ce atom in $CeFe_2$ carries a magnetic moment, and that it is oppositely polarized to the Fe atoms. In this it resembles the ferromagnetic Laves-phase compounds YFe_2 and $ZrFe_2$ in which the Y and Zr atoms carry small 4d moments which are oppositely polarized to Fe [12]. The magnetic moment of the Fe atoms in $CeFe_2$ at 10 K in an applied field of 4.6 T is 1.174(10) μ_B, rather smaller than the value 1.43 μ_B given by the spin-polarized band structure calculations. The value of the Ce moment cannot be uniquely determined without making some assumption about the ratio of the numbers of 5d and 4f electrons contributing to its magnetization. The assumption that this ratio is 0.75, as given by the band structure calculations leads to a total Ce moment of $-0.14(3)$ μ_B of which $-0.10(2)$ μ_B are due to 4f spin, 0.03(2) μ_B to 4f orbital moment and $-0.07(2)$ μ_B to 5d spin. This ratio of 4f orbital to spin moments agrees well with the band structure

calculations although the sizes of the moments are almost an order of magnitude smaller than those calculated. Thus it seems that, as is the case for Laves phases of actinide compounds [13], the relativistic spin-polarized band structure calculations correctly predict the ratios of spin to orbital moments of Ce or an actinide, but systematically overestimate their absolute magnitudes.

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