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## A single-crystal neutron diffraction study of the magnetization density in Fe<sub>2</sub>Zr

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**Abstract.** A single-crystal neutron diffraction study of the cubic Laves phase Fe<sub>2</sub>Zr at 4.2 K has been made using both polarized and unpolarized incident beams. The samples were prepared from high-purity zirconium and iron and exhibited resistance ratios ( $\rho_{293\text{ K}}/\rho_{4.2\text{ K}}$ ) of typically 95, indicative of samples with good long-range order and homogeneity. The material has a Curie temperature of 604(2) K and a cell dimension of  $a = 7.063(1)$  Å at ambient temperature in agreement with previous measurements for this composition by others. The saturation magnetization of 3.46(1)  $\mu_B$ /formula unit at 4.2 K is higher than previously observed. The magnetization density of the sample has been fitted by a weighted least-squares procedure to a multipole model of the iron moment based on free-atom wavefunctions for Fe<sup>2+</sup>. The symmetry at the iron site is  $\bar{3}m$  and the independent symmetry-allowed multipoles up to  $l = 4$  are  $Y_{00}$ ,  $Y_{20}$ ,  $Y_{40}$  and  $Y_{43-}$ : these have amplitudes 2.11(3), 0.03(2), 0.16(4) and  $-0.30(4)$   $\mu_B$  respectively. The magnetization at the Zr site is negative and is modelled by a single spherical term,  $Y_{00} = -0.32(5)$   $\mu_B$ . The remaining magnetization of  $-0.44$   $\mu_B$ /formula unit is associated with diffuse density. These findings are discussed in the light of band structure calculations and previous studies of magnetic Laves phases.

### 1. Introduction

The wide variety of magnetic behaviour exhibited by simple binary cubic alloys is striking, ranging from exchange-enhanced paramagnets such as TiBe<sub>2</sub>, through weak ferromagnets like ZrZn<sub>2</sub> to high-temperature, strongly magnetic materials such as Fe<sub>2</sub>Y and Fe<sub>2</sub>Zr. In all cases, the determination of the distribution of magnetization within the unit cell by neutron diffraction techniques has proved invaluable in the interpretation of the bulk phenomena. In this article we report the results of both polarized and unpolarized neutron diffraction measurements on high-quality single crystals of Fe<sub>2</sub>Zr which were undertaken to shed light on its disputed magnetic structure. In this controversy we find some experimental results [1–5] interpreted on the premise that Fe<sub>2</sub>Zr is an itinerant ferromagnet with moments localized solely about the iron sites, whereas other work [6, 7] taken together with spin-polarized band structure calculations [8–10] suggests that both atom species have magnetic moments with different magnitudes and opposite (ferrimagnetic) alignment.

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$\text{Fe}_2\text{Zr}$  crystallizes in the cubic,  $\text{Cu}_2\text{Mg}$  (C15) Laves phase structure and is stable over a narrow range of composition about the ideal of 66.7 at.% Fe [11]. The space group is  $Fd\bar{3}m$  with  $Z = 8$ . Referred to a centre ( $\bar{3}m$ ) at the origin, the atomic positions are fixed at:

Atom	Site	Symmetry	$x$	$y$	$z$
Fe	16(d)	$\bar{3}m$	0	0	0
Zr	8(a)	$\bar{4}3m$	1/8	1/8	1/8

Its bulk magnetic properties have been studied by several groups [12–21]. In particular, Svechnikov *et al* [20], Brückner *et al* [18, 19] and Kai *et al* [17] have studied the correlations between the cell dimension, the bulk phase Curie temperature ( $T_C$ ) and the atomic composition. The saturation magnetization at room temperature (300 K) has been reported by a Piegger and Craig [21] and by Brückner *et al* [18, 19]: both sets of authors find a value of  $2.60 \mu_B$ /formula unit at the composition  $\text{Fe}_2\text{Zr}$ . The rate of change of this quantity with composition is much higher ( $0.25 \mu_B/\text{at.}\%$  increase in Fe) than at low temperature ( $0.048 \mu_B/\text{at.}\%$  in Fe) due to the proximity of the composition-dependent  $T_C$ . An ambient-temperature polarized neutron study by Kocher and Brown [5] of a large-grained, polycrystalline specimen found that the moment distribution at the Fe site corresponded to a more extended form factor than that in  $\alpha$ -iron and that there was no significant moment at the Zr site. No value for the iron moment was given, but the value of the saturation magnetization at 4.2 K and ambient temperature were measured as  $3.12$  and  $2.56 \mu_B$  per formula unit, respectively.

## 2. Experimental details

The bulk single crystals were prepared from Johnson–Matthey Specpure iron and zirconium by radio-frequency heating in a copper boat under an atmosphere of purified argon. The constituent metals were brought to a temperature of  $1650^\circ\text{C}$  over a period of some 15 minutes and then cooled and annealed at  $1500^\circ\text{C}$  for a period of 3 days. Using this method, three single crystals of  $\text{Fe}_2\text{Zr}$  were obtained with dimensions of approximately  $2 \times 0.75 \times 0.5 \text{ mm}^3$ . The crystals were characterized by x-ray diffraction, low-temperature saturation magnetization ( $3.46(1) \mu_B$  per formula unit at 4.2 K), direct measurement of  $T_C$  (604 K) and by their electrical resistivity ratio ( $\rho_{293 \text{ K}}/\rho_{4.2 \text{ K}} \simeq 95$ ). We find our values of the lattice parameter ( $7.063(1) \text{ \AA}$ ) and  $T_C$  to lie midway between the extremes given by Svenchikov *et al* and Brückner *et al* and close to the values given by Kai *et al*. The high resistance ratios, typically 95, that we obtain for our samples give us confidence that we are dealing with stoichiometric single crystals of high quality.

Both unpolarized and polarized neutron diffraction measurements have been made at 4.2 K on a single-crystal pillar elongated parallel to (110) with dimensions  $1.0 \times 0.5 \times 0.5 \text{ mm}^3$ . The unpolarized integrated intensity data were collected on the D15 diffractometer at the Institut Laue–Langevin (ILL), Grenoble, using a wavelength of  $1.175 \text{ \AA}$ . A total of 396 reflections were measured out to a  $(\sin \theta)/\lambda$  limit of  $1.0 \text{ \AA}^{-1}$ : after averaging over equivalents, which gave a merging  $R$ -factor of

Table 1. The refined parameters for the structure of Fe<sub>2</sub>Zr at room temperature derived from unpolarized neutron integrated intensity data (ITF is the isotropic temperature factor).

Atom	Parameter	Value
Fe	ITF	0.12(1) Å <sup>2</sup>
	Moment	2.06(5) μ <sub>B</sub>
Zr	ITF	0.15(1) Å <sup>2</sup>
	Moment	0.00(fixed)
Inverse mosaic spread parameter		0.077(3) × 10 <sup>-4</sup> rad <sup>-1</sup>

2.9% on  $F_o^2$  and a  $\chi^2$  of 19, these data reduced to 97 unique observed moduli of structure factors,  $F_o$ . These observables were used in a weighted least-squares refinement of a model in which the variables were the isotropic temperature factors on Fe and Zr, the Fe magnetic moment, a scale factor and a mosaic spread parameter to describe the small degree of extinction in the sample using the Becker-Coppens [22] formalism. The weighting scheme was  $1/\sigma^2$ , where  $\sigma$  is the standard deviation in  $F_o$  derived from the agreement between equivalent reflections or the counting statistics, whichever was the higher. The nuclear scattering lengths were taken to be  $b(\text{Fe}) = 0.954$  and  $b(\text{Zr}) = 0.716 \times 10^{-12}$  cm. The form factor of the Fe moment was calculated from the wavefunctions for Fe<sup>2+</sup> 3d given by Clementi and Roetti [23]. In the refinement, Zr was assumed to carry no moment and the excellent final  $R$ -factor of 1.08%, weighted  $R$ -factor,  $R_w = 1.03\%$ , and  $\chi^2 = 2.6$  showed that these data are insensitive to the presence of any small, radially diffuse moment at the Zr site. The refined values for the temperature factors and the mosaic spread, which are listed in table 1, were then used to derive the observed magnetic structure factors from the polarized beam flipping ratios measured on the D3 instrument, also at the ILL. These measurements were also made at 4.2 K with an incident wavelength of 0.84 Å and in a field of 1.5 T, sufficient to saturate the sample with its pillar axis vertical, parallel to the omega rotation axis of the normal-beam instrument and to the applied field direction. A total of 283 flipping ratios were averaged over the equivalent reflections to produce 55 unique magnetic structure factors, corrected for imperfect incident beam polarization (0.975).

### 3. The moment distribution

The magnetic structure factors derived from the D3 measurements provided the observed data for an initial weighted least-squares refinement of a magnetic model with the Fe 3d form factor specified above and a Zr 4d form factor calculated from wavefunctions from the same source [23]. The final  $R$ -factor was 11.1%,  $R_w = 8.5\%$  and a  $\chi^2$  of 23 with Fe and Zr moments of 2.14(4) and  $-0.16(8)$  μ<sub>B</sub>, respectively. The weighting scheme was again  $1/\sigma^2$ . At this stage in the refinement there was no indication of a significant expansion or contraction of the observed form factor relative to the model. One reflection 111, has a magnetic structure factor close in magnitude to its nuclear one. In these circumstances, the polarized beam technique gives poor accuracy and this reflection was omitted from the refinement to leave 54 observed magnetic structure factors. Difference Fourier sections parallel to (001) through both the Fe and Zr atoms were then computed in the belief that they would

show the deficiencies of our model: in the latter case, the data were restricted to those reflections having  $(\sin \theta)/\lambda < 0.5 \text{ \AA}^{-1}$ , since these would be most affected by any weak moment on the Zr. The maps indicated no major departure from spherical symmetry about the iron site due to the action of the crystal field, in contrast with the case of  $\text{LuFe}_2$  [24], and were too sensitive to missing reflection data to give reliable information about the zirconium site.

**Table 2.** The multipole amplitudes and their standard deviations for the best least-squares fit to the magnetization in  $\text{Fe}_2\text{Zr}$ .

Atom	Spherical harmonic	Coefficient (units of $\mu_B$ )
Fe	$Y_{00}$	$2.11(3) + 0.027(22)\langle j_2 \rangle$
	$Y_{20}$	$0.03(2)$
	$Y_{40}$	$0.16(4)$
	$Y_{43-}$	$-0.30(4)$
Zr	$Y_{00}$	$-0.32(5)$

To investigate the magnetization in more detail we modelled the moment distribution centred on Fe by a multipolar expansion of products of spherical harmonics and radial integrals,  $\langle j_n \rangle$  [25]. The site symmetry is  $\bar{3}m$  which leads to three independent multipoles  $Y_{20}$ ,  $Y_{40}$  and  $Y_{43-}$  (referred to quantum axes  $Z$  parallel to  $[111]$  and  $X$  parallel to  $[110]$ ) in addition to the  $Y_{00}$  ( $j_0$ ) spherical term. The coefficients of these products were refined using the least-squares program MPLSQ within the Cambridge Subroutine Library of Subroutines and Programs [26] and a significant improvement in fit was obtained:  $R = 7.9\%$ ,  $R_w = 5.1\%$  with  $\chi^2 = 9$  for 6 basic variables and the 54 observations. Table 2 gives the values of the parameters of this model and their standard deviations; there is a slight, but barely significant, indication of some expansion of the Fe radial form factor as indicated by the coefficient for  $\langle j_2 \rangle$  which was added to  $\langle j_0 \rangle$  as the multiplier of  $Y_{00}$  to model this effect. A section of the magnetization density passing through the centres of both the Fe and Zr atoms and calculated from the coefficients in table 2 is illustrated in figure 1(a). The aspherical nature of the iron density is seen more clearly in the difference density map, figure 1(b). The detail around the Zr site is due to series termination.

#### 4. Discussion

Both the polarized and unpolarized neutron single-crystal diffraction studies present us with a picture of  $\text{Fe}_2\text{Zr}$  in which the majority of the moment sits at the iron sites,  $2.11(3) \mu_B$  per iron atom, with an oppositely aligned moment on the zirconium site of  $-0.32(5) \mu_B$  giving a net moment of  $3.90(8) \mu_B$  per formula unit. This is significantly greater than the saturation magnetization of  $3.46(1) \mu_B$ , measured on our sample with the kind collaboration of Professor J Crangle, and would suggest the presence of a spatially diffuse background magnetization of  $-0.44 \mu_B$  per formula unit. This result qualitatively supports the hypothesis of a ferrimagnetic state obtained in the calculations of Mohn and Schwartz [10] and Yamada and Shimiza [9], whilst apparently disagreeing quantitatively since these authors predict integrated moments of  $1.90(1.87)$  and  $-0.56(-0.53) \mu_B$  respectively on the iron and zirconium sites. It should, however, be pointed out that a diffuse negative magnetization amounting to

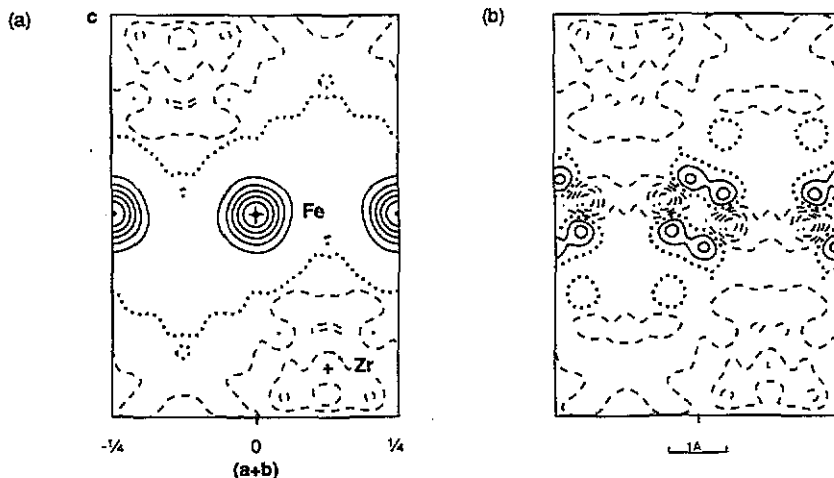


Figure 1. Magnetization density in the (110) plane of Fe<sub>2</sub>Zr, averaged over a cube of side 0.5 Å, computed from the observed magnetization and the calculated amplitudes for all reflections to a limit in  $(\sin \theta)/\lambda$  of  $1.0 \text{ \AA}^{-1}$ . (a) The total density with positive contours (solid lines) at  $0.5 \mu_B \text{ \AA}^{-3}$  intervals and negative contours at  $0.02 \mu_B \text{ \AA}^{-3}$  intervals; the zero contour is dotted. (b) The density without the spherically symmetric moment on Fe; all contours at  $0.02 \mu_B \text{ \AA}^{-3}$  intervals.

some  $-0.22 \mu_B$  is observed in iron itself [27] and this might reasonably be scaled to  $-0.21 \mu_B/\text{Fe}$  in Fe<sub>2</sub>Zr to give a total moment of  $1.90(3) \mu_B/\text{Fe}$  in agreement with the calculations [10]. Allocating the remaining diffuse density of  $-0.02 \mu_B$  to Zr would produce a total moment of  $-0.34(4) \mu_B$  as compared with the calculated value of  $-0.56 \mu_B$ . In this case, the difference might reasonably be taken to indicate a more extended distribution of localized moment on the Zr atom than that corresponding to a free-atom 4d electrons. Figure 1 shows the magnetization distribution corresponding to our model. It is computed in the (110) plane which passes through both the Fe and Zr atoms using a data set complete to  $(\sin \theta)/\lambda = 1 \text{ \AA}^{-1}$  and it is averaged over a cube of side 0.5 Å to reduce the effects of series termination.

We conclude that it is therefore essential to use self-consistent spin-polarized algorithms in the band structure codes, since the strong 3d–4d hybridization implies that rigid-band splitting models [28] cannot be used. We hope that these results will stimulate further experiments and refinements in band structure calculations and contribute to a deeper understanding of the interacting many-electron problem.

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