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Magnetism in ludlamite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$

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Abstract. The magnetic structure of the weak ferromagnet ludlamite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, has been re-examined by both polarized and unpolarized neutron diffraction from single crystal samples of the mineral. The crystal structure has been refined from three dimensional data collected at 20 K, the unit cell being monoclinic, $a = 10.542(8)$, $b = 4.650(2)$, $c = 9.278(7)$ Å, $\beta = 100.75(7)^\circ$ at this temperature. At 4.2 K the contributions to the weak b -axis ferromagnetic moment produced by an external field of 1.5 T parallel to [010], determined from $\{h0l\}$ polarized beam flipping ratios, are 1.73(3) and 0.62(2) μ_B for the Fe^{2+} ions at the centre of symmetry and in a general position, respectively. Limited three-dimensional unpolarized data collected at 4.0 K were used to refine the complete magnetic structure. The moments on the closely linked triads of ions are predominantly ferromagnetically coupled, with the inter-moment angle of $26(2)^\circ$. The total moment at 4 K and in zero field is best fitted by the values: Fe1, 4.51(6) μ_B at angles $\Theta = 30(2)$ and $\varphi = 48(2)^\circ$; Fe2, 4.00(5) μ_B at $\Theta = 6(2)$, $\varphi = 90(7)^\circ$, where Θ is measured from the c axis and φ from the a - c plane. The orientations and magnitudes of the ionic moments are related to the competition between exchange and spin-orbit coupling.

1. Introduction

We have recently determined the antiferromagnetic structures of three first group transition metal anhydrous phosphates, $\text{Co}_3(\text{PO}_4)_2$, $\text{Co}_2\text{P}_2\text{O}_7$ and $\text{Cu}_3(\text{PO}_4)_2$ (Forsyth *et al* 1988, 1989, 1990), from single-crystal diffraction data as part of a programme to study the competition between single-ion anisotropy and exchange in determining the magnetization in salts containing single or linked phosphate groups. The quality or size of the crystals available limited the accuracy of our data for the first and last of these materials. However, our refinement of $\text{Co}_2\text{P}_2\text{O}_7$ enabled us to determine the orbital contribution to the magnetic scattering from its two crystallographically independent Co^{2+} ions, finding a radial expansion of the form factor compared to that for the free ion and relating the non-collinear moment directions to their local environment.

Orbital moment also plays a significant role in iron(II) salts and we have now extended our work to the study of a hydrated Fe^{2+} phosphate. Both the octahydrate (Forsyth *et al* 1970) and tetrahydrate (Abrahams 1966), Forsyth *et al* 1971) have non-collinear antiferromagnetic structures which again show the competing influences of exchange and single-ion anisotropy. A free $\text{Fe}^{2+} 5\text{D } 3d^6$ ion in a weak octahedral field

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has the configuration $4t_{2g}, 2e_g$ in its $5T_{2g}$ ground state. In lower symmetry sites the t_{2g} and e_g orbital degeneracies are lifted to produce a manifold of fifteen low-lying levels if the effect of spin-orbit coupling is included. Strong magnetic exchange or large low symmetry components of the crystal field can, however, simplify this picture by separating some levels sufficiently far from the ground state energy that they no longer play a significant role in the magnetization. The crystal structure of $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ was established by the room temperature single-crystal x-ray study of Abrahams and Bernstein (1966) and is illustrated in figure 1. The unit cell is monoclinic, space group $P2_1/a$

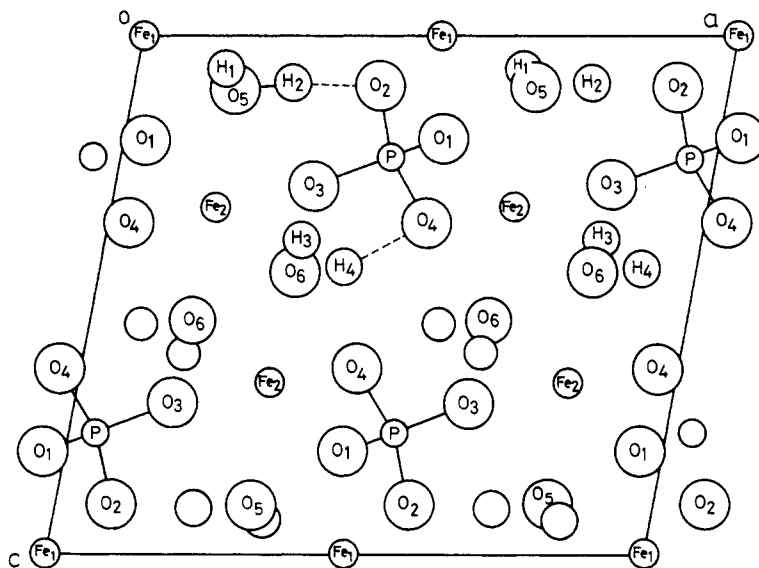


Figure 1. The [010] projection of the structure of ludlamite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. The numbering corresponds to that in tables 1 and 2.

and it contains two crystallographically inequivalent Fe^{2+} ions, Fe1 on centres of symmetry at the origin and $(\frac{1}{2}, \frac{1}{2}, 0)$ and Fe2 at a fourfold site with no symmetry. The companion neutron study at 4.2 K by Abrahams (1966) showed that the magnetic structure below the Néel point at 15 K has the same space group, with the moments on the two triads of Fe^{2+} ions which are related by a 2_1 axis having their approximately parallel a , c components reversed but their small b components ferromagnetically aligned. This model can therefore account for the large ferromagnetic component of magnetization of some $0.8 \mu_B/\text{Fe}^{2+}$, first reported by Mays (1957) and later shown to develop along b by Bozorth and Kramer (1959), as being due to canting of the antiferromagnetic sublattices. However, Abrahams' measurements, which were limited to $\{h0l\}$ and $\{hk0\}$ reflections, did not permit him to model the magnetization more precisely, or to determine whether the a , c components of the moment on the two crystallographically independent iron ions are truly parallel and their b components really equal.

We have now obtained a more accurate and extensive set of magnetic structure factors for the tetrahydrate, using Abrahams' single crystal samples. Furthermore, we have made polarized beam flipping ratio measurements on $\{h0l\}$ reflections to determine

the distribution of the ferromagnetic component of magnetization. We now report these measurements and their interpretation in terms of the single-ion anisotropy of the two Fe^{2+} ions and the exchange coupling between them.

2. Integrated intensity measurements at 20 K and 4 K

Abrahams (1966) found in his refinement of the crystal structure from 1.036 Å neutron data that the natural crystals always exhibited strong extinction, which he modelled using Zachariasen's (1963) method. For this reason, we have used the D9 diffractometer on the hot source at the Institut Laue–Langevin, Grenoble to collect integrated intensity data from the two crystals at both 0.84 and 0.48 Å so that the extinction could be characterized with more certainty. Both samples have cylindrical form, one with [010] as cylinder axis having dimensions 3.02 mm in length and 1.78 mm in diameter: the second has a [001] axis and is 2.77 mm long and 1.98 mm in diameter. Data were collected at 20 K to reduce the effects of thermal vibration. After averaging over equivalent reflections, the 0.84 Å data sets refined to agreement factors $R = 0.074$ without any corrections for extinction: however, its presence was obvious in the strong, low angle data and was modelled following the treatment of Becker and Coppens (1974). The domain radius for both samples was fixed at a large value and a single mosaic spread parameter refined for the combined 0.84 and 0.48 Å data for each sample. The final values for this parameter were not significantly different for the two specimens, which came from the same mineral crystal, so the final refinement was carried out on the total data set of 3732 reflections (this finding is in contrast to that of Abrahams and Bernstein who used extinction factors which differed by a factor of 1.85 to describe the extinction in the two samples). With isotropic thermal parameters on all atoms, two scale factors and the single mosaic spread parameter, a total of 54 variables refined to $R = 0.053$, a χ^2 of 6.6 and a weighted R -factor of 0.040. Finally, the hydrogen and oxygen atoms forming the water molecules were allowed to have anisotropic thermal parameters which increases the number of variables to 84. The final R -factor dropped to 0.046 with a χ^2 of 5.4 and weighted R factor of 0.035.

The Displex two-stage refrigerator of the D9 diffractometer did not allow us to work at the temperature sufficiently below the Néel temperature of ludlamite (15 K) for it to be used to study the magnetic structure. The D15 diffractometer at the ILL has a lifting detector and an ILL 'Orange' liquid helium cryostat. The normal-beam geometry allowed us to collect data at 4.0 K from the zeroth to fourth layers from the samples rotating about their cylinder axes [010] and [001]. The magnetic symmetry is such that the $\{h0l\}$ reflections with h odd, which are absent above the Néel temperature due to the a glide, have purely magnetic intensity at low temperature. In general, however, reflections contain both nuclear and magnetic contributions. After averaging over equivalents, a total of 699 inequivalent reflections were measured from the [001] crystal and 510 from the [010] sample.

3. Polarized beam measurements at 4.2 K

The D3 polarized beam diffractometer at the ILL was used to collect data from the [010] axis crystal at 4.2 K in a magnetic field of 1.5 T applied parallel to [010]. A wavelength of 0.905 Å was used for the majority of the measurements but, as a further check on the

extinction in the sample, some reflections were remeasured at the shorter wavelength of 0.718 Å.

4. The nuclear structure

Table 1 contains the final positional and thermal parameters obtained from the refinement of the 20 K D9 data. At this temperature, the cell dimensions were determined to

Table 1. (a) comparison between the atomic positional parameters (fractions $\times 10^5$) found in the present study with those determined by Abrahams (1966) denoted SCA (fractions $\times 10^4$). In each case the estimated standard deviation (ESD) is given in parentheses. (b) the isotropic temperature factors (ITF) found in the present study compared to those found by Abrahams. Also given are the results of a refinement using anisotropic thermal vibration parameters B_{ij} in the expression

$$\exp\{-\frac{1}{3}[B_{11}(ha^*)^2 + \dots + 2B_{23}(kb^*lc^*) + \dots]\}$$

for the atoms of the water molecules: in all cases the units are Å⁻².

(a) Atom	x		y		z				
	This work	SCA	This work	SCA	This work	SCA			
Fe1		0		0		0			
Fe2	17309(5)	1727(2)	6975(10)	729(25)	32962(6)	3287(2)			
P	45275(9)	4524(3)	96768(17)	9274(16)	23818(10)	2372(5)			
O1	3410(9)	353(3)	78676(15)	7837(12)	19819(9)	2003(4)			
O2	40808(9)	4086(3)	15493(16)	1544(13)	9962(10)	989(4)			
O3	33162(9)	3324(3)	85359(16)	8515(16)	29023(9)	2919(4)			
O4	3487(8)	344(3)	35225(15)	3551(14)	35948(9)	3596(5)			
O5	17008(9)	1702(4)	24349(17)	2412(15)	10213(11)	992(5)			
O6	32757(9)	3265(3)	38715(16)	3846(12)	45516(10)	4539(5)			
H1	14696(19)	1429(11)	43692(34)	4321(36)	6605(24)	639(14)			
H2	26375(18)	2650(8)	21350(35)	2035(25)	9195(24)	918(10)			
H3	33064(19)	3304(8)	55716(33)	5676(95)	38947(20)	3953(11)			
H4	40780(19)	4064(7)	28043(36)	2780(27)	44931(22)	4443(9)			

(b) Atom	ITF							
	This work	SCA	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe1	0.21(1)	0.18(5)						
Fe2	0.20(1)	0.26(4)						
P	0.24(1)	0.30(6)						
O1	0.27(1)	0.64(7)						
O2	0.27(1)	0.39(6)						
O3	0.31(1)	0.33(6)						
O4	0.29(1)	0.70(6)						
O5	0.33(1)	0.39(6)	0.42(3)	0.39(2)	0.39(2)	0.00(2)	0.00(4)	0.00(2)
O6	0.36(1)	0.38(6)	0.42(3)	0.39(2)	0.30(3)	0.00(2)	0.00(4)	0.00(2)
H1	1.63(3)	2.26(19)	1.51(7)	0.98(5)	2.50(9)	0.46(6)	0.29(10)	0.30(3)
H2	1.31(2)	1.60(12)	1.12(7)	1.39(5)	1.66(9)	0.07(6)	0.06(10)	0.17(5)
H3	1.33(2)	1.42(14)	1.44(7)	1.15(5)	1.25(7)	0.31(5)	0.37(9)	0.01(5)
H4	1.37(2)	1.33(12)	1.14(6)	1.53(5)	1.80(5)	-0.18(5)	0.02(8)	0.47(5)

be $a = 10.542(8)$, $b = 4.650(2)$, $c = 9.278(7)$ Å, $\beta = 100.75(7)^\circ$ from the least-squares fit to the diffraction angles of the reflections used to derive the 0.8494 Å crystal orientation matrix. The values obtained by Abrahams (1966) from this neutron study at 4.2 K are also included in Table 1. It can be seen that the estimated standard deviations (ESDs) in the present study are some two to three times smaller for the x and z parameters than in the earlier work and some five times smaller for the y parameters. In most instances the positional parameters agree within 2–3 ESDs, but exceptions are the x parameters of H1 and the z parameters of O1, O3, H3 and H4. Our refinement with isotropic thermal parameters results in the oxygen values being more nearly equal, with the O5, O6 water oxygens having values slightly larger than the remainder. The largest hydrogen isotropic temperature factor (ITF) is on H1, as was found in the earlier study. Table 2 summarises the interatomic distances and angles corresponding to the parameters in table 1.

Table 2. The interatomic distances and bond angles in ludlamite at 20 K.

Fe(1)–O(1) = 2.061(1)Å	P–O(1) = 1.546(2)Å
Fe(1)–O(2) = 2.168(1)	P–O(2) = 1.551(2)
Fe(1)–O(5) = 2.182(1)	P–O(3) = 1.541(2)
	P–O(4) = 1.534(2)
Fe(2)–O(1) = 2.168(1)	
Fe(2)–O(3) = 2.041(2)	O(5)–H(1) = 0.975(2)
Fe(2)–O(4) = 2.019(1)	O(5)–H(2) = 1.019(3)
Fe(2)–O(5) = 2.255(2)	O(6)–H(3) = 1.002(2)
Fe(2)–O(6) = 2.341(1)	O(6)–H(4) = 0.991(3)
Fe(2)–O(6) = 2.171(2)	
	O(2) . . . O(5) = 2.547(2)
Fe(1)–Fe(2) = 3.272(1)	O(2) . . . O(5) = 2.696(2)
Fe(2)–Fe(2) = 4.015(1)	O(3) . . . O(6) = 2.660(2)
	O(4) . . . O(6) = 2.743(2)
O(1)–P–O(3) = 109.9(1)°	
O(3)–P–O(4) = 110.2(1)	O(5)–H(2) . . . O(2) = 171.8(3)°
O(1)–P–O(4) = 109.3(1)	O(5)–H(1) . . . O(2) = 144.5(2)
O(2)–P–O(3) = 108.2(1)	O(6)–H(3) . . . O(3) = 175.6(2)
O(1)–P–O(2) = 109.1(1)	O(6)–H(4) . . . O(4) = 155.1(2)
O(2)–P–O(4) = 110.1(1)	
H(1)–O(5)–H(2) = 106.2(2)	
H(3)–O(6)–H(4) = 103.7(2)	

The crystal structure of ludlamite is well described by Abrahams and Bernstein (1966). The modifications to their conclusions required by the new study result from its higher precision. The average Fe–O bond distance in the distorted octahedron about Fe1 composed of 4 phosphate and 2 water oxygens is 2.137 Å compared to that about Fe2, composed of 3 phosphate and 3 water oxygens, which is 2.166 Å. These are both less than the room temperature x-ray values found by Abrahams and Bernstein by some 0.004 Å, whereas Abrahams neutron study suggested that the reduction was only 0.002 Å for Fe2. We find that the sum of the P–O bond lengths in the phosphate group at 20 K is 6.172(4) Å, which is not significantly different from the 298 K value of 6.169(4), but larger than the 4 K value of 6.158(14) Å. The hydrogen bonding scheme remains unchanged, but the average O–H . . . O angle is 161.7° rather than 163.4°. The H–O–H angle in the two water groups are found to be less different than in the previous 4.2 K

study, viz $105(1.7)^\circ$ compared to $107.9(4.8)^\circ$. In the above discussion the standard deviation quoted for average distances is that given by

$$\left(\sum_i (x_i - \bar{x})^2 / (n - 1) \right)^{1/2}.$$

5. Spatial distribution of the weak ferromagnetism

The contributions to the weak ferromagnetism made by the two crystallographically distinct iron ions have been determined from the polarized beam flipping ratio measurements. These were first converted to values of γ , the ratio between magnetic and nuclear structure factors, taking into account some lack of complete polarization in the input beam and the measured flipping efficiency and including an extinction correction derived from the mosaic spread parameter obtained from our unpolarized beam data. The average γ for equivalent reflections was then multiplied by the appropriate nuclear structure factor calculated from our refined 20 K structure. Reflections with small nuclear structure factors were not used in the subsequent refinement, since they are relatively inaccurate and experience has shown us that they are also liable to be subject to the effects of multiple scattering.

A total of 141 independent magnetic structure factors were available for subsequent modelling. Of these, 65 had values of $\sin \Theta / \lambda < 0.5 \text{ \AA}^{-1}$ and were fitted to a simple model with the two independent iron moments as variables. Using an Fe^{2+} magnetic form factor derived from the Clementi–Roetti (1974) Hartree–Fock wavefunctions for the free ion, a least squares refinement based on unit weights gave an R -factor of 0.081 for moments of 1.68(2) and 0.63(2) μ_B for Fe1 and Fe2 respectively. The radial dependence of the form factor was then allowed to vary by including a contribution with a $\langle j_2 \rangle$ radial dependence (Watson and Freeman 1961). This contribution is of the correct form to model any orbital scattering in the dipole approximation and may also take into account changes in radial distribution between the free ion and the solid state. A refinement of the all data out to $\sin \Theta / \lambda = 0.8 \text{ \AA}^{-1}$ gave $\langle j_2 \rangle$ contributions of 0.13(9) and 0.17(7) for Fe1 and Fe2, respectively. Repeating the first refinement with the inclusion of these terms improved the R -factor slightly to 0.079.

The first order effect of covalency in a ferromagnetic environment is the transfer of moment from the magnetic ion to its ligands. A simple model in which this effect was included by having the same moment on each oxygen with the radial dependence of an $\text{O}^- 2p$ wavefunction (Clementi and Roetti 1974) improved the low angle data refinement still further to 0.069 for the 5 parameters and 65 observations. The final values for the ferromagnetic components produced by the canting of the Fe1 and Fe2 moments out of the a - c plane are:

Ion	Ferromagnetic component of moment (μ_B)	$\langle j_2 \rangle$ (μ_B)
Fe1	1.73(3)	0.13(9)
Fe2	0.62(2)	0.17(9)
O1–O2	0.02(1)	

Some indication of asphericity in the projection of the Fe1 magnetization was evident in a difference Fourier based on the above model, with the moment being contracted in the direction of the 05 water oxygens and elongated in the general direction of the oxygen ligands which form part of the phosphate group. No attempt was made to include this effect by multipole modelling, however, since its significance was no greater than other features of the map for which no physical explanation could be found.

6. The magnetic model of ludlamite

A preliminary magnetic structure refinement was made in which the observational data were limited to the 366 reflections measured from the two samples at 4 K which had $\sin \Theta/\lambda \leq 0.4 \text{ \AA}^{-1}$. The extinction and nuclear structural parameters were constrained to the values obtained from the refinement of the D9 data measured at 20 K and the magnetization was modelled using the free-ion form factors. An R -factor of 0.032, $R_w = 0.027$, was reached in this low angle refinement based on observations for which the magnetic contribution is generally larger.

Several additional refinements were then made, the first being one in which the atomic positional parameters were refined using the 843 data for which $\sin \Theta/\lambda \geq 0.4 \text{ \AA}^{-1}$ whilst fixing the parameters of the magnetic model to the values obtained from the initial refinement. No significant changes in the atomic positional parameters could be associated with the onset of magnetic order, so these parameters were fixed at their 20 K values in all the subsequent refinements.

The true radial dependence of the Fe1 and Fe2 form factors was then investigated. Refinements carried out using the low angle data set to $\sin \Theta/\lambda = 0.4 \text{ \AA}^{-1}$, a purely magnetic $\{h0l\}$ data set with h odd and $\sin \Theta/\lambda \leq 0.5 \text{ \AA}^{-1}$ and finally all 1209 data, all indicated that the observed form factors are better modelled by including a contribution with a $\langle j_2 \rangle$ radial dependence (Watson and Freeman 1961) and that this contribution is larger for Fe2 than for Fe1. The final R -factor for the total data set was 0.044, $R_w = 0.031$ and $\chi^2 = 26$. In no case did the addition of these components significantly modify the moment directions, the final magnetic model parameters being:

Ion	Θ (deg)	Φ (deg)	Moment (μ_B)
Fe1	30(2)	48(2)	4.51(6)
Fe2	6(2)	90(7)	4.00(5)

Here, the moment direction is specified by the polar angles Θ , Φ with Θ measured from [001] and Φ from the plane containing [001] and a^* .

The magnitudes of the $\langle j_2 \rangle$ contributions were less well defined, with mean values of 0.6(3) and 1.0(3) μ_B for Fe1 and Fe2 respectively. Since the moments found on the two ions imply that the orbital contribution is significant for Fe1 but quenched for Fe2, we may conclude that the $\langle j_2 \rangle$ contribution to Fe1 is in complete accord with a dipole approximation to the scattering by its orbital moment, but that the $\langle j_2 \rangle$ contribution to Fe2 indicates that its spin-only form factor is expanded relative to that of the free ion due to a contraction in the radial dependence of the Fe2 3d wavefunctions of some 8%. It should be noted that similar indications are given by the amplitudes of the $\langle j_2 \rangle$

contributions to the ferromagnetic components of moment reported in section 5, though the uncertainties are greater.

7. Discussion

A combination of unpolarized and polarized beam diffractometry has allowed us to establish a more accurate magnetic model for ludlamite. The ferromagnetic components of moment implied by the model are $1.67(3)$ and $0.42(2) \mu_B$ for Fe1 and Fe2, respectively, compared to the values of $1.73(3)$ and $0.62(2) \mu_B$ found in the D3 experiment. The average ferromagnetic moment in zero field given by our unpolarized beam refinement is therefore $0.84(2) \mu_B/\text{Fe}^{2+}$, in excellent agreement with the zero field extrapolation of $0.83(1)$ made by Meijer *et al* (1968) from their 4.2 K magnetization data.

Our model also shows that non-collinearity is not confined to the canting of the moments away from the *a-c* plane produced by the Dzyaloshinsky–Moriya interaction. The components of the Fe1 and Fe2 moments in the *a-c* plane make angles of $21(2)^\circ$ and $0(1)^\circ$ to $[001]$ in β obtuse, respectively. The average moment direction in the *a-c* plane is therefore 7.5° from $[001]$ in β obtuse, which agrees with Abrahams' conclusion that it was within 10° of this direction. However, the differences between both the in-plane and out of plane angles of the moments results in an angle of $26(2)^\circ$ between the moments on the inequivalent iron ions in the predominantly ferromagnetically coupled triads illustrated in figure 2. The average value for the Fe^{2+} moment is $4.17(6) \mu_B$, somewhat lower than the value of $4.6(2) \mu_B$ found by Abrahams (1966).

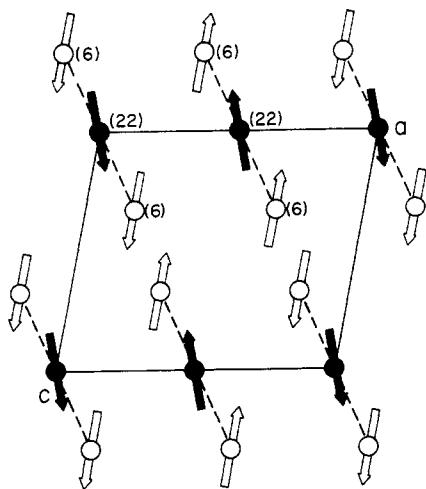


Figure 2. The $[010]$ projection of the magnetic coupling in ludlamite. The Fe1 atoms are shown as solid and the Fe2 atoms as open circles. The angles in degrees made by the moments to the (010) plane are given in parentheses.

The much larger contribution to the weak ferromagnetism made by Fe1 suggests that its moment direction is more strongly influenced by the spin–orbit coupling to the electric field from its coordinating anions than is Fe2. This observation is consistent with the higher moment and hence higher orbital contribution found for Fe1, so we may therefore expect that its magnetization direction will be close to its axis of quantization. Inspection of figure 3, in which the moment directions on the two Fe^{2+} sites are related to their atomic environment, shows clearly that for Fe1 the moment is parallel to the pseudo

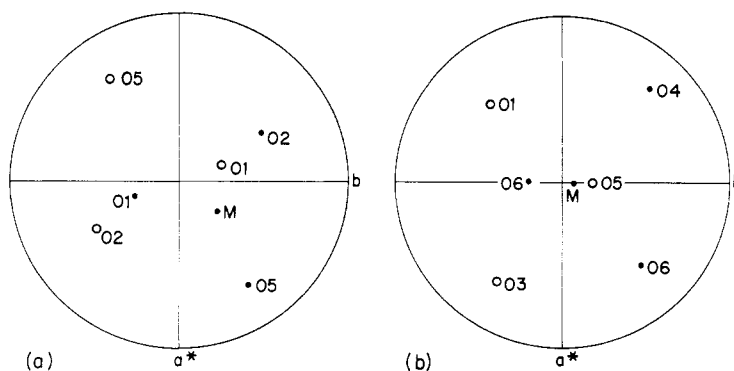


Figure 3. Stereograms showing the orientation of the iron moments, M , with respect to the local coordination: (a) Fe1 and (b) Fe2.

inverse triad axis formed by the two triangular arrays of atoms O1, O2 and O5 and their centrosymmetrically related partners. Calculation shows that the perpendicular distances from Fe1 to the four groups of three oxygen atoms defining the faces of the coordination octahedron are 1.102(2), 1.206(2), 1.235(2) and 1.348(2) Å with the O1, O2 and O5 atoms defining the longest of them. This distortion would appear to be sufficient to remove a large part of the orbital degeneracy responsible for quenching the orbital moment in higher symmetry materials. Further evidence for the large single-ion anisotropy of Fe1 is provided by the differences between the zero field and 1.5 T ferromagnetic components of moment found for the two Fe^{2+} sites; the field induced component of moment appears to be much larger for Fe2 than for Fe1, the magnitude of the whole moment is little changed. It is perhaps remarkable that the lower symmetry of the Fe2 site is less effective in raising the orbital degeneracy. Evidence for large Fe^{2+} single-ion anisotropy has recently been found by Figgis *et al* (1990) who made polarized beam measurements of the aligned paramagnetic moment in deuterated ferrous ammonium Tutton salt at 1.5 K, 4.6 T. Their analysis clearly shows that the Fe^{2+} moment remains effectively locked to a particular direction, which is again a pseudo triad defined by three of the six coordinating water oxygens.

The magnitude of the small average moment of 0.02(1) μ_B on the oxygen ligands in the ferromagnetic moment distribution and the expansion of the Fe^{2+} form factor compared to that of the free ion are in agreement with the more detailed study of covalency in the hexaaqua Fe^{2+} ion by Figgis *et al* (1990) which showed that there is delocalisation of the moment away from the iron atom onto the water ligands of 6.5% and a radial contraction of the 3d wavefunctions on the Fe^{2+} ion of some 10%.

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