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Zn location in the *W*-type hexagonal ferrite $SrZnCoFe_{16}O_{27}$

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The title compound, $SrZnCoFe_{16}O_{27}$ (ZnCo-*W*), strontium zinc cobalt hexadecairon oxide, crystallizes in space group $P6_3/mmc$, with the Sr atom at a site with $\bar{6}m2$ symmetry and Zn^{2+} located at two tetrahedral sites (4*e* and 4*f*, each with $3m$ symmetry) of the spinel blocks. The Zn occupancy is 36% on equipoint 4*e* and 14% on 4*f*. The enrichment of diamagnetic ions on one of seven sublattices is thought to be responsible for the high temperature dependence of the saturation magnetization.

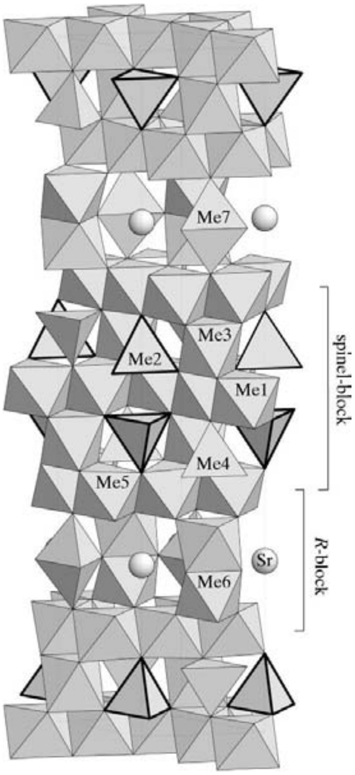

Figure 1
A polyhedral representation of the $SrZnCoFe_{16}O_{27}$ *W*-type hexagonal ferrite. Me1–Me7 denote the different polyhedra.

Comment

W-Type hexagonal ferrites are ferrimagnetic oxides in which the cations are distributed over seven sublattices (one bipyramidal, two tetrahedral and four octahedral sites, Fig. 1). At low temperatures, Zn-containing *W* ferrites have the highest saturation magnetization of all ferrites. According to their well known site preference, the diamagnetic Zn^{2+} ions are incorporated in the tetrahedral interstices of the close packing of O atoms. They exclusively reduce the magnetic moments of the minority sublattice so that the resulting total magnetization is enhanced. In the solid solution series $SrZn_xCo_{2-x}Fe_{16}O_{27}$, no further increase of the low-temperature saturation magnetization is found for $x > 1.5$, indicating that the diamagnetic dilution becomes high enough to weaken severely the magnetic superexchange interactions and disturb the otherwise collinear spin arrangement. The magnetization of Zn_xCo_{2-x}-*W* ferrites with high Zn contents shows a relatively strong decrease with increasing temperature, so that, at room temperature, their saturation magnetization is no higher than that of Zn-free *W* ferrites (Graetsch *et al.*, 1984).

Partial combined substitution of Li^+/Fe^{3+} for Zn^{2+} into Zn_2-*W* ferrite, however, yields an approximately 15% higher saturation magnetization at room temperature for the composition $SrZnLi_{0.5}Fe_{16.5}O_{27}$, whereas both compounds have approximately the same saturation magnetization at 0 K (Ram & Joubert, 1991). This has been ascribed to a selective incorporation of Li^+ in the octahedral sites of the *R* blocks (Ram & Joubert, 1991; Albanese *et al.*, 1994), which also belong to the minority sublattice. The distribution of diamagnetic cations over several sites of the minority sublattice obviously reduces the temperature dependence of the saturation magnetization.

The present crystal structure refinement of $SrZnCoFe_{16}O_{27}$ (ZnCo-*W*) was undertaken in order to obtain more information about the cation distribution, which might be useful in elucidating more details of the magnetization behaviour.

In contrast with magnetoplumbite and spinel, the tetrahedral sites in the spinel blocks of the *W*-type structure are not symmetrically equivalent. In $SrZn_2Fe_{16}O_{27}$, 50% of the available tetrahedral sites are occupied by Zn ions. Zn is enriched on equipoint 4*e* with an occupancy of about $\frac{3}{4}$, compared with $\frac{1}{4}$ on 4*f* (Graetsch *et al.*, 1986). The old data set for Zn_2-*W* has been reprocessed using *SHELXL*97 (Sheldrick, 1997). Application of an extinction correction yielded more precise site-occupancy factors of 0.695 (2) and 0.305 (2) for equipoints 4*e* (Me2 tetrahedron) and 4*f* (Me4 tetrahedron), respectively. The corresponding values for ZnCo-*W* are 0.3557 (1) for Me2 and 0.1443 (1) for Me4 (Fig. 1). Thus, the ratio of Zn atoms on the Me2 and Me4 tetrahedral sites is approximately constant in ZnCo-*W* and Zn_2-*W*, with a value of 2:1. Both tetrahedra are distorted towards trigonal pyramids, elongated along the *c* axis for Me4 and shortened for Me2. The mean M—O distances are slightly longer for the Zn-rich Me2 polyhedron (1.917 Å, compared with 1.908 Å for Me4).

Due to the small difference in the X-ray scattering factors for Co^{2+} and Fe^{3+}, the location of the Co ions in ZnCo-*W* could only be detected by the different sizes of the ions and

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the corresponding interatomic Me—O distances. Comparison with $BaCo_2Fe_{16}O_{27}$, $SrZn_2Fe_{16}O_{27}$ and $SrFe_{12}O_{19}$ indicated an enrichment of Co^{2+} (high-spin state) in the Me1 octahedra within the spinel blocks. This finding is in accordance with the results of a neutron diffraction study on $BaCo_2Fe_{16}O_{27}$ (Collomb *et al.*, 1986).

The trigonal bipyramid in the *R* blocks of hexagonal ferrites is known to show some disorder, which is mainly of dynamic origin. The position of the central cation (Fe7) is described by a split-atom model, where Fe^{3+} ions with half-occupancy are displaced from the centre of the bipyramid and the horizontal mirror plane in either direction along the *c* axis. The distance between the positions of the split atoms is 0.301 (2) Å in ZnCo-*W*, which is in the range of other *W*-type and magnetoplumbite-type hexaferrites (Graetsch & Gebert, 1996). The displacement ellipsoids of the three horizontal O7 and two apical O6 atoms are elongated perpendicular and parallel to the *c* axis, respectively, indicating that the O atoms are affected by the vibrations of Fe7 through the triangle formed by O7 atoms on the horizontal mirror plane.

Experimental

ZnCo-*W* crystals with a size of up to *ca* 3 mm were grown from an SrO/B_2O_3 flux by slow cooling of the melt in a platinum crucible from 1613 to 1223 K at a rate of 2.5 K h^{-1}. The crystals were removed from the solidified flux with hot dilute HNO_3. Chemical analysis showed that deviation from stoichiometric $SrZnCoFe_{16}O_{27}$ was negligible and that the FeO content was less than 1% of the starting amount of Fe_2O_3 (Graetsch *et al.*, 1984).

Crystal data

$SrZnCoFe_{16}O_{27}$
$M_r = 1537.52$
Hexagonal, $P6_3/mmc$
$a = 5.902$ (1) Å
$c = 32.78$ (1) Å
$V = 988.9$ (4) Å^3
$Z = 2$
$D_x = 5.164$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 30 reflections
$\theta = 2.5$–42.5°
$\mu = 16.14$ mm^{-1}
$T = 293$ (2) K
Plate, black
0.33 × 0.15 × 0.05 mm

Data collection

Oxford Xcalibur diffractometer with a Sapphire2 CCD area-detector
ω and φ scans
Absorption correction: numerical after shape optimization (*CrysAlisRED*; Oxford Diffraction, 2002)
$T_{\min} = 0.085$, $T_{\max} = 0.468$
16 610 measured reflections
687 independent reflections
659 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$
$\theta_{\max} = 31.4^\circ$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -45 \rightarrow 45$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.056$
$S = 1.30$
687 reflections
62 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0178P)^2 + 2.9005P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 0.85$ e Å^{-3}
$\Delta\rho_{\min} = -0.68$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00828 (18)

Lattice parameters were refined from a Guinier X-ray powder diagram using Si as the internal standard. Soft constraints were used in order to restrict the sum of the Zn atoms on both tetrahedral sites to one Zn atom per formula unit, and to fix full occupancy of the Me2 and Me4 tetrahedral sites by both Zn^{2+} and Fe^{3+}. From interatomic distance considerations, it was assumed that Co occupies one third of the octahedral Me1 positions.

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2002); cell refinement: *LCLSQ* (Burnham, 1963); data reduction: *CrysAlisRED* (Oxford Diffraction, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS for Windows* (Dowty, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1585). Services for accessing these data are described at the back of the journal.

References

Albanese, G., Sanchez Ll, J. L., Lopez, G., Diaz, S., Leccabue, F. & Watts, B. E. (1994). *J. Magn. Magn. Mater.* **137**, 313–321.

Burnham, C. W. (1963). *LCLSQ*. Carnegie Institution, Washington, DC, USA.

Collomb, A., Lambert-Andron, B., Boucherle, J. X. & Samaras, D. (1986). *Phys. Status Solidi A*, **96**, 385–395.

Dowty, E. (1994). *ATOMS for Windows*. Version 3.0. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Graetsch, H. & Gebert, W. (1996). *Z. Kristallogr.* **211**, 25–30.

Graetsch, H., Gebert, W. & Sahl, K. (1986). *Z. Kristallogr.* **175**, 139–144.

Graetsch, H., Haberey, F., Leckebusch, R., Rosenberg, M. S. & Sahl, K. (1984). *IEEE Trans. Magn.* **12**, 495–500.

Oxford Diffraction (2002). *CrysAlisCCD* and *CrysAlisRED*. Versions 1.69. Oxford Diffraction, Oxford, England.

Ram, S. & Joubert, J. C. (1991). *J. Magn. Magn. Mater.* **99**, 133–144.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.