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Redetermination of the iron–zinc phase $FeZn_{13}$

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In iron tridecazinc, the $FeZn_{13}$ unit cell contains two Zn_{12} icosahedra which are Fe-centred and two Zn_2 dumb-bells coordinated by eight icosahedra. Zn_{12} icosahedra form chains along the *c* axis by vertex-sharing, and are further interlinked through octahedra-sharing and vertex-to-vertex bonds.

Comment

In our general study of icosahedron-based intermetallic phases, we have reinvestigated the Fe—Zn binary system. Several phases, *e.g.* cubic γ-Fe_3Zn_{10} (Brandon *et al.*, 1974) and monoclinic ζ-$FeZn_{13}$ (Brown, 1962), were known but their structures poorly determined, while hexagonal δ-$FeZn_{10}$ has not yet been structurally characterized. For $FeZn_{13}$, intensities have been determined visually from Weissenberg photographs and the structure refined in the monoclinic space group *C*2/*m* with reflections from the [010] and [001] projections. Agreement factors *R*(*F*) were 0.121 ([010] projection) and 0.098 ([001] projection). Such refinements based on a restricted number of intensities led to an incomplete description of the structure. Since the limited quality of the data did not allow any atomic differentiation, positions 2*a* and 2*c* were ambiguously assigned to Fe and/or Zn atoms. Difficulty in obtaining good quality single crystals (having sharp reflections) was underlined by Brown (1962) who prepared $FeZn_{13}$ by an electrochemical process. With a flux method, we have obtained needles which display satisfactory diffraction spots. Structural refinement has allowed location of Fe atoms at only the 2*c* position, the centre of the zinc icosahedron. In the structure, icosahedra are packed in chains along the *c* axis by sharing opposite vertices. Furthermore, their linking is achieved by octahedra-sharing in planes parallel to ($\bar{4}02$) and by vertex-to-vertex bonding in planes parallel to (001). Each icosahedron is then surrounded by 12 alike units. Zn3 atoms form dumb-bells which complement the metallic bonding.

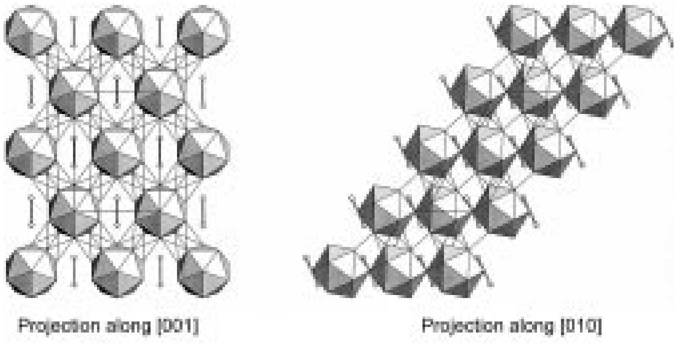
Projection along [001] Projection along [010]

Figure 1
Representation of the atomic packing in the $FeZn_{13}$ unit cell.

Experimental

Single crystals of $FeZn_{13}$ were obtained using a flux method. A Fe/Zn mixture containing 98 at.% Zn was melted at 1000 K in a silica tube, homogenized for 10 d and then air quenched. The resulting ingot (2.9 g) was inserted with dried $ZnCl_2$ (5 g) in a silica tube, flame sealed, heated to 973 K for a week and then cooled at a rate of 3 K h^{-1} to room temperature for crystal growth. The nearly spherical ingot obtained displayed on its surface, at the interface with $ZnCl_2$, some small flat needles. Chemical analysis, $FeZn_{13.08\,(6)}$, indicated the ζ phase, which has a very narrow range in the phase diagram (Bastin *et al.*, 1974, 1977).

Crystal data

$FeZn_{13}$
$M_r = 905.66$
Monoclinic, $C2/m$
$a = 13.394$ (3) Å
$b = 7.5980$ (9) Å
$c = 5.066$ (2) Å
$\beta = 127.23$ (2)°
$V = 410.49$ (19) Å^3
$Z = 2$
$D_x = 7.327$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.40$–20.59°
$\mu = 38.817$ mm^{-1}
$T = 293$ (2) K
Triangular platelet, metallic grey
0.10 × 0.05 × 0.02 mm

Data collection

Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: numerical (*SHELX*76; Sheldrick, 1976)
$T_{\min} = 0.118$, $T_{\max} = 0.462$
1091 measured reflections
604 independent reflections
439 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.059$
$\theta_{\max} = 29.91$°
$h = -18 \rightarrow 18$
$k = 0 \rightarrow 10$
$l = -7 \rightarrow 7$
3 standard reflections every 100 reflections intensity decay: none

Table 1
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2).

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
Zn1	0	0	0	0.0134 (5)
Fe2	0	0	1/2	0.0045 (5)
Zn3	0.11406 (12)	1/2	0.2942 (3)	0.0109 (4)
Zn4	0.22002 (13)	0	0.0693 (4)	0.0148 (4)
Zn5	0.07635 (9)	0.29477 (17)	0.8340 (3)	0.0172 (3)
Zn6	0.17545 (9)	0.17895 (15)	0.5486 (3)	0.0114 (3)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.109$
$S = 1.025$
604 reflections
40 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 2.147$ e Å^{-3}
$\Delta\rho_{\min} = -1.499$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0019 (5)

Table 2
Selected bond lengths (Å).

Zn1—Fe2	2.5330 (10)	Zn4—Zn6^{i}	2.6939 (19)
Zn1—Zn6	2.6819 (14)	Zn4—Zn5^{i}	2.7137 (15)
Zn1—Zn4	2.7488 (17)	Zn4—Zn6^{iii}	2.8945 (14)
Zn1—Zn5^{i}	2.7946 (14)	Zn4—Zn5^{iii}	2.9143 (18)
Fe2—Zn4^{ii}	2.5919 (17)	Zn4—Zn6	3.139 (2)
Fe2—Zn6	2.5945 (11)	Zn5—Zn6	2.6358 (17)
Fe2—Zn5	2.6136 (12)	Zn5—Zn5^{v}	2.694 (3)
Zn3—Zn4^{iii}	2.582 (2)	Zn5—Zn6^{v}	2.8277 (17)
Zn3—Zn5^{i}	2.5878 (17)	Zn5—Zn6^{vii}	2.8797 (18)
Zn3—Zn6	2.6468 (13)	Zn5—Zn5^{viii}	3.119 (3)
Zn3—Zn3^{iv}	2.683 (3)	Zn5—Zn6^{ix}	3.135 (2)
Zn3—Zn5^{v}	2.7119 (16)	Zn6—Zn6^{iii}	2.567 (2)
Zn3—Zn6^{vi}	2.7775 (16)	Zn6—Zn6^{x}	2.719 (2)

Symmetry codes: (i) $x, y, z-1$; (ii) $-x, -y, -z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (iv) $-x, 1-y, -z$; (v) $-x, y, 1-z$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (vii) $\frac{1}{2}-x, \frac{1}{2}-y, 2-z$; (viii) $x, 1-y, z$; (ix) $x, y, 1+z$; (x) $x, -y, z$.

Refinement with a Zn atom at the 2*a* position and an Fe atom at the 2*c* position gives $R(F) = 0.0417$, while the opposite (Fe at 2*a* and Zn at 2*c*) leads to $R(F) = 0.0534$. Refinement of Fe/Zn statistical site occupation would give 86 (2)% Zn on the 2*a* site and 91 (5)% Fe on the 2*c* site with $R(F) = 0.0415$. Within the 3σ limits, we consider the 2*a* and 2*c* sites fully occupied by Zn and Fe, respectively.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: local program; program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1065). Services for accessing these data are described at the back of the journal.

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