Siemens (1989). *P3/PC Diffractometer Program*. Version 3.13. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1991). *XDISK. Data Reduction Program*. Version 3.11. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Yarmolyuk, J. R., Gryn, J. N. & Gladyshevskii, E. I. (1979). *Dopov. Akad. Nauk Ukr. RSR Ser. A*, pp. 771–775.

(Fe,Ni)Zn$_{6.5}$, a Superstructure of γ-Brass

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Abstract

The structure of (Fe,Ni)Zn$_{6.5}$ (Pearson symbol $cF412$) is closely related to that of Fe$_{22}$Zn$_{78}$ [$cF408$; Koster & Schoone (1981). *Acta Cryst.* B37, 1905–1907]. Both structures may be considered as superstructures of γ-brass, but in the title structure the occupation of two fourfold positions that are vacant in Fe$_{22}$Zn$_{78}$ leads to further distortions away from the parent structure.

Comment

The binary systems Fe–Zn and Ni–Zn contain a plethora of complex phases, several being structurally related to γ-brass. To date, few of the compounds reported from these systems have been structurally characterized (Bastin, van Loo & Rieck, 1974).

In an attempt to grow crystals of suitable quality and size for an X-ray crystallographic study of the Zn-rich phases in the Fe–Zn system, Zn, in large excess, and Fe were mixed with equal portions (by volume) of ZnO to provide a porous matrix for the easier extraction of single crystals. The mixture was placed in stainless steel ampoules and sealed under Ar, heated to 1300 K in 2 h and cooled to room temperature at a rate of 30 K h^{-1}. The reaction product contained thin hexagonal plates, stacked together like a deck of playing cards. Single crystals were separated by cutting the 'deck' with a scalpel. The crystals were subjected to primary X-ray analysis (symmetry, crystal quality) using photographic methods. Microprobe analysis gave an approximate composition of FeNiZn$_{18}$, showing that the Zn had attacked the ampoule material.

The reciprocal lattice was examined meticulously for signs of further superstructure. A doubling of the unit cell along the ⟨111⟩ direction would yield a hexagonal unit cell, about 60 × 12.5 × 12.5 Å; this is a possible candidate for the structure of the phase 'FeZn$_{10}$' (Bastin, van Loo & Rieck, 1974). No signs of superstructure reflections were detected, however, either by X-ray or electron diffraction.

The crystal structure of (Fe,Ni)Zn$_{6.5}$ is closely related to that of Fe$_{22}$Zn$_{78}$ (Koster & Schoone, 1981) and both may be considered as superstructures of γ-brass. One salient feature that all three structures have in common is a cluster built up from four slightly distorted icosahedra meeting around an empty central tetrahedron (Westman, 1972). In Fig. 1(*a*) the structure of γ-brass is shown as two identical interpenetrating f.c.c. (diamond) nets (grey–green and marine–light blue) of such clusters. Between the two nets a separating surface may be inserted. This is the infinite periodic minimal surface *D*, first described by Schwarz (1890). If one of the cluster nets that make up γ-brass is exchanged for a net consisting of truncated tetrahedra (light blue) and icosahedra (dark blue) meeting four-by-four around an octahedron, the structure of Fe$_{22}$Zn$_{78}$ is achieved (Fig. 1*b*). The dark blue icosahedra form pieces of the pyrochlore structure. The truncated tetrahedra (light blue) are empty and hence constitute a 16-atom f.c.c. block. In the structure of (Fe,Ni)Zn$_{6.5}$, two of the fourfold positions in the spacegroup $F\bar{4}3m$ (No. 216) are occupied. The position at the origin, which is the centre of the empty tetrahedron in one of the remaining γ-brass clusters (there are two symmetrically inequivalent γ-brass clusters in Fe$_{22}$Zn$_{78}$), is partially occupied (about $\frac{2}{3}$) and this leads to a split position and two different configurations around this site (*cf.* Table 1). If the origin is unoccupied, a classical γ-brass cluster results and the position of the Fe,Ni3 atom is that of Fe,Ni32. Where the origin is occupied, the cluster of icosahedra distorts to a cluster of four rhombic dodecahedra (grey, Fig. 1*c*), each missing one vertex (Fig. 2). The rhombic faces are slightly bent as can be seen in Fig. 2. This cluster constitutes a substantial b.c.c. block.

Further, in the title compound the position $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ is fully occupied and the positions at the faces of the truncated tetrahedron are forced outwards, generating a Frihauf polyhedron. This change is clearly seen in Figs. 1(*b*) and 1(*c*). The faces of the truncated tetrahedron (light blue) are planar in Fig. 1(*b*), while the corresponding faces of the Frihauf polyhedron in Fig. 1(*c*) are convex, showing only the outer positions. This Frihauf polyhedron is unusual in the sense that the vertices and the centre are occupied by
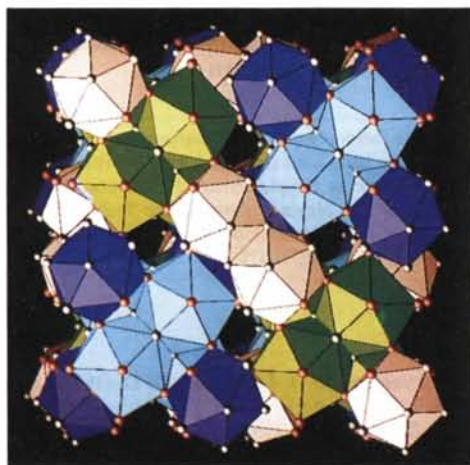
(a)
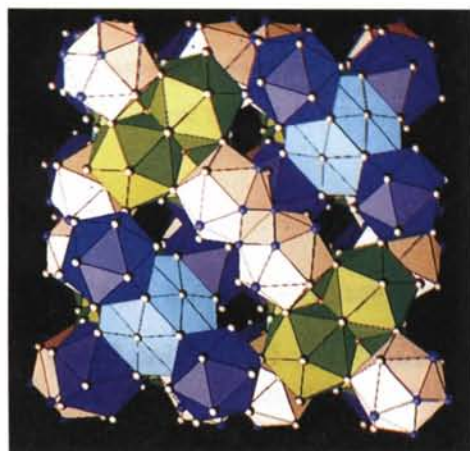
(b)
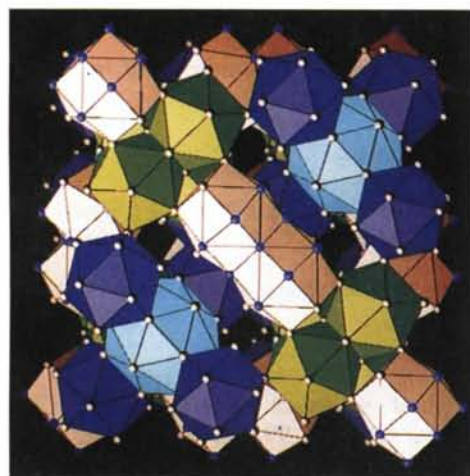
(c)

Fig. 1. The three structures compared: (a) γ-brass, grey spheres are Cu, red spheres are Zn, all clusters (green, grey, marine and light blue) are equivalent; (b) $Fe_{22}Zn_{78}$; (c) $(Fe,Ni)Zn_{6.5}$, the position at the origin is occupied.
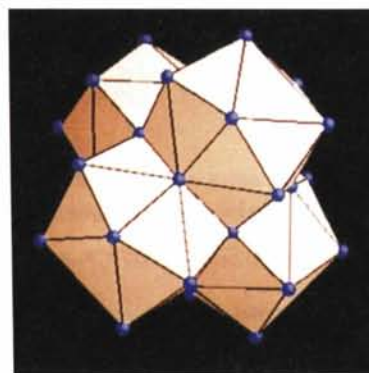

Fig. 2. The full cluster of four rhombic dodecahedra formed by the addition of one atom to a γ-brass cluster. Half of this unit is seen at the centre of Fig. 1(c). Note that one vertex is missing from each rhombic dodecahedron.

the same element (Zn). Hence the ratio of the two different vertex-to-centre distances is unusual (the fourfold vertex position is closer to the centre than the twelvefold position is. The complete structure of $(Fe,Ni)Zn_{6.5}$ is shown in Fig. 1(c) and the distances in the polyhedra are given in Table 2.

Experimental

Crystal data

$(Fe,Ni)Zn_{6.5}$
$M_r = 482.2$
Cubic
$F\bar{4}3m$
$a = 18.0838\ (53)$ Å
$V = 5913.8\ (51)$ Å^3
$Z = 55$
$D_x = 4.48$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 69
  reflections
$\theta = 8.6–23.1°$
$\mu = 39.56$ mm^{-1}
$T = 298$ K
Triangular plate
$0.26 \times 0.26 \times 0.14$ mm
Metallic

Data collection

Huber diffractometer
$\omega/2\theta$ scans
Absorption correction:
  by integration from crystal
  shape
  $T_{min} = 0.029$, $T_{max} = 0.308$
5414 measured reflections
316 independent reflections

210 observed reflections
  $[F_o^2 > 3\sigma(F_o^2)]$
$R_{int} = 0.144$, $R_w = 0.098$
$\theta_{max} = 25°$
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 21$
3 standard reflections
  frequency: 60 min
  intensity variation: 4%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.057$
$S = 1.3162$
210 reflections

Extinction correction: Becker
  & Coppens (1975)
  isotropic
Extinction coefficient:
  0.1948×10^4

64 parameters
$w = 1/[\sigma^2(F_o) + (0.05F_o)^2]$
$(\Delta/\sigma)_{max} = 0.013$
$\Delta\rho_{max} = 2.42$ e Å^{-3}
$\Delta\rho_{min} = 1.63$ e Å^{-3}

Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1974, Vol. IV)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	x	y	z	U_{eq}
Zn1	1.0	0.0941 (2)	0.0941 (2)	0.2305 (3)	0.015 (1)
Zn2	1.0	0.0590 (2)	0.0590 (2)	0.7321 (3)	0.016 (1)
Zn3	1.0	0.1617 (3)	0.1617 (3)	0.9783 (4)	0.040 (2)
Zn4	1.0	0.1437 (2)	0.1437 (2)	0.4698 (3)	0.012 (1)
Zn5	1.0	0.2010 (2)	0.2010 (2)	0.5936 (3)	0.016 (1)
Zn6	1.0	0.3916 (4)	0	0	0.010 (2)
Zn7	1.0	0.0722 (4)	1/4	1/4	0.021 (2)
Zn8	1.0	0.0850 (3)	0.0850 (3)	0.0850 (3)	0.027 (2)
Zn9	1.0	0.1978 (3)	0.1978 (3)	0.1978 (3)	0.017 (1)
Zn10	1.0	0.3352 (3)	0.3352 (3)	0.3352 (3)	0.016 (1)
Zn11	1.0	0.8339 (4)	0.8339 (4)	0.8339 (4)	0.023 (2)
Zn12	1.0	3/4	3/4	3/4	0.006 (3)
Fe,Ni1	1.0	0.1586 (7)	0	0	0.039 (3)
Fe,Ni2	1.0	0.5998 (3)	0.5998 (3)	0.5998 (3)	0.005 (1)
Fe,Ni31	0.25 (2)	0.926 (2)	0.926 (2)	0.926 (2)	0.04 (1)
Fe,Ni32	0.53 (2)	0.945 (1)	0.945 (1)	0.945 (1)	0.036 (5)
Fe,Ni4	0.68 (1)	0	0	0	0.016 (1)

Table 2. *Centre-to-vertex distances* (Å) *in the polyhedra in Fig.* 1(c)

Rhombic dodecahedra (grey)	Zn8 —3 Zn1	2.64
	—3 Zn3	2.75
	—3 Fe,Ni1	2.55
	—3 Fe,Ni3	2.89
	— Fe,Ni4	2.66
Icosahedra (green)	Zn10—3 Zn1	2.62
	—3 Zn4	2.49
	—3 Zn7	2.75
	—3 Zn9	2.62
Icosahedra (marine)	Fe,Ni2—3 Zn2	2.61
	—3 Zn4	2.61
	—3 Zn4	2.59
	—3 Zn6	2.56
Frihauf polyhedra (light blue)	Zn12—12 Zn5	3.09
	—4 Zn11	2.62

The composition was determined by means of energy dispersive X-ray analysis with a Jeol 840 scanning electron microscope. Since Fe and Ni are near neighbours in the Periodic Table, straddling Co, the mixed (Fe,Ni) positions were refined as pure Co. The final composition (1:6.5) differs from the microprobe analysis (1:9), but the deviation is within the uncertainty of the analysis and further details of the nature of the atomic species in the split position are uncertain, as is the nature of the atom at the origin that generates the split. The structure (Table 1) was refined from a starting model based on the structure of Fe$_{22}$Zn$_{78}$. All atoms except the (Fe,Ni) at the split position were refined anisotropically; the occupancy factors were refinable, but varied little from unity, with the exception of the occupancy at the origin and the split position. The nature of the atoms at the different positions was determined from the occupancy refinement and this determination was in agreement with the interatomic distances. The minimum Zn—Zn distance is 2.49 Å (2.64 Å in the element), minimum Zn—(Fe,Ni) 2.43 Å and min-

imum (Fe,Ni)—(Fe,Ni) 2.32 Å [Fe—Fe is 2.48 Å in the element and Ni—Ni is 2.40 Å (Donohue, 1974)]. All computer programs used are as described by Lundgren (1982).

References

Bastin, G. F., van Loo, F. J. J. & Rieck, G. D. (1974). *Z. Metallk.* **65**, 656–660.
Becker, P. J. & Coppens, P. (1975). *Acta Cryst.* A31, 417–425.
Donohue, J. (1974). In *The Structures of the Elements.* New York: Wiley.
Koster, A. S. & Schoone, J. C. (1981). *Acta Cryst.* B37, 1905–1907.
Lundgren, J.-O. (1982). Report No. UUIC-B13-4-05. Univ. of Uppsala, Sweden.
Schwarz, H. A. (1890). *Gesammelte Matematische Abhandlungen,* 2nd ed. Berlin: Springer Verlag.
Westman, S. (1972). Thesis, Univ. of Stockholm, Sweden.

Neutron and X-ray Diffraction Study of Magnesium Phosphite Hexahydrate, [Mg(H$_2$O)$_6$]$^{2+}$ [PHO$_3$]$^{2-}$

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Abstract

The original structure determination [Corbridge (1956). *Acta Cryst.* **9**, 991–994] indicated an ordered structure of [PHO$_3$]$^{2-}$ and [Mg(H$_2$O)$_6$]$^{2+}$ ions lying on threefold symmetry axes. Current refinement of H-atom positions allows full elucidation of the hydrogen-bonding network. This network connects each [PHO$_3$]$^{2-}$ anion to seven [Mg(H$_2$O)$_6$]$^{2+}$ cations by nine hydrogen bonds. Each [Mg(H$_2$O)$_6$]$^{2+}$ com-