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Refinement of the Structure of β-Manganese and of a Related Phase in the Mn–Ni–Si System*

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β-Manganese is cubic, space group $P4_132$ or $P4_332$, a = 6·315 (2) Å, 20 atoms per cell, *A*13 *Strukturbericht* type, D_x = 7·24 g cm^{-3}. Full-matrix least-squares refinement leads to $R(F)$ = 0·030 for all 142 independent reflections. β-$Mn_{66}Ni_{20}Si_{14}$ is cubic, $P2_13$, a = 6·292 (2) Å, structure derived from β-Mn, 20 atoms per cell, D_x = 6·92 g cm^{-3}. Refinement leads to $R(F)$ = 0·043 for all 372 independent reflections, Friedel pairs separated. In the elemental structure Mn(1) is in icosahedral coordination in an eightfold position, which is split into two fourfold positions in the ternary phase, respectively occupied by (mainly) Si and (mainly) Ni. In the elemental and ternary compounds Mn(2) occupies a twelvefold position, on a twofold axis and a pseudo twofold axis respectively. The coordination polyhedron of this Mn atom is a highly distorted form of the CN 14 polyhedron type which occurs in tetrahedrally close-packed structures. There are per unit cell four interstices with the shape of 'metaprisms' and a rotation angle between end faces of 34°.

Introduction

β-Manganese is the form of Mn stable between 727 and 1095 °C. Its structure was first determined by Preston (1928) from single-crystal data. A cell with doubled cell dimensions was described for β-Mn by Wilson (1935). Several binary and ternary alloys with the β-Mn structure have been described. Bardos, Malik, Spiegel & Beck (1966) found large β-Mn phase fields in ternary systems at 1000 °C of transition elements with Si, Ge, or Sn. Professor Beck kindly sent us a sample of material in the Mn–Ni–Si system of composition $Mn_{52}Ni_{29}Si_{19}$, and called by him the *W* phase; however, this was reported to contain a small amount of a second phase. All fragments selected from the sample for diffraction work were found to be single crystals with the β-Mn-type structure. The powder diffraction diagram of the bulk sample contains β-Mn lines, as does also the diagram published by Bardos *et al.* (1966). Evidently the bulk sample contains at least two phases, and the minority β-Mn-type phase component happened to be selected for diffraction because its fragments were more visually attractive for that purpose. The composition of the β-Mn-type component cannot be accurately determined by non-diffraction means because of the virtual impossibility of separating out a sufficiently large specimen for analysis, but presumably lies within the phase field established by Bardos *et al.* (1966). In the present study, a composition within this field is strongly implied by the results of position-occupancy refinement. The structure of the *W* phase component itself remains to be determined.

The present study was undertaken to establish and refine the correct β-Mn structure, both in the elemental state and in the ternary Mn–Ni–Si system. In both cases no evidence was found for the cell with doubled cell dimensions. Also, no evidence for doubled cell dimensions was found by Kasper & Roberts (1956) in their neutron powder diffraction study of β-Mn.

Experimental

β-Mn was prepared by heating Mn flakes (99·97%) sealed in a quartz tube under Ar in a Varian–Marshall tube furnace over a period of 5 d from 690 to 740 °C, keeping the temperature at 850 °C for three more days, and then quenching in water. The crystal fragment of β-Mn used in the X-ray study had an irregular shape with average radius 0·003 cm. The crystal fragment of the ternary phase had an average radius of 0·002 cm. The crystal data for both phases are given in Table 1. Intensity data were collected with Mo $K\alpha$ radiation on an automated Syntex $P\bar{1}$ diffractometer equipped with a graphite monochromator. θ–2θ scans were used, the scan speed was 1° min^{-1}, and the 2θ range was 2·0° plus the $\alpha_1\alpha_2$ angular separation. Background readings were made at the beginning and the end of each scan range; the ratio of background time to scan time was 1 to 2. All reflections in a half sphere of reciprocal space were measured out to 2θ = 70°. Approximately 2500 reflections were averaged for β-Mn to 142 independent

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reflections, for β-(Mn–Ni–Si) to 372 with the Friedel pairs separated. The real and imaginary parts of the anomalous dispersion were taken into account for the ternary phase (Cromer & Liberman, 1970). Spherical absorption corrections were applied with $\mu r = 0{\cdot}75$ for β-Mn and 0·50 for β-(Mn–Ni–Si). A secondary-extinction correction factor of the form $F_o^{\rm corr} = F_o(1 + gI_o)$ (Zachariasen, 1963) was applied only to the Mn–Ni–Si data. The largest correction was 1·6%.

Data treatment and refinement

The data reductions and refinements were carried out as described for the *R* phase (Shoemaker & Shoemaker, 1978). The composition of the ternary β phase was assumed to be $Mn_{63}Ni_{20}Si_{17}$ or $Mn_{12}Ni_4(Mn_{0\cdot6}Si_{3\cdot4})$, which according to the phase diagram (Bardos *et al.*, 1966) is in equilibrium with the *W* phase and is the composition in the β-phase field closest to the composition given for the *W* phase, $Mn_{52}Ni_{29}Si_{19}$. Mn was put in the 12(*b*) position, Ni in the 4(*a*) position with $x = 0{\cdot}690$ and Si in the 4(*a*) position with $x = 0{\cdot}054$, in agreement with the Si assignment in $(Ni_6Fe_{10})Si_4$ (Hladyshevskii, Kripyakevich & Kuzma, 1962). The occupancies of the three sites were allowed to vary. The final refinement cycles were performed on the Lawrence Berkeley Laboratory CDC 7600 computer from a remote terminal with the programs *LESQ* and *NUCLS* contained in A. Zalkin's XRAY 76 program system. Table 2 lists the agreement factors obtained and Table 3 gives the final parameters. The refinement of the occupancies shows that the 12(*b*) position is entirely occupied by Mn, that the Si position has some Ni and/or Mn mixed in with it, and that the Ni position similarly has some Mn and/or Si mixed in with it. The site compositions given in Table 3 are those yielding the overall composition that is closest to that in the phase diagram in equilibrium with the *W* phase, consistent with the determined occupancy parameters. They are also consistent with the fact that in alloys of this type Si and Ni avoid coordinations other than icosahedral, while Mn may show a variety of coordinations. The fact that in this arrangement Si atoms mainly avoid direct contact with other Si atoms is consistent with behavior shown by Si in tetrahedrally close-packed (t.c.p.) structures. The mixed occupancies of the fourfold positions probably apply throughout the large β-Mn field.

The data for the ternary phase were refined with $+f''$ and $-f''$ and the *R*-factor ratio showed that a significantly better agreement at the 0·005 level was obtained with $+f''$. The interatomic distances are given in Table 4.*

Table 1. *Crystal data*

	β-Mn	β-($Mn_{66}Ni_{20}Si_{14}$)
FW/atom	54·938	51·93
a (Å)	6·315 (2)	6·292 (2)
V (Å^3)	251·8 (2)	249·1 (2)
Space group	$P4_132(O^7)$ or $P4_332(O^6)$	$P2_13(T^4)$
Atoms/cell	20	20
D_x (g cm^{-3})	7·24	6·92
F(000)	505·9	486·0
μ(Mo *Kα*) (cm^{-1})	251	243

Table 2. *Agreement factors for the least-squares refinements*

	NO	Thermal parameters	NV	*R*(*F*)	$R_w(F)$	*S**
β-Mn	142	Anisotropic	9	0·030	0·022	1·87
β-(Mn–Ni–Si)	372	Anisotropic	19†	0·043	0·031	1·43

* $S = [\Sigma\, w(F_c - F_o)^2/(n_{\rm refl} - n_{\rm var})]^{1/2}$.
† Including one extinction parameter.

Table 3. *Atomic parameters*

			x	*y*	*z*	B_{11}*	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
β-Mn	Mn(1)	8(*c*)	0·06361 (10)	*x*	*x*	0·572 (16)	B_{11}	B_{11}	−0·001 (16)	B_{12}	B_{12}
	Mn(2)	12(*d*)	$\frac{1}{8}$	0·20224 (11)	$\frac{1}{4}+y$	2·060 (41)	0·766 (21)	B_{22}	0·429 (21)	$-B_{12}$	−0·210 (28)
β-(Mn–Ni–Si)	'Si'	4(*a*)	0·06383 (20)	*x*	*x*	0·601 (27)	B_{11}	B_{11}	0·007 (32)	B_{12}	B_{12}
	'Ni'	4(*a*)	0·68551 (13)	*x*	*x*	0·856 (18)	B_{11}	B_{11}	−0·019 (20)	B_{12}	B_{12}
	Mn	12(*b*)	0·12370 (14)	0·20302 (14)	0·45276 (14)	1·655 (32)	0·863 (32)	0·859 (31)	0·302 (28)	−0·258 (28)	−0·147 (25)
			RMSD1†	RMSD2†	RMSD3†	f_o‡	%Mn	%Si	%Ni		
β-Mn	Mn(1)		0·085	0·085	0·085						
	Mn(2)		0·084	0·094	0·172						
β-(Mn–Ni–Si)	'Si'		0·087	0·087	0·088	18·1 (2)	0·	71·	29·		
	'Ni'		0·102	0·105	0·105	27·2 (2)	28·	0·	72·		
	Mn		0·095	0·102	0·153	25·0 (1)	100·	0·	0·		

* The B_{ij} are the coefficients in the temperature-factor expression $\exp(-\Sigma_{i,j}B_{ij}a_i^*a_j^*h_ih_j/4)$.
† Root mean-square vibrational amplitudes in the directions of the principal axes.
‡ Previously assumed scattering factor (at $2\theta = 0$) multiplied by occupancy factor from refinement.

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* Lists of structure factors for both phases have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33863 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Interatomic distances* (Å) *for* β-Mn *and* β-(Mn–Ni–Si)

'Ni' and 'Si' in this table stand for 'mainly Ni' and 'mainly Si'. Estimated standard deviations of distances in β-Mn are in all cases less than 0·002 Å. Estimated standard deviations of distances in the ternary phase are not given because of uncertainty in the composition.

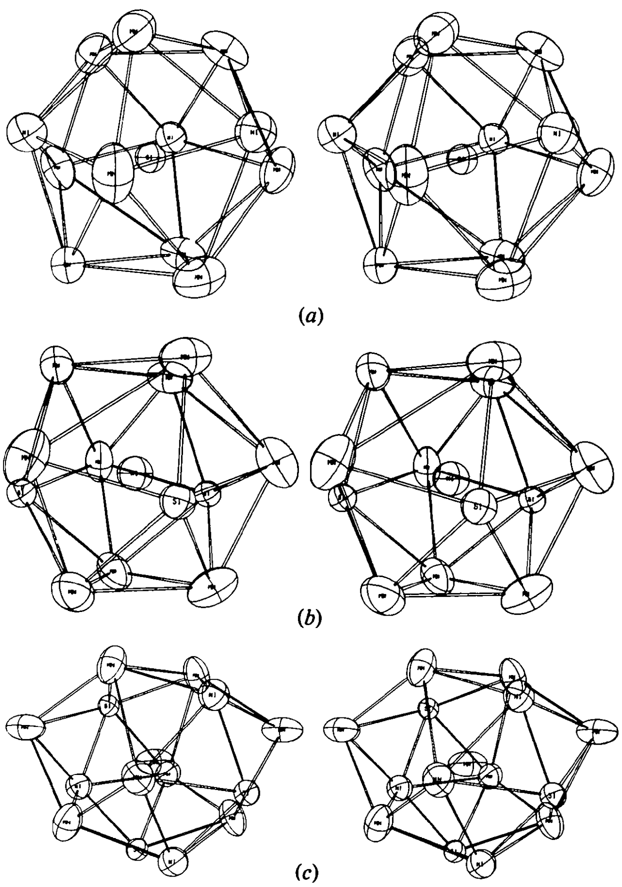
Atom (1)	Atom (2)	β-Mn	Mn–Ni–Si	Atom (2)	Atom (1)
Mn(1)	Mn(1)	2·364 (3×)	2·353 (3×)	'Ni'	'Si'
	Mn(2)	2·576 (3×)	2·561 (3×)	Mn	
	Mn(2)	2·634 (3×)	2·626 (3×)	Mn	
	Mn(2)	2·680 (3×)	2·678 (3×)	Mn	
			2·353 (3×)	'Si'	'Ni'
			2·576 (3×)	Mn	
			2·624 (3×)	Mn	
			2·666 (3×)	Mn	
Mn(2)	Mn(1)	2·576 (2×)	2·561	'Si'	Mn
			2·576	'Ni'	
	Mn(1)	2·634 (2×)	2·626	'Si'	
			2·624	'Ni'	
	Mn(1)	2·680 (2×)	2·678	'Si'	
			2·666	'Ni'	
	Mn(2)	2·646 (4×)	2·647 (2×)	Mn	
			2·634 (2×)	Mn	
	Mn(2)	2·672 (2×)	2·653 (2×)	Mn	
	Mn(2)	3·271 (2×)	3·256 (2×)	Mn	

Discussion

A description of the structure of β-Mn (*A*13 type) has been given by Kripyakevich (1960). In the ternary phase, along the threefold axes, two icosahedra centered alternately by (mainly) Si and (mainly) Ni share triangular faces formed by Mn atoms at one end and are separated at the other end by a distorted octahedral hole formed by Mn atoms. In the elemental structure Mn(2) lies on a true twofold axis of the structure; in the ternary phase the Mn atom is on a pseudo twofold axis, relating Mn with Mn and Si with Ni. The coordination polyhedron of this Mn atom is like the CN 14 polyhedron in t.c.p. structures (Shoemaker & Shoemaker, 1971), except that two Mn atoms are much farther away.

Recently an elegant description of β-Mn has been given by O'Keeffe & Andersson (1977) in terms of a body-centered cubic packing of rods along threefold axes, each rod consisting of a distorted octahedron followed by four Mn(1)[Mn(2)]$_3$ tetrahedra (parts of the icosahedra along the threefold axes). The distorted octahedral hole is called by these authors a 'metaprism' since it is intermediate between a trigonal prism (rotation angle between end faces zero) and an octahedron (rotation angle 60°). In our refined structure of β-Mn the rotation angle is 34·0°.

The anisotropic thermal refinement shows that the icosahedral atoms have essentially isotropic thermal motion, but the Mn atom in the twelvefold position has an anisotropic thermal ellipsoid with the shortest axis along the twofold or pseudo twofold axis and the longest axis making angles of 16·7° with the lines


(*a*)

(*b*)

(*c*)

Fig. 1. Stereoscopic views produced by *ORTEP* (Johnson, 1965) of the coordination polyhedra in β-(Mn–Ni–Si). 99% probability ellipsoids are shown. (*a*) The 'Si' icosahedron. The threefold axis is vertical in the paper. The bottom triangle of Mn atoms is shared with the 'Ni' polyhedron, the top triangle is part of the empty metaprism. (*b*) The 'Ni' icosahedron. The triangle shared with 'Si' is at the top. The bottom triangle is part of the empty metaprism. (*c*) The Mn CN 14 polyhedron. The pseudo twofold axis is vertical in the paper. One extra Mn atom outside each of the quadrangular faces will complete the two metaprisms to which the center atom belongs.

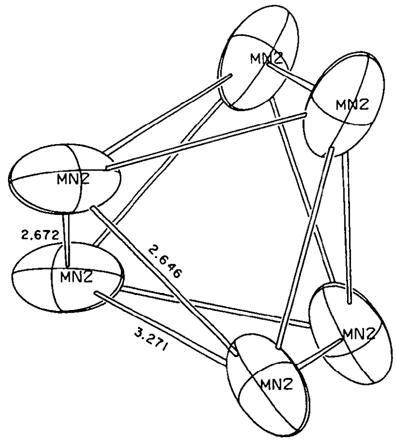


Fig. 2. Projection down the threefold axis of the Mn(2) metaprism in β-Mn. 99% probability ellipsoids are shown.

connecting it with the centers of the two metaprisms to which it belongs. In interstitially 'filled-up' β-Mn structures the metaprisms are occupied by C or N, as in Mo_3Al_2C (Jeitschko, Nowotny & Benesovsky, 1964). The distance from the Mn atoms to the center of the hole is 1·98 Å in the elemental structure. The coordination polyhedra for the ternary phase are given in Fig. 1(*a*)–(*c*). The metaprism in the elemental structure is shown in Fig. 2.

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X-ray Crystal Structure of the Monoclinic Form of *cyclo*-Tetrakis[di-μ-acetato-platinum(II)]: A Square-Cluster Platinum Complex

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The structure of the monoclinic form of $[Pt(CH_3COO)_2]_4$ has been determined from X-ray diffractometer data. This polymorph has a unit cell $a = 12{\cdot}031$ (1), $b = 10{\cdot}583$ (1), $c = 20{\cdot}090$ (2) Å, $\beta = 91{\cdot}10$ (1)°, space group $P2_1/c$, $Z = 4$ tetrameric molecules. Refinement of 3908 independent reflexions has reached $R = 0{\cdot}043$. A strongly metal–metal bonded square of Pt atoms, with Pt–Pt distances in the range 2·493–2·501 Å, forms the basis of the molecular structure in which eight bridging acetate groups are distributed round the square. The arrangement is such that four groups are approximately in the cluster plane, while four are alternately above and below it. Pt—O bonds which are perpendicular to the Pt cluster have normal lengths with a mean of 2·014 Å, while the eight which are nearly coplanar with the Pt atoms are all rather long, with a mean distance of 2·157 Å. The molecular structure is very similar to that found in the tetragonal form, but shows a slightly greater twisting distortion away from ideal $\bar{4}2m$ (D_{2d}) point symmetry.

Introduction

We have recently reported details of the crystal structure of the tetragonal form of Pt acetate (Carrondo & Skapski, 1976, 1978), and have shown it to have an unusual tetrameric geometry based on a strongly metal–metal bonded Pt square cluster. The background to this work and the reasons for determining the structure of this compound have been set out in the previous publication.

Starting with a specimen of Pt acetate obtained by the Ag acetate method (ICI Ltd, 1970), crystallization from glacial acetic acid yielded both a tetragonal and a monoclinic form, as well as a blue-black apparently amorphous solid (Phillips & Skapski, 1975).

We report here the determination of the structure of the monoclinic polymorph, in which essentially the same molecular structure is found as in the tetragonal form. The molecule shows a similar twisting distortion, but to a slightly greater degree. This difference can be