would thus reveal no more about the position or the bonding of the OH group. Comparison with the data for Cs[SbF_6] (*Index to Powder Diffraction Files*, 1971) shows only a slight change in the cell dimensions, which is not unexpected since F and O atoms are of comparable size. The similarity in space groups, however, is surprising and does not account for the presence of the OH group as the infrared spectra do.

References

BEAUCHAMP, A. L., BENNETT, M. J. & COTTON, F. A. (1969). *J. Am. Chem. Soc.* **91**, 297–301.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

Index to Powder Diffraction Files (1971). ASTM, Pennsylvania.

KEMMITT, R. D. W., RUSSELL, D. R. & SHARP, D. W. A. (1963). *J. Chem. Soc.* pp. 4408–4413.

KOLDITZ, V. L. & REHAK, W. (1959). *Z. Anorg. Allg. Chem.* **300**, 322–330.

KRUGER, G. J., PISTORIUS, C. W. F. T. & HEYNS, A. M. (1976). *Acta Cryst.* B**32**, 2916–2918.

MAZEIKA, W. A. & NEUMANN, H. M. (1966). *Inorg. Chem.* **5**, 309–311.

PALMER, W. G. (1970). *Experimental Inorganic Chemistry*, p. 306. Cambridge Univ. Press.

STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

VOGEL, A. I. (1961). *A Textbook of Quantitative Inorganic Analysis*, 3rd ed., p. 269. London: Longmans.

Acta Cryst. (1979). B**35**, 1210–1212

Structure of Iron Selenide 3*C*-Fe_7Se_8

BY JOHN B. PARISE, ASAO NAKANO, MASAYASU TOKONAMI AND NOBUO MORIMOTO

Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, *Japan*

(*Received* 18 *December* 1978; *accepted* 6 *February* 1979)

Abstract. 3*C*-Fe_7Se_8 (a high-temperature form) trigonal, $P3_121$, $a = 7{\cdot}2613\ (9)$, $c = 17{\cdot}675\ (5)$ Å, $Z = 3$, $D_x = 6{\cdot}31$ Mg m^{-3}. The structure of synthetic 3*C*-Fe_7Se_8 has been refined on the assumption of twinning of domains with $P3_121$ and $P3_221$ by rotation about the *c* axis. The weighted *R* factor converged to 0·036 for 1550 intensities generated from the 527 observed. The average Fe—Se bond length is 2·57 Å. 3*C*-Fe_7Se_8 is isostructural with 3*C*-Fe_7S_8.

Introduction. Single crystals of $Fe_{1-x}Se$ have been studied systematically by Okazaki & Hirakawa (1956) and Okazaki (1961). These authors proposed a defect NiAs-type structure of 3*C*-Fe_7Se_8 based on the inspection of the X-ray photographs of single crystals. Here 3*C* refers to the number of times the NiAs-type subcell repeats along the *c* axis. The present study has been undertaken using precise intensity data collected by a four-circle diffractometer in order to elucidate atomic shifts and correlations in the structure of 3*C*-Fe_7Se_8.

Small chips were taken from a large synthetic crystal, heated for 12 h at 573 K in evacuated silica-glass capsules, quenched in ice water and then crushed. Because the Laue symmetry is 6/*mmm* and 00*l* reflections appear only when $l = 3n$, the space group is apparently $P6_222$ (or $P6_422$). A small specimen was chosen for intensity measurements; it had an almost triangular-prismatic form and was about 0·1 mm in height and on edge. 1054 intensities in two dependent sectors were collected with the ω–2θ scan technique ($2\theta_{\max} = 60°$) and Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å), monochromatized by pyrolytic graphite. Weak intensities with $F_o < 2\sigma(F_o)$ were measured three times. After averaging the equivalent reflections the data set contained 527 independent reflections of which 113 had zero intensity. A spherical absorption correction ($\mu r = 2{\cdot}1$) was made on the assumption that the specimen crystal was spherical.

The observed symmetry of 6/*mmm* is inconsistent with the possible ordering of vacancies in the defect NiAs-type superstructure for the 3*C* type which gives space group $P3_121$ (or $P3_221$). It has been assumed that the observed symmetry arises from the twinning of small domains, with point symmetry 32, related by 180° rotation about the *c* axis. This would give apparent symmetry 622. Since the anomalous-dispersion term for Se is large ($f'' = 2{\cdot}223$), the observed symmetry 6/*mmm* [in which $I(hkl) = I(\bar{h}\bar{k}\bar{l})$] has been attributed to the existence of two enantiomorphs ($P3_121$ and $P3_221$) in the specimen crystal. This is equivalent to reflection across (100) which transforms symmetry 622 to 6/*mmm*. Accordingly, the

0567-7408/79/051210-03$01.00

Table 1. *Final fractional atomic coordinates and isotropic thermal parameters* ($Å^2$), *with standard deviations in parentheses*

	x	y	z	B
Fe(1)	0·0175 (15)	0	$\frac{1}{3}$	1·6 (1)
Fe(2)	0·0322 (20)	0	$\frac{5}{6}$	3·0 (2)
Fe(3)	0·4567 (8)	0	$\frac{5}{6}$	0·76 (9)
Fe(4)	0·0137 (14)	0·5361 (9)	0·8282 (2)	1·83 (8)
Fe(5)	0·0047 (10)	0·5172 (9)	0·3363 (2)	0·38 (4)
Se(1)	0·1587 (6)	0·3318 (8)	0·7519 (1)	0·56 (3)
Se(2)	0·1675 (5)	0·8371 (5)	0·7391 (1)	0·74 (3)
Se(3)	0·6666 (7)	0·3371 (6)	0·7534 (2)	0·42 (4)
Se(4)	0·6640 (8)	0·8384 (6)	0·7562 (1)	0·63 (3)

observed intensities were divided into the individual twin components, $|F_o(hkl)|^2$, $|F_o(khl)|^2$, $|F_o(\bar{h}\bar{k}\bar{l})|^2$ and $|F_o(\bar{k}\bar{h}\bar{l})|^2$, using the relation: $|F_o(hkl)|^2 = kE_s[I_o(hkl)A\,\mathrm{Lp}^{-1}]\,I_c(hkl)/[I_c(hkl) + I_c(khl) + I_c(\bar{h}\bar{k}\bar{l}) + I_c(\bar{k}\bar{h}\bar{l})]$, where k is a scale factor, E_s is an isotropic secondary-extinction parameter [$C = 0{\cdot}78\ (2) \times 10^{-6}$; Zachariasen, 1963], A is an absorption correction, Lp is the Lorentz–polarization correction and $I_c(hkl)$ and $I_o(hkl)$ are the calculated and observed intensities respectively. Neutral-atom scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974). For 1550 generated reflections, the least-squares refinement converged to 0·105 and 0·036 for unweighted and weighted R factors respectively. These values were 0·061 and 0·035, respectively, when unobserved reflections with $F_o = 0$ were excluded. The final atomic parameters are presented in Table 1 and bond lengths and angles in Table 2.*

Discussion. The structure of 3C-Fe_7Se_8 is essentially that reported by Okazaki & Hirakawa (1956). Fe atoms shift from their ideal positions in the NiAs-type structure, not only to reduce the space around the vacancies, but also to form a particular distribution of Fe clusters. Although the atoms in the filled layers (Fig. 1*a*) move slightly towards the vacant sites in the adjacent layers [the Fe(4) atom in Fig. 2 moves 0·1 Å in this direction], the major shifts are in the basal plane where atoms move towards each other to form four-atom clusters. On the other hand, for the atoms in the vacancy-containing planes (Fig. 1*b*) the shift is mainly towards the vacancy; Fe(1) and Fe(5) move 0·13 Å in this direction.

Distances between Fe atoms tend to be short along the c axis. Infinite [–Fe(1)–Fe(2)–] and short five-atom [Fe(4)–Fe(5)–Fe(3)–Fe(5)–Fe(4)] rods are formed in the structure (Fig. 2). The short five-atom rods are separated from each other along the c axis by intervening vacancies. In the basal layers, with the exception of the short Fe(2)–Fe(3) distance (3·082 Å), Fe atoms are more than 3·2 Å apart. The Fe(2)–Fe(3) couple, which is rotated through 120° in successive filled layers of Fe atoms, serves to link the five-atom and infinite rods. This results in infinite columns running parallel to **c**.

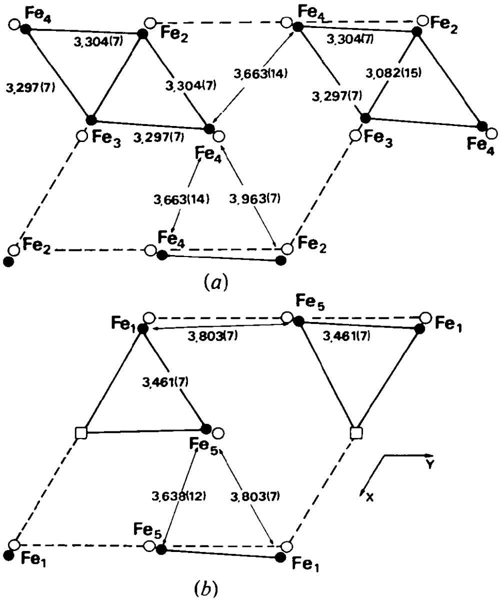

Fig. 1. Distribution of Fe–Fe distances (Å) with e.s.d.'s in parentheses. In (*a*) the filled iron plane is at $z = \frac{5}{6}$ and in (*b*) the vacancy-containing plane is at $z = \frac{1}{3}$. Open circles represent ideal positions in the NiAs-type structure, solid circles iron atoms and squares vacancies. Broken lines outline the unit cell.

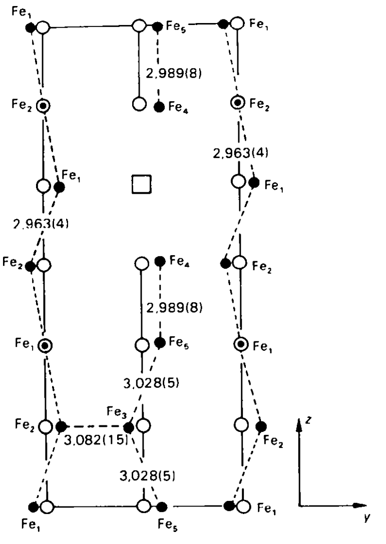

Fig. 2. Distribution of Fe–Fe distances (Å), with e.s.d.'s, in the *yz* plane at $x = 0$. Broken lines depict the 'infinite' and 'five-atom' rods (see text).

---

* Lists of structure factors and Table 2 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34260 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

3C-Fe_7Se_8 is isostructural with 3C-Fe_7S_8 (Fleet, 1971; Nakano, Tokonami & Morimoto, 1979). The directions of the cation shifts from the ideal positions are almost the same in both cases. However, Se is more polarizable than S and the magnitudes of the shifts of Fe in the Se sublattice are a little larger than those in the S sublattice. The similarity of the two structures suggests that the enantiomorphic pair exists not only in the specimen of 3C-Fe_7Se_8 but also in that of 3C-Fe_7S_8.

We are indebted to Professor A. Okazaki, Kyushu University, for providing the synthetic Fe_7Se_8 and to Drs K. Koto and H. Horiuchi for help throughout this work. JBP wishes to acknowledge the Australia–Japan Business Cooperation Committee for a study grant and the staff of the Science Faculty of Osaka University who made the stay in Japan possible.

References

Fleet, M. E. (1971). *Acta Cryst.* B**27**, 1864–1867.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Nakano, A., Tokonami, M. & Morimoto, N. (1979). *Acta Cryst.* B**35**, 722–724.

Okazaki, A. (1961). *J. Phys. Soc. Jpn*, **16**, 1162–1170.

Okazaki, A. & Hirakawa, K. (1956). *J. Phys. Soc. Jpn*, **11**, 930–936.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1979). B**35**, 1212–1214

Structure of Disodium Dihydrogen 1-Hydroxyethylidenediphosphonate Tetrahydrate: A Bone Growth Regulator

By B. L. Barnett and L. C. Strickland

The Procter & Gamble Company, Miami Valley Laboratories, PO Box 39175, *Cincinnati, Ohio* 45247, *USA*

(*Received* 5 *October* 1978; *accepted* 2 *January* 1979)

Abstract. $2Na^+.C_2H_6O_7P_2^{2-}.4H_2O$, $Na_2H_2[C_2H_4O_7P_2].4H_2O$, M_r = 322·055, monoclinic, $P2_1/c$, a = 10·598 (4), b = 5·993 (2), c = 18·262 (6) Å, β = 91·77 (1)° [$\lambda(\mathrm{Cu}\,K\alpha_1) = 1{\cdot}54051$ Å], V = 1159·34 Å^3, Z = 4, D_x = 1·845 Mg m^{-3}. The structure was solved with *MULTAN* and refined to $R(F_o) = 0{\cdot}040$ for 1397 reflections measured with Cu $K\alpha$ radiation. The ligand can act as a tridentate and bidentate chelator. When functioning as a tridentate ligand, the hydroxyl group of 1-hydroxyethylidenediphosphonate (hedp) participates in the coordination. A conformation of the ligand that may influence its polydentate nature is the *W* conformation. The *W* conformation has the phosphonate groups eclipsed so that an O—P—C—P—O linkage forms a planar *W*. For the first time, the multifunctional hedp ligand has been observed to exhibit a tridentate capability where three coordination sites on an atom are occupied by a single ligand. The triangular face, which this ligand provides, furnishes an optimal binding geometry for half of the Ca atoms in the ⟨001⟩ surface of calcium hydroxyapatite, the major constituent in bone. Complex formation in this manner establishes a foundation for the chemisorption of hedp onto calcium hydroxyapatite, which is an essential element in the crystal growth inhibition mechanism of hedp.

Introduction. Disodium dihydrogen 1-hydroxyethylidenediphosphonate, Na_2H_2hedp, has demonstrated the ability to inhibit either dissolution or crystal growth of calcium hydroxyapatite, depending upon the concentration of Na_2H_2hedp (King, Francis & Michael, 1971). We have investigated the crystal structure of Na_2H_2hedp.$4H_2O$ (etidronate disodium, USP) in order to understand the interaction between the hedp ligand and calcium hydroxyapatite, the major constituent of bone.

Crystals of Na_2H_2hedp.$4H_2O$ suitable for X-ray analysis were obtained by slow evaporation from aqueous solution. Four solid phases (three crystalline and one amorphous) of Na_2H_2hedp can be prepared and all form the tetrahydrate from water at room temperature. An elongated parallelepiped of dimensions 0·10 × 0·15 × 0·45 mm was chosen for all X-ray investigations. Preliminary data, which were taken from an intensity-weighted plot of reciprocal space, indicated the Laue group to be $P2/m$ and the systematic absences to be consistent with the uniquely defined space group $P2_1/c$ (No. 14).

Cell dimensions were obtained from least-squares refinement of three instrument angles of 15 general reflections with 85° < 2θ < 110°. All X-ray data were measured with Cu $K\alpha$ (1·54178 Å) radiation employ-

0567-7408/79/051212-03$01.00