

X-Ray and Neutron Diffraction Studies on Γ -Ni, Zn and Γ -Fe, Zn

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The body centered cubic Γ -Ni,Zn structure has a novel ordering type, with Ni occupying the outer tetrahedral position yielding a structure without Ni-Ni contacts. Thus, the basic stoichiometry is Ni₄Zn₂₂. The solution mechanism for excess Ni remains obscure.

The Γ -Fe,Zn phase has a crystal structure based upon a Cu₅Zn₈-type ordering scheme. It is body-centered cubic. The inner tetrahedral position is occupied exclusively by Fe, and the octahedral position by a random distribution of Fe and Zn (~35 to ~70 % Fe).

In 1938, Schramm¹ published phase analyses of the Fe-Zn, Co-Zn, and Ni-Zn systems and reported the homogeneity ranges of the gammabrass like phases² in these systems. The cubic lattice parameter of Γ -Fe,Zn was found to decrease linearly from 9.018 Å to 8.974 Å over the region 24-31 atomic % Fe, whereas the lattice parameter *versus* composition graph for the Γ -Ni,Zn phase, extending from 15 to approximately 20 atomic % exhibited a pronounced maximum, $a=8.926$ Å at 17 atomic % Ni. (The above lattice parameter values have been recalculated from values given in kX units by Schramm).

The T₅Zn₂₁ composition proposed for these phases on the basis of electron concentration considerations (21/13 valence electrons per atom) corresponds to 19.2 atomic % transition metal, T, and the "ideal structural" stoichiometries (see Fig. 2 and section describing the Ni₄Zn₂₂ structure) T₄Zn₂₂, T₆Zn₄₀, T₈Zn₁₈ and T₁₀Zn₁₆ to 15.4, 23.1, 30.8, and 38.4 atomic % T, respectively.

No ordering scheme for the atoms in the above phases has previously been determined and reported in the literature. The present investigation has been aimed at establishing the crystal structures of Γ -Ni,Zn and Γ -Fe,Zn, *i.e.* the identification of Ni, Fe, and Zn atoms and the determination of their position parameters in the crystallographic unit cells.

EXPERIMENTAL

Weighed amounts of nickel (Kebo, puriss. powder 99.8 % Ni—carbonyl nickel) and zinc (Mallinkrodt, zinc metal. Dust min. 95.0 % Zn, analyzed 98.1 % Zn) were mixed together and heated in sealed evacuated silica capsules at $405 \pm 10^\circ\text{C}$ for 1–2 weeks. Some specimens which had obviously not reached equilibrium after this period were re-heated at 800°C for 2–3 days, whereupon the temperature was again slowly lowered to $\sim 400^\circ\text{C}$. After the heat-treatment the capsules were quenched in water.

The nickel content of these preparations was determined by dimethyl glyoxime precipitation.³

The Γ -Fe,Zn phase was synthesized from iron (Baker and Adamson, Fe metal wire 99.90 %) and zinc (granular, Mallinkrodt Analytical Reagent). The components were reacted in sealed evacuated silica capsules at $720 \pm 10^\circ\text{C}$ for 2–3 weeks. The tubes were quenched in water, the reaction product extracted, finely ground and subsequently re-heated, in the same manner, at 720°C for one month.

The iron content was determined³ by NH_3 precipitation of the hydroxide, which was ignited and weighed as Fe_2O_3 .

Density measurements were performed by weighing of the alloy specimens in air and in CHCl_3 .

X-Ray powder diffraction photographs were taken with a Guinier-Hägg type focusing camera of 80 mm diameter, using monochromatized $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54050 \text{ \AA}$) and KCl ($a = 6.2919 \text{ \AA}$) as an internal standard.

Single crystal X-ray data for the Γ -Ni,Zn phase have been collected with a Weissenberg camera ($\text{CuK}\alpha$ radiation) employing the multiple film technique. The diffracted intensities were estimated visually by comparison with an intensity scale obtained from the same crystal, and were put on a common basis by intercomparison of symmetry-equivalent reflexions from photographs of several layer lines, the result being a list of 56 independent reflexions. No absorption correction was attempted, since the crystal was a tiny (max. diameter 0.03 mm), irregular fragment.

When a single crystal of Γ -Fe,Zn (a fragment of max. diameter 0.06 mm) was investigated, we had at our disposal a General Electric Diffractometer equipped with a full circle Single Crystal Orienter and a scintillation counter. Nickel-filtered $\text{CuK}\alpha$ radiation, with pulse height discrimination, was used for the intensity measurements. Pulses were counted for 400 sec during a $\theta - 2\theta$ scan across each diffraction peak. The 167 measured intensities were corrected for absorption ($\mu = 774 \text{ cm}^{-1}$) by approximate numerical integration and converted to 66 independent structure factors.

Neutron powder diffractograms ($\lambda = 1.07 \text{ \AA}$) of two Ni,Zn alloys and one Fe,Zn specimen were recorded by the neutron diffraction group at the Swedish Research Councils' laboratory in Studsvik. The sample holder was a cylindrical aluminium container, diameter = 10 mm. The diffracted intensities were determined by graphical integration of the areas under the diffractometer chart peaks.

Atomic scattering factors for the X-ray case were taken from Cromer and Waber⁴ (corrected for dispersion according to Cromer⁵) and for the neutron case from Bacon's⁶ tabulation, viz. $b_{\text{Ni}} = 1.03 \times 10^{-12} \text{ cm}$, $b_{\text{Zn}} = 0.59 \times 10^{-12} \text{ cm}$, and $b_{\text{Fe}} = 0.96 \times 10^{-12} \text{ cm}$. Bacon⁶ also gives the expression for calculated neutron intensity computation.

Ten-cycle, full matrix least-squares refinements of the atomic positional and thermal parameters were carried out on the Uppsala CDC 3600 computer with the program LALS (World list⁷ No. 384) in which Cruickshank's weighting function $w = (2|F_o|_{\min} + |F_o| + 2|F_o|_{\max}^{-1} \cdot |F_o|^2)^{-1}$ was used.

The derivation of calculated neutron intensities was performed on the computer TRASK for the Γ -Ni,Zn structure and initially on the CDC 3600, subsequently on the recently installed IBM 1800 computer at this institute for the Γ -Fe,Zn phase. The program FIS employed for the calculations was written for the present problem type. Scaling and adjustment of an over-all temperature factor for the calculated neutron intensities was performed, using a Wilson plot of $\log I_o/I_c$ versus $\sin^2\theta$, for each Γ -Fe,Zn structure model tried. This procedure was not possible to apply to the Γ -Ni,Zn data, since the number of observed reflexions was appreciably smaller. In this case, the X-ray B value was used, and only a scale factor calculated from $\sum I_o / \sum I_c$.

Table 1. Phases observed in preparations of analyzed composition $\text{Ni}_x\text{Zn}_{100-x}$. Lattice parameter of the cubic Γ phase. Densities are given for the samples investigated by neutron diffraction.

x	Phases	a Å	d_{obs}	d_{calc}
12.2	$\Gamma + \Gamma_1$	8.9173		
15.9	Γ	8.9195		
16.1	Γ	8.9191		
16.4	Γ	8.9218		
16.8	Γ	8.9228	7.7	7.81
17.2	Γ	8.9231		
17.4	Γ	8.9220		
17.7	Γ	8.9206		
18.0	Γ	8.9166	7.7	7.82
18.8	Γ	8.9112		
19.7	Γ	8.9024		

THE Γ -Ni,Zn STRUCTURE

In Table 1 are listed the phases observed in the various Ni—Zn preparations together with the lattice parameter of the cubic Γ phase. For the specimens investigated by neutron diffraction, the measured densities and the densities calculated for 52 atoms per unit cell are given. The number of atoms per unit cell calculated from the data in the table is, in both cases >51 .

Fig. 1 presents the lattice parameter information graphically, emphasizing the a maximum at 17 at. % Ni. The shape of the graph agrees closely with that published by Schramm.¹ No two-phase preparation was obtained on the high-Ni side of the homogeneity range.

The single-phase range commences, on the low-Ni side, at approximately 15.8 at. % Ni, *i.e.* at a nickel content only slightly higher than the composi-

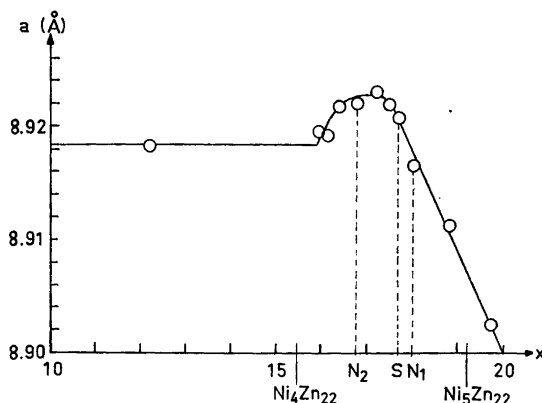


Fig. 1. Lattice parameter a (Å) of the cubic $\text{Ni}_x\text{Zn}_{100-x}$ phase. The compositions of the two samples investigated by neutron diffraction are indicated on the x axis (N_1 and N_2). Also indicated (S) is the composition of the sample from which the single crystal was picked for X-ray analysis.

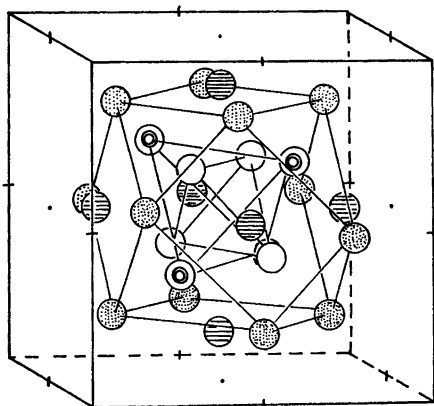
tion $\text{Ni}_4\text{Zn}_{22}$ (15.4 at. %), and does certainly not continue up to $\text{Ni}_6\text{Zn}_{20}$ (23.1 at. %). Therefore, a crystal structure based upon the former stoichiometry appears reasonable. This is borne out by the neutron diffraction data; *vide infra*.

The crystal investigated by X-ray diffraction was selected from the single-phase sample of 17.7 at. % Ni content and with $a=8.9206 \pm 2$ Å. The symmetry was found to be body-centered cubic from both X-ray and neutron diffraction data. Thus, there was ample reason to expect that the structure could be described,⁸ in space group $I43m$ (No. 217), in terms of an Inner Tetrahedral (IT), an Outer Tetrahedral (OT), an OctaHedral (OH) and a Cubo-Octahedral (CO) position, all centered around the origin of the unit cell and repeated at the body center of the cell (see Fig. 2)

IT	8(c)	$x x x$	etc	$x \approx 0.10$	
OT	8(c)	$x x x$	etc	$x \approx -0.17$	
OH	12(e)	$x 0 0$	etc	$x \approx 0.35$	
CO	24(g)	$x x z$	etc	$x \approx 0.30$	$z \approx 0.05$

The most reasonable structure, *vide infra*, which also turned out to be the correct one, refined to $R=0.101$. For observed and calculated X-ray structure factors, see Table 2. Positional and thermal parameters after refinement are given in Table 6, and interatomic distances in Table 7.

Observed neutron diffraction intensities from a sample containing 18.0 atomic % Ni ($a=8.9166$ Å) and calculated intensities for five different ordering schemes with reasonable stoichiometries are listed in Table 3. Because of the scaling difficulty the models should be compared both on the basis of an



○	= IT	0.10	0.10	0.10
⊙	= OT	-0.17	-0.17	-0.17
▨	= OH	0.35	0	0
⊘	= CO	0.30	0.30	0.05

Fig. 2. Atomic sites in the cluster of atoms around the origin.

IT=inner tetrahedral, OT=outer tetrahedral, OH=octahedral and CO=cubo-octahedral position.

Table 2. X-Ray structure factors for final refined model of Γ -Ni,Zn (see Table 6)
 $R=10\%$.

hkl	$ F_o $	$ F_c $	hkl	$ F_o $	$ F_o $
222	234	241	466	63	38
013	27	38	127	155	178
123	76	87	237	83	83
233	195	190	147	153	154
024	52	59	257	96	77
224	124	136	457	64	55
134	55	49	477	118	110
334	66	54	008	74	74
044	75	78	028	91	80
244	155	147	228	71	81
015	107	116	338	66	54
125	52	54	358	146	93
235	59	53	178	45	47
345	70	62	088	73	98
055	202	211	149	58	53
255	107	97	459	37	34
455	70	58	369	46	61
116	86	92	00.10	75	83
136	128	130	11.10	63	67
336	208	198	22.10	81	86
046	90	77	24.10	51	47
246	72	64	15.10	67	74
446	81	73	35.10	16	24
066	170	157	03.11	28	32
266	128	112			

$R_I=100 \cdot \sum |I_o - I_c| / \sum I_o$ (the sum taken over all reflexions with I_o or $I_c > 3$ except the 330, 411 pair, which could not easily be obtained on exactly the same scale as the others) and by inspection of the matching of critically sensitive individual reflexions.

The models tried are:

- | | |
|--|---------------|
| A) Ni_4Zn_{22} with Ni in IT | $R_I = 125\%$ |
| B) Ni_4Zn_{22} with Ni in OT | $R_I = 13\%$ |
| C) Ni_8Zn_{20} with Ni in OH | $R_I = 36\%$ |
| D) Ni_4Zn_{22} with Ni randomly distributed in CO | $R_I = 80\%$ |
| E) Ni_4Zn_{22} with Ni randomly distributed over all sites | $R_I = 57\%$ |

It is easily observed, then, that the best fit is obtained for model B, with Ni in the OT (outer tetrahedral) position, corresponding to an Ni_4Zn_{22} stoichiometry. This identification of the atoms is employed in Tables 6 and 7. The observed structure type is probably adopted since, in it, there are no Ni-Ni contacts. In general, Γ -type structures with the minimum number of like-atom contacts appear to be favored.

The neutron intensities diffracted by an alloy specimen (16.8 at.% Ni, $a=8.9228 \text{ \AA}$) with a composition lying on the other (low-Ni) side of the a maximum of the a versus x (in Ni_xZn_{100-x}) graph were not measurably different from those recorded in Table 3. Hence, we have not been able to deduce

Table 3. Observed and calculated neutron diffraction intensities for Γ -Ni,Zn. Arbitrary scale.

A) $\text{Ni}_4\text{Zn}_{22}$ with Ni in IT. B) $\text{Ni}_4\text{Zn}_{22}$ with Ni in OT. C) $\text{Ni}_4\text{Zn}_{30}$ with Ni in OH. D) $\text{Ni}_4\text{Zn}_{22}$ with Ni randomly distributed in CO. E) $\text{Ni}_4\text{Zn}_{22}$ with Ni randomly distributed over all sites.

$h k l$	I_o	A	B	I_c C	D	E
1 1 0	9	34	10	1	0	5
2 0 0	—	0	4	7	1	0
2 1 1	22	1	24	23	1	2
2 2 0	—	0	0	0	2	0
3 1 0	—	0	1	12	2	1
2 2 2	8	32	8	12	24	20
3 2 1	3	21	5	11	20	14
4 0 0	—	3	1	0	0	0
4 1 1 3 3 0	(365)	313	367	402	321	362
4 2 0	—	4	1	2	3	3
3 3 2	22	44	22	26	27	31
4 2 2	27	18	23	22	12	18
5 1 0 4 3 1	6	28	7	7	14	14
5 2 1	—	2	1	1	7	3
4 4 0	—	5	2	1	2	2
5 3 0 4 3 3	7	1	6	4	7	4
6 0 0 4 4 2	45	17	40	46	26	41
$R_1 =$		125 %	13 %	36 %	80 %	57 %

anything about the solution mechanism from our observed data, and the reason for the existence of the α maximum remains obscure.

THE Γ -Fe,Zn STRUCTURE

The alloy investigated by neutron diffraction had an analyzed iron content of 29.5 atomic %, approximating the stoichiometric formula $\text{Fe}_8\text{Zn}_{18}$. The sample consisted of a mixture of several batches synthesized separately. The average lattice parameter, and its largest deviation from the mean were $a = 8.986 \pm 4$ Å, a value corresponding exactly to the one derivable from Schramm's¹ lattice parameter graph for the above composition.

The batch from which the single crystal was picked out had a measured lattice parameter value of $a = 8.9822 \pm 12$ Å.

A comparison of measured and calculated densities yields $d_{\text{obs}} = 7.4 \pm 1$ g cm^{-3} ; $d_{\text{calc}} = 7.45$ g cm^{-3} for the above analyzed composition, assuming 52 atoms per unit cell. The calculated value of $z = 51.7$ atoms per unit cell.

Both X-ray and neutron diffraction data show that Γ -Fe,Zn is body-centered cubic.

At first, it was assumed that Γ -Fe,Zn was analogous with Γ -Ni,Zn, although more transition metal could be dissolved in the structure, possibly with a random distribution over all Zn sites.

Thus, a refinement of positional and thermal parameters was carried out in space group $I\bar{4}3m$ (No. 217) for a Ni_4Zn_{22} -type structural model, which refined to an R value of 9.9 %. The final values of the individual temperature factors were such, however, as to induce one to think that a better model could be constructed by an interchange of Fe and Zn atoms between the OT and IT positions:

$$\begin{array}{ll} B_{n,IT} & = 4.0 \text{ \AA}^2 \\ B_{Zn,OH} & = 2.9 \text{ \AA}^2 \end{array} \qquad \begin{array}{ll} B_{Fe,OT} & = 1.7 \text{ \AA}^2 \\ B_{Zn,CO} & = 3.0 \text{ \AA}^2 \end{array}$$

Another refinement was immediately carried out for the new model, yielding a slightly higher R value, *viz.* 10.5 %. All the thermal parameters, however, became equal to within one half standard deviation: $B=3.0 \pm 2 \text{ \AA}^2$ ($\sigma=0.4 \text{ \AA}^2$). The ambiguity was resolved by the use of neutron powder diffraction data. First, four different structure models, each containing Fe in just one of the different crystallographic positions, and one model with Fe randomly distributed over all available atomic sites were compared on the basis of an R_I value: $R_I=100 \sum |I_o - I_c| / \sum I_o$ (the sums were taken over all reflexions with I_o or $I_c > 4$ except the 330, 411 pair). The following result was obtained:

A) Fe_4Zn_{22} with Fe in OT (Ni_4Zn_{22} model)	$R_I = 26 \%$
B) Fe_4Zn_{22} with Fe in IT	$R_I = 12 \%$
C) Fe_8Zn_{20} with Fe in OH (assumed in the literature)	$R_I = 35 \%$
D) Fe_8Zn_{18} with Fe randomly distributed over CO	$R_I = 43 \%$
E) Fe_8Zn_{18} with Fe randomly distributed over all sites	$R_I = 19 \%$

Even though its stoichiometry deviates considerably from Fe_8Zn_{18} , model B, with Fe in the inner tetrahedral position, is by far the most realistic one. The stoichiometry was adjusted towards the analytical composition by the substitution of Fe for Zn in the other positions, according to the following models:

F) Fe_8Zn_{18} with Fe in IT and OT	$R_I = 15 \%$
G) $Fe_{10}Zn_{16}$ with Fe in IT and OH (Cu_5Zn_8 model)	$R_I = 10 \%$
H) Fe_8Zn_{18} with Fe in IT and randomly in CO	$R_I = 17 \%$
I) Fe_8Zn_{18} with Fe in IT and randomly over all other sites	$R_I = 11 \%$

A few other models of the Fe_8Zn_{18} composition have also been tried, with Zn in the IT position. All these trials have yielded R_I values in the 30–40 % region.

Although the composition of model G is not the analytical one, this model seems to be the best one. Its stoichiometry can be brought to match Fe_8Zn_{18} as follows:

J) Fe_8Zn_{18} Fe in IT, $\frac{3}{4}Fe + \frac{1}{4}Zn$ randomly in OH	$R_I = 7 \%$
K) Fe_8Zn_{18} $\frac{1}{2}Fe + \frac{1}{2}Zn$ randomly in IT, Fe in OH	$R_I = 24 \%$
L) Fe_8Zn_{18} $\frac{4}{3}Fe + \frac{1}{3}Zn$ randomly over IT and OH	$R_I = 11 \%$

Table 4. Observed and calculated neutron diffraction intensities for Γ -Fe₅Zn₈. Arbitrary scale. Model J with Fe in IT, $\frac{2}{3}$ Fe + $\frac{1}{3}$ Zn in OH. $R_I=7\%$.

<i>hkl</i>	I_o	I_c
110	102	81
200	—	0
211	—	0
220	—	0
310	—	0
222	35	47
321	30	29
400	—	0
330, 411	(600)	854
420	—	0
332	131	140
422	92	88
510, 431	78	72
521	—	0
440	—	0
433, 530	—	0
600, 442	50	51
611, 532	58	51
620	—	0
541	—	0
622	—	0
631		
444		
550, 543, 710	294	271
640		
552, 633, 721	331	333
642		
730	—	0
732, 651		
800	100	101
554, 741, 811		
644, 820	159	152
653		
822, 660		
831, 750, 743	171	173
662		
752	37	44

The final model, thus, is model J, for which observed and calculated neutron intensities are listed in Table 4. Refined positional and thermal parameters for this model are given in Table 6, and interatomic distances in Table 7. The X-ray structure factors are listed in Table 5.

The structure, thus, approximates the Cu₅Zn₈ type, Fe being located in the IT and OH positions. It may reasonably be conjectured that the Fe occupancy remains constant at 100 % in the IT position and varies from ~35 % to ~70 % (the rest being Zn) in the OH position over the homogeneity region (24–31 atomic % Zn) of the phase.

Table 5. X-Ray structure factors for final refined model of Γ -Fe,Zn (see Table 6).
 $R=11\%$.

hkl	$ F_o $	$ F_c $	hkl	$ F_o $	$ F_c $
011	49	48	046	46	44
002	6	21	246	65	67
112	33	42	446	72	68
022	22	16	156	70	73
222	199	209	356	41	40
013	64	45	556	10	19
123	92	90	066	190	152
033	587	595	266	71	100
233	178	197	466	50	46
004	31	18	017	33	29
114	421	407	127	176	181
024	42	34	037	43	35
224	165	162	237	82	83
134	53	59	147	146	131
334	8	36	347	37	37
044	73	68	057	38	30
244	131	139	257	97	84
444	332	328	457	49	61
015	115	101	167	25	22
125	29	37	367	15	22
035	60	61	008	112	94
235	67	70	118	23	11
145	43	41	028	110	92
345	49	48	228	65	93
055	269	220	138	30	32
255	97	87	338	63	55
455	59	54	048	26	11
006	259	213	248	26	16
116	77	82	158	47	46
026	46	28	019	32	31
226	69	80	129	38	43
136	127	118	039	33	42
336	181	184	239	29	31

Table 6. Atomic distributions, positional and thermal parameters of the refined structures.

		Γ -Ni,Zn	Γ -Fe,Zn
	$a \pm \sigma$ Å	8.9206 ± 2	8.9822 ± 12
IT	Atom	Zn	Fe
	$x \pm \sigma$	0.1052 ± 15	0.0973 ± 15
	$B \pm \sigma$ Å ²	2.7 ± 4	2.8 ± 5
OT	Atom	Ni	Zn
	$x \pm \sigma$	-0.1701 ± 19	-0.1638 ± 13
	$B \pm \sigma$ Å ²	2.5 ± 5	3.3 ± 5
OH	Atom	Zn	$\frac{2}{3}\text{Fe} + \frac{1}{3}\text{Zn}$
	$x \pm \sigma$	0.3560 ± 16	0.3551 ± 15
	$B \pm \sigma$ Å ²	2.7 ± 3	2.3 ± 4
CO	Atom	Zn	Zn
	$x \pm \sigma$	0.3069 ± 13	0.3029 ± 8
	$z \pm \sigma$	0.0437 ± 13	0.0508 ± 12
	$B \pm \sigma$ Å ²	2.9 ± 3	3.1 ± 4

Table 7. Coordination, number and type of contacts, and interatomic distances (Å), with standard deviations, in the two gamma phases.

		Γ -Ni,Zn	Γ -Fe,Zn
3	IT(A)–IT(A)	Zn–Zn 2.654 ± 30	Fe–Fe 2.471 ± 30
3	–OT(A)	–Ni 2.589 ± 25	–Zn 2.492 ± 17
3	–OH(A)	–Zn 2.601 ± 12	–Fe 2.624 ± 12
3	–CO(A)	–Zn 2.603 ± 23	–Zn 2.644 ± 19
3	OT(A) –IT(A)	Ni–Zn 2.589 ± 25	Zn–Fe 2.492 ± 17
3	–OH(A)	–Zn 2.712 ± 12	–Fe 2.698 ± 10
3	–CO(A)	–Zn 2.572 ± 14	–Zn 2.614 ± 10
3	–CO(B)	–Zn 2.569 ± 23	–Zn 2.598 ± 17
2	OH(A)–IT(A)	Zn–Zn 2.601 ± 12	Fe–Fe 2.624 ± 12
2	–OT(A)	–Ni 2.712 ± 12	–Zn 2.698 ± 10
1	–OH(A)	–Zn 2.570 ± 29	–Fe 2.603 ± 26
4	–CO(A)	–Zn 2.800 ± 10	–Zn 2.798 ± 6
2	–CO(B)	–Zn 2.595 ± 17	–Zn 2.642 ± 11
2	–CO(B)'	–Zn 2.956 ± 17	–Zn 3.059 ± 12
1	CO(A) –IT(A)	Zn–Zn 2.603 ± 23	Zn–Fe 2.644 ± 19
1	–OT(A)	–Ni 2.572 ± 14	–Zn 2.614 ± 10
2	–OH(A)	–Zn 2.800 ± 10	–Fe 2.798 ± 10
1	–OT(B)	–Ni 2.569 ± 23	–Zn 2.598 ± 17

Table. 7 Continued.

		Γ -Ni,Zn	Γ -Fe,Zn
1	-OH(B)	-Zn 2.595 \pm 17	-Fe 2.642 \pm 11
1	-OH(B)'	-Zn 2.956 \pm 17	-Fe 3.059 \pm 12
4	-CO(B)	-Zn 2.696 \pm 7	-Zn 2.754 \pm 5
2	-CO(B)'	-Zn 3.321 \pm 23	-Zn 3.202 \pm 18

Acknowledgements. This investigation has been carried out within a research program sponsored by the *Swedish Natural Science Research Council*.

The authors are also indebted to the *Computer Division of the Swedish Rationalization Agency* for placing computer time at our disposal.

One of us (S.W.) wishes to acknowledge a grant from the *Royal Academy of Sciences (K.V.A.)* out of the *Hierta-Retzius* fund.

We wish to express our gratitude to Professor A. Magnéli, for providing us with the research facilities, for his continued interest in this work and for critical reading of the manuscript.

The valuable help of Mr. Å. Nilsson, who supplied us with the neutron diffraction records, is gratefully acknowledged.

Some of the initial experimental work was performed by Miss B. Linnros.

We also wish to acknowledge the technical assistance of Mrs. G. Winlöf, who took the Guinier photographs.

REFERENCES

- Schramm, J. Z. *Metallk.* **30** (1938) 122.
- Ekman, W. Z. *phys. Chem. Abt. B* **12** (1931) 57.
- See e.g. Vogel, A. I. *A Textbook of Quantitative Inorganic Analysis*, 3rd Ed., London 1961, pp. 479 and 468.
- Cromer, D. T. and Waber, J. T. *Acta Cryst.* **18** (1965) 104.
- Cromer, D. T. *Acta Cryst* **18** (1965) 17.
- Bacon, G. E. *Neutron Diffraction*, 2nd Ed., Oxford 1962, pp. 31 and 96.
- IUCr World List of Crystallographic Computer Programs*, 2nd Ed., Cambridge, Mass. 1966.
- Heidenstam, O. V., Johansson, A. and Westman, S. *Acta Chem. Scand.* **22** (1968) 653.

Received April 4, 1968.