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A Refinement of the Atomic and Thermal Parameters of α-Manganese from a Single Crystal*

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The growth of small single crystals of α-manganese has made possible the confirmation of the structure of this element determined previously by powder methods. This X-ray study has led to a precise structure determination and values for the Debye temperatures of the different atom types. α-Manganese, the low-temperature allotrope, has a body-centered structure with 58 atoms per cell occupying four different symmetry sites in space group $I\bar{4}3m$ (T_d^3). The lattice constant of $8\cdot911 \pm 0\cdot002$ Å leads to a calculated density of 7·463 g.cm^{-3}. Integrated intensities for 1142 reflections (650 independent) were measured by counter methods using Mo $K\alpha$ radiation. The data were refined by the least-squares method to yield a conventional R factor on F^2 of 8·4%.

Introduction

The structure of α-manganese has been studied previously by several workers. Westgren & Phragmén (1925), in an X-ray investigation of the allotropy of manganese, were able to determine the lattice parameter. Bradley & Thewlis (1927), using intensities from Westgren & Phragmén's photographic data of α-manganese powder, correctly determined the space group ($I\bar{4}3m$) and the number of atoms per unit cell (58). Values for the fractional coordinates of the atoms were also determined. These results were confirmed (Preston, 1928) from oscillating crystal photographs of nearly single-crystal samples. Gazzara, Middleton, Weiss & Hall (1967) reported a refinement of these atomic positions based on several sets of X-ray intensities obtained from α-manganese powder using Cr, Mn, and Cu radiation and counter methods. Atomic positions have been refined from single-crystal X-ray data by Kunitomi, Yamada, Nakai & Fujii (1969).‡ The results of these investigations are given in Table 1.

α-Manganese is unusual among metals and elements in the complexity of its crystal structure. The variations in interatomic distance and coordination number among the four atom types makes the structure of α-manganese more like that of an intermetallic compound than an element. The growth of pure single crystals of α-manganese in this laboratory has made possible a more precise determination of the structure of this element. The present X-ray study was undertaken for several reasons. First, it is of intrinsic importance to know the structures of the elements as accurately as possible. Second, antiferromagnetism has been observed in α-manganese below 95°K (Shull & Wilkinson, 1953; Kasper & Roberts, 1956). This present X-ray study was desirable as a prelude to a neutron diffraction study (Oberteuffer, Marcus, Schwartz and Felcher, 1968, 1970; Oberteuffer, 1969) of the magnetic structure. Third, the determination of the individual characteristic temperatures of the four atom types is possible from single-crystal data and is of importance since surprisingly large differences in these temperatures were hypothesized to explain the Mössbauer spectra of ^{57}Fe in an alloy of 5% Fe in α-manganese (Kimball, Phillips, Nevitt & Preston, 1966).

The sample used in this experiment was prepared from a crystal grown by a vapor deposition method (Oberteuffer, Marcus, Schwartz & Felcher, 1970). To minimize absorption effects the crystals were ground into spheres with radii of the order of 0·2 mm. They were then etched in solutions of 10% HCl in methanol to reduce the radius by about half. It was difficult to prevent some asphericity from developing during etching even though the etching solution was agitated. The smallest sphere that could be prepared in this way was about 0·1 mm in radius. The sample used in this experiment was an ellipsoid whose principal axes were 0·11, 0·084 and 0·068 mm. This crystal was mounted with the long axis of the ellipsoidal crystal roughly parallel to the φ axis of a Picker four-circle automatic diffractometer.

Collection and reduction of intensity data

Fourteen reflections were manually centered on the diffractometer and their setting angles formed the basis

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for a least-squares refinement* of cell constant and orientation as previously described (Corfield, Doedens & Ibers, 1967). The lattice constant derived was 8·911(2) Å, based on observations made at 20°C with Mo $K\alpha_1$ radiation ($\lambda=0·70930$ Å).

Intensity data were collected in the manner previously described (Corfield, Doedens & Ibers, 1967). The diffracted beams were filtered through a 3 mil niobium foil. The $\theta-2\theta$ scan technique was used, at a scan rate of 1° per minute, with scans ranging from 0·5° in 2θ below the $K\alpha_1$ peak to 0·5° above the $K\alpha_2$ peak. Stationary-counter, stationary-crystal background counts at the extreme positions were made for 20 seconds each. The pulse height analyzer was set to accept a 90% window. The diffracted beams passed through a counter aperture of dimensions 7 × 7 mm which was positioned 29 cm from the crystal. At a take-off angle of 1·1°, where a typical peak height was 80% of the maximum as a function of take-off angle, the widths at half-height of the scans were only about 0·1° in 2θ. Thus the eventual problems with extinction were not surprising.

During the data collection three reflections were chosen as standards and were observed every 200 reflections. No differences were observed other than those expected from the usual statistical deviations. A total of 1142 reflections was collected out to $\lambda^{-1}\sin\theta$ of 1·3 Å^{-1} (using both the bisecting and parallel geometries). Of these, 129 were less than their standard deviations. This data set consisted of two members of the *hkl* form, specifically *hkl* and *hlk*.

The data were reduced as described previously, using a value for p of 0·03. Absorption effects are significant even with an average sample radius of 0·085 mm since μ is 257 cm^{-1} for α-manganese using Mo $K\alpha$ radiation. The attenuation factor of the radiation over the mean radius is approximately 10. Initially a spherical absorption correction was applied to the data using the mean radius of 0·085 mm for the ellipsoidal crystal. In the final stages of refinement a more realistic absorption correction was applied: The ellipsoidal crystal was approximated by a 30-sided polygon and a numerical absorption correction was made. The transmission factors calculated in this way varied from about 0·06 at low angles to 0·14 at high angles. The anisotropy of the correction because of the non-spherical shape was as large as 50% at low angles and decreased to 20% at high angles. The maximum error in the local radius of the crystal as a result of the polygonal approximation is of the order of 6%, but microscopic examination of the crystal revealed surface irregularities of at least this magnitude. Because of the large absorption much of the intensity of a reflection comes from the surface of the crystal and these surface ir-

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* In addition to various local programs for the CDC 6400 local versions of the following programs were used: *ORFLS* least-squares refinement and *ORFFE* error function programs of Busing & Levy, *GONO* absorption correction program of Hamilton, *FORDAP* Fourier program of Zalkin, and *ORTEP* plotting program of Johnson.

Table 1. *Atomic positional parameters*

	Atom I	Atom II	Atom III	Atom IV	Lattice parameter
Wyckoff notation	2(*a*)	8(*c*)	24(*g*)	24(*g*)	
Site symmetry	$\bar{4}3m$	$3m$	m	m	
Equivalent positions	000	*xxx*	*xxz*	*xxz*	*a*
Bradley & Thewlis	000	$x=0·317$	$x=0·356$ $z=0·042$	$x=0·089$ $z=0·278$	8·894 Å
Gazzara, Middleton, Weiss & Hall	000	$x=0·316$	$x=0·356$ $z=0·034$	$x=0·089$ $z=0·282$	8·9125 (10)*
Kunitomi, Yamada, Nakai & Fujii	000	$x=0·3176$	$x=0·3569$ $z=0·0346$	$x=0·0898$ $z=0·2820$	
Present experiment	000	$x=0·31787$ (10)	$x=0·35706$ (6) $z=0·03457$ (9)	$x=0·08958$ (6) $z=0·28194$ (9)	8·911 (2)

* The numbers in parentheses here and in succeeding Tables are estimated standard deviations.

Table 2. *Results of various refinements*

Refinement number	*hkl, hlk* averaged	Absorption correction	Debye–Waller factors	Scattering factor	R_w	R_1
1	no*	Spherical	Isotropic	Mn^0	16·0%	14·2%
2	no*	Ellipsoidal	Isotropic	Mn^0	13·3	11·8
3	no*	Ellipsoidal	Anisotropic	Mn^0	13·2	11·7
4	yes†	Ellipsoidal	Isotropic	Mn^0	12·4	9·7
5	yes	Ellipsoidal	Isotropic	Mn^{2+}	11·3	9·2
6‡	yes	Ellipsoidal	Isotropic	Mn^{2+}	11·5	8·4

* Number of observations = 1142.

† Number of observations = 650.

‡ $\sigma(F^2)$ adjusted to give an error in an observation of unit weight the value 1·0 for all classes of reflections, as a function of F_o^2, and as a function of θ.

regularities are thus a significant contributor to the uncertainty of the low angle data. At low angles the *R*-factor for averaging equivalent reflections was 8·9 % before the final absorption correction and 8·5 % after. For all reflections, however, averaging *hkl* and *hlk* gave *R* factors of 7·9 % before and 6·1 %after the absorption correction. Thus there is some justification for the use of the more sophisticated absorption correction.

Refinement of the structure

In the full-matrix least-squares refinements, the function minimized was $\sum w(F_o^2-F_c^2)^2$, where w, the weight, is taken as $1/\sigma^2\ (F_o^2)$ and where F_o^2 and F_c^2 are the squares of the observed and calculated structure amplitudes. The conventional and weighted R factors are defined as $R_1=\sum|F_o^2-F_c^2|/\sum F_o^2$ and $R_w^2=\sum w(F_o^2-F_c^2)^2/\sum wF_o^4$. The Mn^0 (and later Mn^{2+}) scattering factors were taken from Watson & Freeman (1961) and Freeman & Watson (1961). The values of $\Delta f'$ and $\Delta f''$ were taken from the calculations of Cromer (1965) and were applied to the calculated structure factors (Ibers & Hamilton, 1964).

The course of the refinement is shown in Table 2. Initially the parameters varied were the overall scale factor, the atomic coordinates of the atoms (starting with those values in Table 1), the isotropic Debye–Waller factors for the four independent atoms, and a one-parameter extinction parameter (Zachariasen, 1968). Space group $I\bar{4}3m$ was assumed.

The final values of F_o^2 and F_c^2 (in electrons² × 0·1) are given in Table 4. The final parameters are listed in Tables 1 and 3. The extinction coefficient in absolute units was $4{\cdot}0(3)\times10^{-5}$. Although the various refinements indicated in Table 2 led to slight differences in the derived Debye–Waller factors, they did not lead to significant differences in the positional parameters.

A final difference Fourier synthesis has no interpretable features. The maximum density is 2·9 e.Å^{-3}, about 1 % of the manganese peaks on an observed electron density map.

Table 3. *Thermal parameters determined for α-manganese*

	Debye–Waller factor B	Debye temperature Θ_D	Root-mean square displacement
I	0·447 (23) Å²	379 (11) °K	0·075 (2) Å
II	0·454 (12)	376 (5)	0·076 (1)
III	0·423 (7)	390 (4)	0·0732 (7)
IV	0·391 (7)	406 (4)	0·0704 (6)
Average	0·414	394	0·0725

The structure

The structure is that deduced from earlier powder data. A stereoscopic view of the unit cell is shown in Fig. 1. The type I atom at the body-centered position is surrounded tetrahedrally by four atoms of type II (these four shown are actually those belonging to the corners of the unit cell). At a somewhat larger distance twelve type III atoms form a polygon whose faces are triangles and rectangles. Closest to atom I are the twelve type IV atoms. Fig. 2 shows the four atom types and their nearest neighbors in stereo pairs. In Table 5 the interatomic distances for the nearest neighbors of the four atom types are listed.

The thermal parameters determined in this experiment are listed in Table 3. A refinement using anisotropic thermal ellipsoids did not improve the value of R_w nor did it lead to values that differed significantly from the spherical model. The Debye temperature was calculated from the simple Debye model for cubic crystals with one atom per unit cell. In a previous determination of the average Debye temperature Gazzara, Middleton & Weiss (1964) found $\Theta_D=390°$ K from X-ray reflection intensity ratios at different temperatures. Kimball, Phillips, Nevitt & Preston (1966) obtained $\Theta_D=410°$ K for Fe atoms in sites III and IV in a 5% Fe–Mn alloy with the α-manganese structure from the temperature variation of the total absorption of Mössbauer spectra. They suggested that atoms III and IV might have the widely different individual

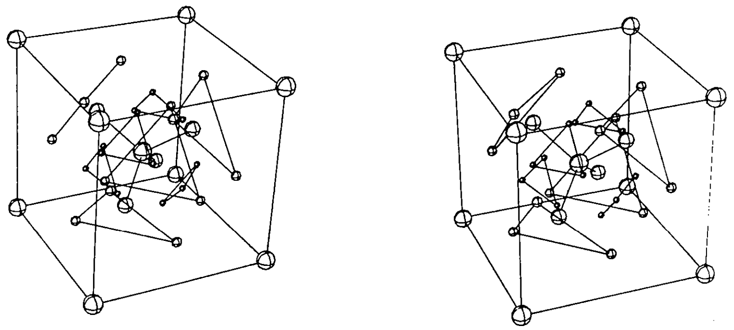

Fig. 1. Stereoscopic view of one half of the unit cell. The 28 nearest neighbors of the type I atom at the body-centered position are shown. The unit-cell corners are defined by 8 type I atoms. Each corner and body-centered position in the lattice has this coordination. The atoms are differentiated by size, type I is the largest, type IV the smallest.

Debye temperatures of 500 and 250° K. The absolute values of the Debye temperatures are sensitive to the magnitude of the absorption correction, which is not precisely known, and to the effects of thermal diffuse scattering, which were ignored in the refinement. But the relative values of Θ_D are insensitive to the absorption correction and are probably not very sensitive to the effects of thermal diffuse scattering. We conclude, therefore, that although some significant variations in the Debye temperatures of the atom types exist, these variations are far smaller than suggested by Kimball, *et al.*

Table 4. *Values of* $0{\cdot}1\ F_o^2$ *and* $0{\cdot}1\ F_c^2$ *(in electrons²) for α-manganese*

H	K	FO	FC
***** L = 0 *****			
1	1	5	1
2	0	26	0
2	2	168	142
3	1	20	11
3	3	6107	6047
4	0	3009	2735
4	2	55	47
4	4	310	317
5	1	1051	933
5	3	2	8
5	5	5849	6387
6	0	85	76
6	2	147	134
6	4	11	6
6	6	4081	4263
7	1	41	24
7	3	1778	1607
7	5	36	28
7	7	0	27
8	0	24	4
8	2	1111	1030
8	4	74	64
8	6	29	16
8	8	447	521
9	1	47	41
9	3	567	544
9	5	24	2
9	7	437	437
9	9	0	0
10	0	83	39
10	2	204	182
10	4	185	151
10	6	1007	997
10	8	278	293
10	10	1697	1870
11	1	2048	1957
11	3	49	73
11	5	274	249
11	7	6	18
11	9	143	167
11	11	1277	1332
12	0	53	37
12	2	128	121
12	4	515	494
12	6	83	73
12	8	115	102
12	10	461	494
12	12	0	7
13	1	13	11
13	3	130	103
13	5	345	319
13	7	793	801
13	9	8	0
13	11	99	88
13	13	328	315
14	0	239	245
14	2	852	736
14	4	17	24
14	6	196	181
14	8	60	70
14	10	30	0
14	12	22	0
14	14	1	0
15	1	34	16
15	3	497	447
15	5	17	19
15	7	303	266
15	9	50	31
15	11	216	236
15	13	239	241
15	15	201	196
16	0	1270	1117
16	2	3	6
16	4	306	283
16	6	538	549
16	8	41	56
16	10	0	2
16	12	9	0
16	14	271	260
16	16	628	627
17	1	103	99
17	3	10	5
17	5	759	725
17	7	18	11
17	9	0	1
17	11	76	78
17	13	41	51
17	15	6	8
18	0	961	755
18	2	59	39
18	4	29	20
18	6	76	72
18	8	19	12
18	10	195	196
18	12	185	180
19	1	10	15
19	3	85	60
19	5	45	26
19	7	67	70
19	9	0	21
19	11	259	232
20	0	31	10
20	2	42	31
20	4	57	48
20	6	0	7
20	8	39	41
20	10	33	26
21	1	138	103
21	3	155	151
21	5	223	250
21	7	31	29
22	0	1069	901
22	2	7	5
22	4	0	2
***** L = 1 *****			
2	1	56	41
3	2	98	83
4	1	6423	6707
4	3	1705	1631
5	2	229	193
5	4	63	56
6	1	59	46
6	3	252	213
6	5	890	973
7	2	3924	4052
7	4	228	221
7	6	572	602
8	1	542	461
8	3	381	355
8	5	782	781
8	7	172	173
9	2	384	371
9	4	404	389
9	6	1960	2024
9	8	334	342
10	1	610	525
10	3	399	373
10	5	879	862
10	7	749	740
10	9	206	204
11	2	554	562
11	4	296	289
11	6	68	50
11	8	244	233
11	10	60	54
12	1	195	156
12	3	767	733
12	5	239	242
12	7	337	323
12	9	273	269
12	11	42	28
13	2	88	87
13	4	362	377
13	6	379	339
13	8	112	110
13	10	38	52
13	12	118	101
14	1	434	365
14	3	358	335
14	5	79	101
14	7	473	466
14	9	331	316
14	11	560	559
14	13	20	29
15	2	595	653
15	4	142	132
15	6	36	26
15	8	16	5
15	10	201	208
15	12	297	324
15	14	69	76
16	1	9	12
16	3	40	41
16	5	463	409
16	7	53	56
16	9	285	314
16	11	14	21
16	13	33	23
16	15	0	1
17	2	21	28
17	4	479	480
17	6	125	109
17	8	115	130
17	10	136	135
17	12	191	179
17	14	57	56
18	1	621	520
18	3	3	3
18	5	56	58
18	7	9	26
18	9	114	114
18	11	17	5
18	13	37	31
19	2	2	6
19	4	180	160
19	6	64	89
19	8	83	65
19	10	74	59
19	12	157	157
20	1	134	161
20	3	139	134
20	5	18	10
20	7	291	272
20	9	42	42
21	2	36	34
21	4	329	307
21	6	52	38
21	8	119	93
22	1	23	36
22	3	19	17
22	5	0	10
***** L = 2 *****			
2	2	334	319
3	3	4049	4143
4	2	2316	2205
4	4	424	464
5	3	254	254
5	5	2131	2570
6	2	1327	1107
6	4	1322	1375
6	6	556	632
7	3	498	485
7	5	569	598
7	7	171	185
8	2	3659	3334
8	4	327	319
8	6	308	323
8	8	32	53
9	3	29	25
9	5	822	802
9	7	127	113
9	9	555	614
10	2	697	565
10	4	1458	1415
10	6	119	107
10	8	368	375
10	10	121	184
11	3	966	956
11	5	437	405
11	7	18	7
11	9	118	155
11	11	44	58
12	2	108	114
12	4	410	403
12	6	845	761
12	8	194	241
12	10	115	127
12	12	158	199
13	3	364	368
13	5	593	602
13	7	340	332
13	9	255	273
13	11	145	188
13	13	151	156
14	2	146	106
14	4	236	241
14	6	191	178
14	8	361	353
14	10	20	30
14	12	64	67
14	14	145	133
15	3	41	44
15	5	94	96
15	7	30	37
15	9	222	243
15	11	0	13
15	13	29	33
15	15	46	48
16	2	204	182
16	4	9	21
16	6	82	75
16	8	290	284
16	10	0	7
16	12	84	73
16	14	14	11
16	16	13	12
17	3	161	147
17	5	161	159
17	7	303	273
17	9	345	324
17	11	141	145
17	13	164	154
17	15	0	23
18	2	208	175
18	4	60	56
18	6	90	74
18	8	464	422
18	10	131	123
18	12	106	103
19	3	493	464
19	5	79	64
19	7	6	6
19	9	15	15
19	11	62	48
20	2	107	85
20	4	140	125
20	6	236	211
20	8	214	214
20	10	56	24
21	3	15	17
21	5	153	126
21	7	136	147
22	2	33	21
22	4	117	103
***** L = 3 *****			
4	3	305	295
5	4	93	89
6	3	2899	2635
6	5	525	594
7	4	292	273
7	6	363	433
8	3	2432	2083
8	5	739	751
8	7	487	550
9	4	179	185
9	6	836	905
9	8	675	813
10	3	485	427
10	5	359	366
10	7	247	262
10	9	130	169
11	4	106	73
11	6	114	111
11	8	279	302
11	10	45	50
12	3	143	100
12	5	149	140
12	7	122	104
12	9	114	103
12	11	15	14
13	4	315	336
13	6	192	166
13	8	905	876
13	10	566	553
13	12	236	245
14	3	651	545
14	5	322	310
14	7	56	55
14	9	175	149
14	11	49	46
14	13	343	365
15	4	456	516
15	6	30	29
15	8	35	51
15	10	234	240
15	12	123	106
15	14	3	21
16	3	168	176
16	5	57	46
16	7	328	290
16	9	44	46
16	11	188	180
16	13	93	103
16	15	92	87
17	4	225	222
17	6	45	41
17	8	118	120
17	10	90	80
17	12	107	99
17	14	32	32
18	3	430	401
18	5	5	1
18	7	284	265
18	9	60	44
18	11	26	30
18	13	184	196
19	4	21	29
19	6	83	68
19	8	314	293
19	10	42	25
19	12	41	42
20	3	97	78
20	5	35	38
20	7	0	4
20	9	20	24
21	4	7	10
21	6	72	62
21	8	16	11
22	3	190	159
22	5	34	38
***** L = 4 *****			
4	4	5828	5865
5	5	256	277
6	4	362	345
6	6	1129	1263
7	5	1228	1320
7	7	1698	1925
8	4	535	505
8	6	155	160
8	8	265	300
9	5	335	316
9	7	279	309
9	9	1514	1715
10	4	72	91
10	6	27	17
10	8	10	9
10	10	392	450
11	5	53	31
11	7	526	567
11	9	337	413
11	11	213	259
12	4	458	413
12	6	215	211
12	8	76	76
12	10	286	339
12	12	670	770
13	5	37	16
13	7	142	141
13	9	237	267
13	11	28	66
13	13	7	2
14	4	473	445
14	6	487	454
14	8	224	200
14	10	137	157
14	12	4	21
14	14	349	390
15	5	184	198
15	7	313	311
15	9	7	13
15	11	4	4
15	13	72	70
15	15	490	452
16	4	9	7
16	6	284	288
16	8	61	47
16	10	7	6
16	12	98	100
16	14	60	92
17	5	39	37
17	7	117	141
17	9	23	32
17	11	150	134
17	13	21	17
18	4	331	331
18	6	272	241
18	8	22	7
18	10	61	47
18	12	148	157
19	5	0	1
19	7	9	7
19	9	94	94
19	11	94	83
20	4	167	102
20	6	59	60
20	8	30	27
20	10	215	213
21	5	46	41
21	7	7	5
22	4	51	56
***** L = 5 *****			
6	5	582	569
7	6	10	11
8	5	1272	1233
8	7	235	302
9	6	245	239
9	8	167	186
10	5	1418	1267
10	7	123	136
10	9	22	25
11	6	1530	1580
11	8	142	176
11	10	269	322
12	5	497	478
12	7	111	117
12	9	251	302
12	11	46	73
13	6	21	29
13	8	334	368
13	10	9	24
13	12	46	36
14	5	64	72
14	7	106	97
14	9	32	34
14	11	155	146
14	13	3	0
15	6	119	123
15	8	339	358
15	10	189	234
15	12	27	21
15	14	40	41
16	5	559	493
16	7	25	22
16	9	22	27
16	11	690	638
16	13	20	27
16	15	10	8
17	6	16	26
17	8	48	44
17	10	91	96
17	12	17	23
17	14	24	22
18	5	218	253
18	7	148	183
18	9	39	28
18	11	36	34
18	13	29	18
19	6	209	196
19	8	90	75
19	10	84	77
20	5	359	286
20	7	18	19
20	9	190	183
21	6	191	169
***** L = 6 *****			
6	6	618	650
7	7	887	935
8	6	335	316
8	8	353	418
9	7	81	76
9	9	342	375
10	6	262	193
10	8	167	168
10	10	248	279
11	7	8	22
11	9	0	3
11	11	197	248
12	6	506	432
12	8	33	27
12	10	153	185
12	12	271	295
13	7	61	46
13	9	149	142
13	11	55	58
13	13	232	252
14	6	49	57
14	8	109	106
14	10	87	87
14	12	115	136
14	14	32	40
15	7	546	524
15	9	240	266
15	11	5	5
15	13	57	68
15	15	71	109
16	6	324	275
16	8	127	112
16	10	443	436
16	12	181	206
16	14	15	10
17	7	136	132
17	9	100	117
17	11	63	65
17	13	45	42
18	6	44	7
18	8	8	1
18	10	60	47
18	12	9	4
19	7	108	115
19	9	400	369
19	11	18	2
20	6	34	18
20	8	19	11
***** L = 7 *****			
8	7	0	15
9	8	20	14
10	7	206	209
10	9	501	558
11	8	188	206
11	10	12	17
12	7	635	614
12	9	741	750
12	11	277	287
13	8	72	70
13	10	106	145
13	12	217	210
14	7	16	25
14	9	11	22
14	11	132	143
14	13	45	49
15	8	62	58
15	10	115	119
15	12	139	144
15	14	76	85
16	7	28	23
16	9	109	102
16	11	56	69
16	13	99	118
17	8	176	171
17	10	41	33
17	12	44	35
18	7	119	111
18	9	123	120
18	11	17	24
19	8	151	155
19	10	9	2
20	7	79	32
***** L = 8 *****			
8	8	3116	3117
9	9	0	6
10	8	421	379
10	10	18	22
11	9	41	45
11	11	431	420
12	8	259	255
12	10	32	37
12	12	65	41
13	9	252	259
13	11	42	41
13	13	500	581
14	8	522	524
14	10	33	49
14	12	2	0
14	14	315	315
15	9	2	12
15	11	99	99
15	13	14	29
15	15	22	41
16	8	50	39
16	10	59	75
16	12	0	5
16	14	28	38
17	9	8	3
17	11	101	99
18	8	25	17
18	10	37	35
19	9	173	148
***** L = 9 *****			
10	9	49	36
11	10	14	5
12	9	583	580
12	11	73	74
13	10	26	24
13	12	21	23
14	9	23	16
14	11	44	39
14	13	29	24
15	10	398	385
15	12	66	85
15	14	41	15
16	9	251	217
16	11	15	6
16	13	74	72
17	10	91	78
17	12	81	95
18	9	29	40
***** L = 10 *****			
10	10	16	6
11	11	737	748
12	10	50	40
12	12	71	57
13	11	40	44
13	13	172	175
14	10	135	149
14	12	188	169
14	14	137	140
15	11	44	35
15	13	190	197
16	10	304	271
16	12	55	65
17	11	5	16
***** L = 11 *****			
12	11	88	73
13	12	0	4
14	11	191	174
14	13	119	117
15	12	30	46
16	11	170	162
***** L = 12 *****			
12	12	205	213
13	13	58	62
14	12	86	100

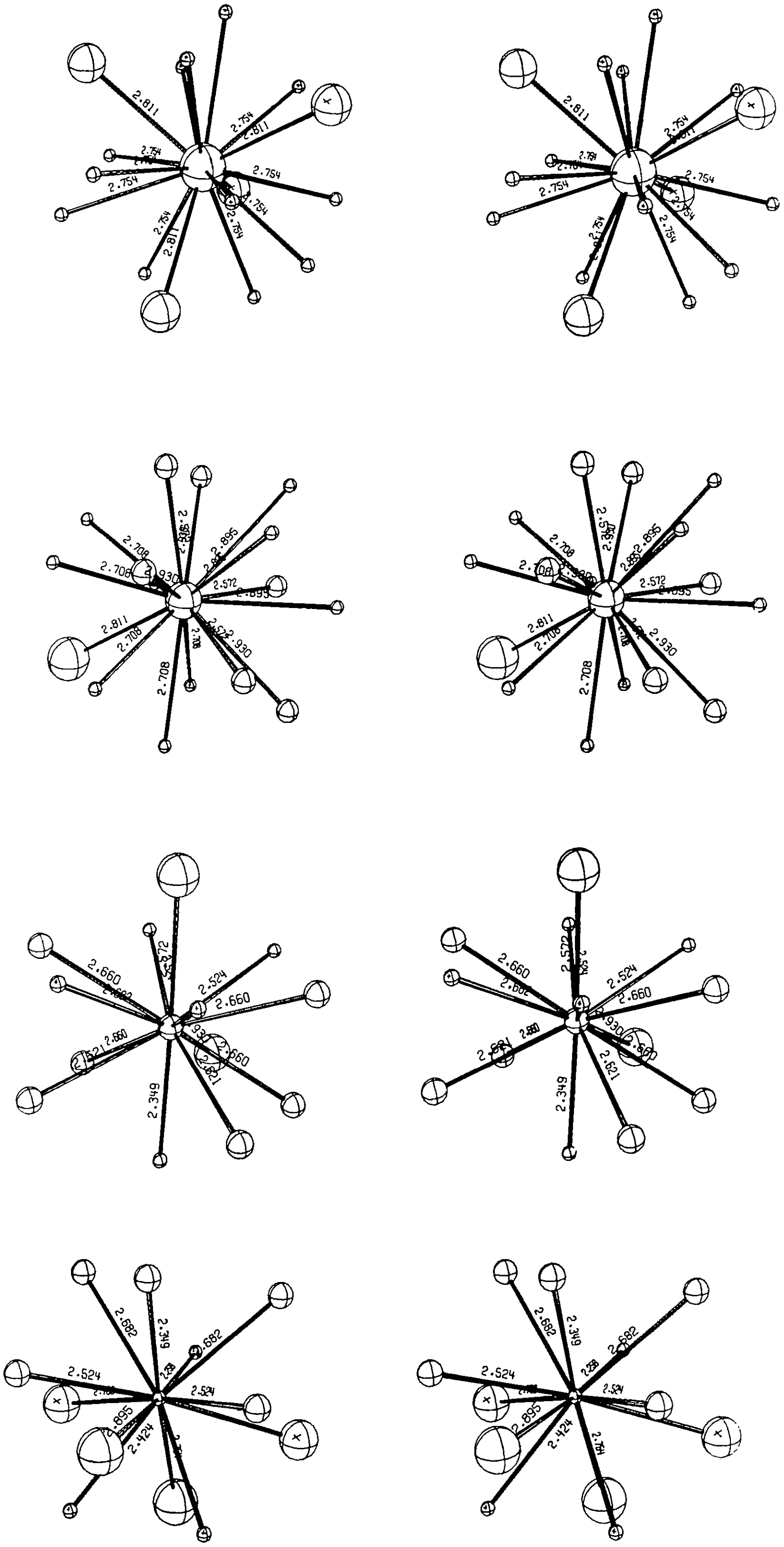

Fig. 2. Stereoscopic views of the coordination of the four atom types. These views are from the same angle as that of Fig. 1. Bond lengths not explicitly indicated are the same as those given for atoms marked with similar symbols.

Table 5. *Interatomic distances for nearest neighbors*

Atomic type	Nearest neighbors Number	 Type	Distance*	Coordination number
I	4	II	2·811 Å	
	12	IV	2·754	16
II	1	I	2·811	
	3	III	2·572	
	3	III	2·930	
	6	IV	2·708	
	3	IV	2·895	16
III	1	II	2·572	
	1	III	2·930	
	2	III	2·622	
	4	III	2·661	
	1	IV	2·349	
	2	IV	2·524	
	2	IV	2·682	13
IV	1	I	2·754	
	2	II	2·708	
	1	II	2·895	
	1	III	2·349	
	2	III	2·524	
	2	III	2·682	
	1	IV	2·258	
	2	IV	2·424	12

* All errors are ±0·001 Å.

One might expect differences to exist in the true scattering factors of the four different types of manganese atoms, since the coordination number and symmetry of their sites are different. Although such effects were looked for in a second data set which consisted of all dependent reflections in the region $\lambda^{-1}\sin\theta < 0\cdot3$ Å^{-1}, no definite conclusions could be reached. This is not surprising since these inner data are most sensitive to the model for extinction and are affected more by the problems of the absorption correction.

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The Crystal and Molecular Structure of α,α′-Diselenobisformamidinium Dichloride

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The crystal structure of α,α′-diselenobisformamidinium dichloride, $[\mathrm{SeC(NH_2)_2}]_2\mathrm{Cl_2}$, has been determined by a three-dimensional X-ray analysis (Cu $K\alpha$). The unit cell of dimensions $a=12\cdot82(2)$, $b=6\cdot01(1)$, $c=12\cdot22(1)$ Å, $\beta=108\cdot1(0\cdot1)°$ contains 4 stoichiometric units (space group $C2/c$). The organic cation is formed by two selenourea groups nearly perpendicular to the Se–Se = 2·380(6) Å bond, the dihedral angle $\mathrm{CSeSe^{i}\wedge SeSe^{i}C^{i}}$ being 89·5°; bond distances in those groups are: Se–C = 1·94 (1), C–N = 1·32 (2) and 1·30 (2) Å.All the hydrogen atoms are involved in N···Cl hydrogen bonds. The molecular structure of the cation is compared with that of the corresponding thio-derivative.

Introduction

In an attempt to prepare silver(I)–selenourea complexes, a few crystals of α,α′-diselenobisformamidinium dichloride were obtained. They were probably formed by oxidation of selenourea by the Ag$^+$ ion or by atmospheric oxygen. As the crystals were too few for a conventional chemical analysis, their nature was deter-