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A Refinement of the Parameters of α Manganese

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The atomic parameters of α manganese, first determined by Bradley & Thewlis (1927), have been refined from an R index of 0.093 to a final R of 0.029 for fifty reflections. This refinement was based on an analysis of the integrated intensities of X-ray diffracted powder peaks measured independently at two laboratories. The lattice constant of α manganese was determined from liquid helium temperature up to room temperature and a change in the thermal expansion coefficient was found in the vicinity of the Néel temperature (95°K) although no structural change was observed in this region.

The structure of α manganese as determined by Bradley & Thewlis (1927) is as follows:

Space group $I\bar{4}3m$ no. 217 in *International Tables for X-ray Crystallography* (1952).

2 Mn(1) in 2(a) 000, etc.
 8 Mn(2) in 8(c) xxx, etc. $x(2)=0.317$
 24 Mn(3) in 24(g) xxz, etc. $x(3)=0.356$, $z(3)=0.042$
 24 Mn(4) in 24(g) xxz, etc. $x(4)=0.089$, $z(4)=0.278$

This result is based on X-ray intensities read from Phragmén-camera photographs taken by Westgren & Phragmén (1925). Kasper & Roberts (1956) checked Bradley & Thewlis's parameters with neutron diffraction data and found them to be accurate enough (± 0.003) to establish the magnetic structure at 4.2, 77, and 298°K.

In an attempt by Gazzara, Middleton & Weiss to determine the characteristic temperature θ of α -Mn it was found desirable to refine the structural parameters by applying modern experimental X-ray diffraction techniques. A refinement was performed on twenty-one Cr $K\alpha$ diffraction peaks from powder specimens. During this same time, a similar refinement was performed by E. O. Hall on α -Mn powders using Cu $K\alpha$

radiation. This report presents the best values of the structural parameters obtained from the two investigations.

Although many powder samples were examined in this X-ray diffraction analysis, the data from only four sources were eventually used:

(1) A pure, carbon-free, electrolytic -400 mesh powder. This showed some diffraction peak broadening and gave intensities identical with those of sample (2).

(2) Electrolytic plate, ground mortar and pestle and sifted to -400 mesh particle size. Although the cold working increased the diffraction peak widths, it reduced extinction effects. The integrated intensity of the Cr $K\alpha$ diffraction peak $\Sigma h^2=18$, for example, was increased 4% through cold working. All calculations involving Cr $K\alpha$ radiation are based on measurements performed on this material.

(3) A portion of powder sample (2) annealed at 440°C for 90 hours in vacuum. All of the diffraction peaks obtainable with Cr $K\alpha$ radiation from this sample could be resolved and accurately measured with Mo $K\alpha$ radiation; many of the high-angle Mo $K\alpha$ diffraction peaks were resolved sufficiently well to be integrated. All results obtained with Mo $K\alpha$ radiation were taken

from sample (3) and extinction effects were assumed to be negligible.

(4) A Johnson-Matthey H.S. manganese flake. This was lightly pickled in hydrochloric acid to remove surface oxide, washed, dried and finally crushed in a mortar. This material was used in the investigation by E. O. Hall.

All samples of Mn were contaminated to some degree with MnO. The MnO peaks frequently occurred at the same angles as the Mn peaks and a correction for their contribution was made. Vacuum fusion analyses of samples (1) to (3) indicated 0.40 wt. % oxygen, whereas neutron activation measurements indicated more than 0.60 wt. % oxygen. The integrated intensity of the resolved MnO 211 peak indicated approximately 0.60 wt. % oxygen or more.

Preferred orientation in the powder samples was examined using a pole figure sample holder. No significant variation in the integrated intensity of diffraction peak $\Sigma h^2=18$ was observed with rotation of the specimen.

The effect of porosity on the integrated intensities was determined from the ratio of the fluorescent intensities of the powder specimens to those from polished electrolytic plates (Cooper, 1962). The ratios were found to be 0.95 ± 0.01 at $(\sin \theta/\lambda)^2=0.057$ and 0.98 ± 0.01 at $(\sin \theta/\lambda)^2=0.984$ with Cr $K\alpha$ radiation. In the refinement calculations the effect of porosity on the values of the atomic parameters was found to be negligible.

A correction for porosity was made by normalizing the intensity of the Cr $K\alpha$ $\Sigma h^2=50$ peak against the reflection $\Sigma h^2=19$ from a standard silicon powder specimen. An interesting observation for this α -Mn study is that the refined parameter values were found to be independent of the normalization factor, used to obtain the absolute values of the intensities.

The intensity data were obtained in four different ways:

(i) Twenty-one of the major diffraction peaks $\Sigma h^2=6$ through 58 from samples (1) and (2) were investigated at 310 and 100°K, using a General Electric XRD-5 Diffractometer, vanadium filtered Cr $K\alpha$ radiation, (40 kV, 35 mA) and a scintillation counter. The integrated intensities were measured using a technique reported by Gazzara (1960).

(ii) Using the apparatus in (1) with a Mo-target tube (40 kV, 35 mA) and Zr filter. This provided the most reliable intensity data. Several samples were investigated using both a counting technique, and automatic ratemeter chart recordings of 2θ scans. Of the high angle diffraction peaks $\Sigma h^2 > 58$, twenty-nine were resolved and integrated graphically.

(iii) Using a Phillips X-ray generator with a Mo-target tube and a LiF monochromator. This system was not sufficient to resolve diffraction peaks $\Sigma h^2=54, 56, 58$.

(iv) Using a Phillips PW 1010 X-ray set with a Cu-target tube for step-scanning diffraction peaks $\Sigma h^2=6$

through 58. This apparatus was used by E. O. Hall on sample (4).

The lattice constant measurements from 5 to 298°K were made on sample (3) using a cryostat manufactured by Materials Research Corporation, Orangeburg, New York. The lattice constants were refined by Cohen's (1955) least-squares method; the weighted r.m.s. deviations are indicated in Fig. 1 with vertical bars. The assumed wave lengths were 2.28962 Å (Cr $K\alpha_1$), 2.29351 Å (Cr $K\alpha_2$), 0.70926 Å (Mo $K\alpha_1$) and 0.713543 Å (Mo $K\alpha_2$).

The dispersion corrections used were $\Delta f' = 1.8$ and $\Delta f'' = 0.8$ for Cr $K\alpha$ radiation; $\Delta f' = 0.4$ and $\Delta f'' = 0.8$ for Mo $K\alpha$ radiation; and $\Delta f' = -0.5$ and $\Delta f'' = 3.0$ for Cu $K\alpha$ (Dauben & Templeton, 1955). The scattering factors were taken from Freeman & Watson (1961). All measured intensities were converted to the Mo $K\alpha$ scale and corrected for thermal diffuse scattering (Chipman & Paskin, 1958).

The function Y_j is defined by:

$$Y_j = \frac{I_j}{(\text{LP})G_j^2 e^{-2M}}$$

where

I_j = normalized integrated intensity of peak j

LP = Lorentz Polarization factor

$e^{-2M} = \exp\{-2B(\sin \theta/\lambda)^2\}$ = Debye-Waller factor

G_j = square root of the structure factor term for powder peak j or $G_j = (\sum_i m_i F_i F_i^*)^{\frac{1}{2}}$

m_i = multiplicity

$F_i F_i^*$ = the structure factor times its complex conjugate for $(hkl)_i$.

In the refinement of the atomic parameters, the condition was imposed that the slope of $\ln Y_j$ vs. $(\sin \theta/\lambda)^2$ be the same for both sets of intensity data taken at 100 and 310°K for one computed value of B . This resulted in a value of $B = 0.47 \pm 0.05$ Å² with a characteristic temperature $\Theta = 380 \pm 20$ °K.

The value of B and the characteristic temperature Θ were more accurately determined from measurements of the ratio of the integrated intensities at 100 to 310°K

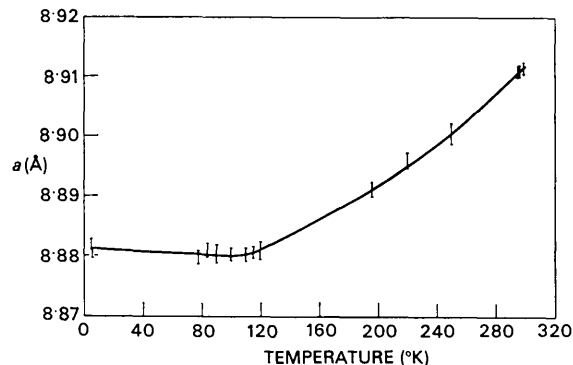


Fig. 1. Lattice parameter, a , versus temperature for α manganese. The a values were obtained from Cohen least-squares calculations.

Table 1. Values of G_j , where $G_j = (\sum m_i F_i F_i^*)^2$, corresponding to the observed powder reflections (column 1), calculated with the atomic parameters of Bradley & Thewlis (column 2), and calculated with the atomic parameters reported in the present investigation (column 3)

Σh_i^2	G_j			Σh_i^2	G_j			Σh_i^2	G_j		
	Observed	Bradley and Thewlis	Present Work		Observed	Bradley and Thewlis	Present Work		Observed	Bradley and Thewlis	Present Work
2		18	22	108			582	218		1106	
4		40	15	110	1053	1253	1027	222		775	
6	125	123	123	114	1395	1245	1377	224		323	
8	165	168	164	116			440	226		638	
10		78	89	118	1556	1518	1548	228		757	
12	206	209	207	120			1214	230	1425	1391	
14	231	210	236	122	1272	1386	1359	232		328	
16	552	590	546	126	1535	1360	1482	234		965	
18	2870	2868	2897	128			375	236		642	
20		204	109	130			485	238		285	
22	1584	1633	1570	132			263	242	1472	1489	
24	1032	1033	1022	134			1408	244	1460	559	
26	1328	1273	1329	136			807	246		1019	
30	355	389	382	138			706	248		906	
32	257	164	255	140			319	250		1103	
34	317	381	321	142			486	254		762	
36	418	463	446	144			421	256		454	
38	466	567	467	146			944	258		834	
40		226	231	148			201	260		689	
42		248	149	150	1447	1210	1435	262		297	
44	648	687	679	152			290	264		839	
46	414	342	391	154	1242	1454	1318	266		843	
48	1163	1093	1172	158			603	268		208	
50	1385	1330	1392	160			509	270		556	
52		38	41	162			313	272		612	
54	2647	2615	2625	164			892	274	1274	1245	
56	1096	1104	1083	166			760	276		555	
58	830	897	794	168			583	278	1254	1311	
				170			651	280	1487	534	
62	1067	1161	1116	172			308	282		820	
64			55	174			495	286		736	
66			664	176			481	288		79	
68			769	178	1122	987	1136	290		879	
70			724	180			250	292		726	
72	1799	1712	1770	182	1588	1515	1603	294		626	
74			702	184	1075	779	988	296		504	
76			534	186	1151	1062	1149	298		225	
78			551	190			433	300		202	
80			146	192			874	302		551	
82	1029	999	1014	194			1274	304		831	
84			477	196			607	306	1505	1442	
86	1082	972	1042	198			1090	308	568	698	
88			790	200	1090	1088	1130	310	1136	1157	
90	1535	1467	1508	202			449	312	568	486	
94			692	204			386	314	1704	1783	
96			435	206	904	1134	985	318	1042	1103	
98	1073	912	1038	208			188	320	1219	238	
100			131	210			554				
102			606	212			546				
104			627	214			720				
106			448	216			866				

Table 2. Interatomic distances in α manganeseThe lattice parameter a was taken as 8.9125 Å at 298°K.

Atoms*	Interatomic distance, d , using Bradley & Thewlis's parameters (Å)	Interatomic distance, d , using present parameters (Å)	Coordination number
Mn(1)-4Mn(2) 12Mn(4)	2.83 2.72	2.84 ₀ 2.75 ₂	16
Mn(2)-1Mn(1) 3+3Mn(3) 6+3Mn(4)	2.83 2.50; 2.96 2.70; 2.89	2.84 ₀ 2.56 ₃ ; 2.91 ₁ 2.72 ₀ ; 2.87 ₇	16
Mn(3)-1+1Mn(2) 6Mn(3) 1+2+2Mn(4)	2.50; 2.96 2.67 2.45; 2.51; 2.67	2.56 ₃ ; 2.91 ₁ 4-2.65 ₅ ; 2-2.63 ₇ 2.35 ₁ ; 2.51 ₈ ; 2.69 ₁	13
Mn(4)-1Mn(1) 2+1Mn(2) 1+2+2Mn(3) 1+2Mn(4)	2.72 2.70; 2.89 2.45; 2.51; 2.67 2.24; 2.38	2.75 ₂ 2.72 ₀ ; 2.87 ₇ 2.35 ₁ ; 2.51 ₈ ; 2.69 ₁ 2.24 ₄ ; 2.43 ₃	12

* The number and type (in parentheses) of neighbors are listed.

(Gazzara, Middleton & Weiss, 1964) of diffraction peaks $\Sigma h^2=314-(0,5,17)(1,12,13)(3,4,17)(3,7,16)(5,8,15)(7,11,12)(8,9,13)$ and $\Sigma h^2=318-(1,11,14)(2,5,17)(7,10,13)$. These have large values of $\sin \theta/\lambda$ and G_j and were well resolved. Furthermore, the effects of anisotropy on the Debye-Waller factor were considered to be negligible since each peak consists of so many different combinations of h , k , and l . The characteristic temperature was found to be $390 \pm 10^\circ\text{K}$ with a corresponding value of $B=0.445 \pm 0.022 \text{ \AA}^2$. This value was subsequently used in the calculations of Y_j .

A least-squares analysis program was written for an IBM 1620 or 7090 computer in which the atomic parameters were systematically varied so as to maximize the correlation coefficient, r (Weatherburn, 1957), which is defined in terms of Y_j and $(\sin \theta/\lambda)^2$, and to minimize the R index:

$$R = \frac{\sum_j |G_j(\text{observed}) - G_j(\text{calculated})|}{\sum_j G_j(\text{observed})}$$

In the analysis, each peak was given a weight inversely proportional to the probable error of its absolute intensity.

A refinement utilizing an average of the intensities measured according to all four methods described above and one employing those intensities obtained from method (ii) alone resulted in the same atomic parameters: $x(2)=0.316$, $x(3)=0.356$, $z(3)=0.034$, $x(4)=0.089$, $z(4)=0.282$, space group $I\bar{4}3m$. For the reflections $\Sigma h^2=6$ through 58, the atomic parameters of Bradley & Thewlis yielded an R index of 4.9% and an r index of 0.29 compared with an R of 1.4% and an r of 0.76 using the refined parameters. For all fifty reflections listed in Table 1, R is 9.3% with Bradley & Thewlis's parameters and 2.9% with our parameters. No significant change in the atomic parameters was found between 310 and 100°K . Although the plot shown in Fig. 1 reveals a marked change in the lattice constant in the vicinity of the Néel temperature, no structural change could be detected on examination of the intensities of the diffraction peaks $\Sigma h^2=16,18,26$ above and below the Néel temperature. The lattice constant at 298°K was found to be 8.9125 \AA , in agreement with the reported values of $a=8.9139 \text{ \AA}$ (Carapella & Hultgren, 1942) and $a=8.9120$ (Carlile, Christian & Hume-Rothery, 1949). The values of G_j calculated both with the atomic parameters of Bradley & Thewlis and with our refined parameters are given in Table 1 together with those values of G_j that correspond to the observed absolute intensities.

The interatomic distances are given in Table 2 for $a=8.9125 \text{ \AA}$ at 298°K .

A special tribute should be extended to A. J. Bradley and J. Thewlis for the accuracy of their diffraction work and computations without the use of modern diffraction equipment and high speed computers. Indeed, except for the $z(3)$ parameter, there would have been little justification to perform this refinement.

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