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The Magnetic Susceptibilities of Alpha- and Beta-Manganese*

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Pure alpha-manganese was prepared by distillation. Beta-manganese was prepared by melting a sample of the alpha-manganese in vacuum, and quenching it in water from about 1000°C. The mass susceptibilities of these two specimens were measured by a null-reading, astatic magnetometer, and found to be $9.60(10)^{-6}$ and $8.80(10)^{-6}$ respectively. These results eliminate the possibility that the ferromagnetic manganese found by some investigators is either the alpha-or the beta-crystal form.

Introduction

IN THE periodic table manganese lies in the same transition series as the ferromagnetic elements, iron, cobalt, and nickel, and adjacent to them, and also might be expected to exhibit ferromagnetism. However, although the magnetic properties of manganese have been the subject of several investigations, the results have disagreed even in such an important respect as to whether it is or is not ferromagnetic. Undoubtedly many of the discrepancies are attributable to chemical impurities, especially in the work of the early investigators. Manganese is a very active element chemically, and many of its alloys and chemical compounds are ferromagnetic. Iron as an impurity is not so important as carbon and nitrogen, as 18 percent of manganese in iron causes the iron to lose its ferromagnetism, while carbon and nitrogen, which form highly ferromagnetic compounds with manganese, are more likely than iron to be overlooked.

Honda[1] and Owen[2] found the susceptibilities of their specimens to be $10.6(10)^{-6}$ and $8.93(10)^{-6}$ respectively. Both these investigators were very careful to avoid iron. Honda and Soné,[3] and Ishiwara,[4] using similar specimens of Kahlbaum's manganese, measured susceptibilities of 9.70 and 9.66 $(10)^{-6}$. Kuh,[5] who prepared a sample electrolytically, found it to be ferromagnetic, as did Hadfield.[6] Freese[7] repeated Kuh's work, suspecting that the ferromagnetism might be due to hydrogen, since the last step in the preparation was heating a manganese amalgam in hydrogen. He also prepared specimens by sputtering in hydrogen, but found no consistent effect of the hydrogen.

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[1] K. Honda, Ann. d. Physik [4] **32,** 1027 (1910).

[2] M. Owen, Ann. d. Physik [4] **37,** 657 (1912).

[3] K. Honda and T. Soné, Sci. Rep. Tohoku Imp. Univ. [1] **2,** 27 (1913).

[4] T. Ishiwara, Sci. Rep. Tohoku Imp. Univ. [1] **5,** 53 (1916).

[5] E. Kuh, Diss. Zurich (1911).

[6] R. Hadfield, C. Chéveneau, and Ch. Géneau, Proc. Roy. Soc. [A] **94,** 65 (1917).

[7] H. Freese, Phys. Zeits. **29,** 191 (1928).

Since the magnetic susceptibilities of many substances have been found to vary in different crystal forms, the object of this research was to investigate what difference in susceptibility might exist between the alpha- and beta-crystal forms of manganese at room temperature. Manganese exists in three crystal forms, alpha, beta, and gamma. The alpha form is the low temperature modification, stable up to 742°C.[8] The beta form is stable from 742° to 1191°[9] and can be obtained in specimens quenched at room temperature from this temperature interval. Both these forms are cubic, having 58 and 20 atoms per unit cube respectively.[10] The gamma form is present in specimens prepared electrolytically, but changes back to alpha automatically in a couple of weeks. It is stable above 1191°, but has never been obtained in pure manganese by quenching.

The susceptibility of manganese as a function of the temperature was measured by Shimizu[11] who found unusually low values for his samples, which were prepared by distillation and were 99.9 percent pure. Some of his results are as follows:

Crystal form	alpha	beta	gamma
Temperature	20°C	810°C	1100°C
Susceptibility	$7.53(10)^{-6}$	$6.01(10)^{-6}$	$8.41(10)^{-6}$

None of these exhibited ferromagnetism in the temperature interval in which they were stable, but he did not investigate the high temperature forms at room temperature.

PREPARATION OF SAMPLES

Two samples of manganese were used for these researches, both prepared by the method of distillation, which yields manganese with a very small percentage of impurities. The first specimen was very kindly supplied by Dr. Walters of the Carnegie Institute of Technology, and was stated to have the following impurities: C, 0.009 percent; Fe, Al, Si, spectroscopic traces. Some manganese was purified similarly in an Ajax 30 KVA induction furnace. In general the method consisted in placing the crude manganese in a magnesia crucible with a second inverted crucible resting on it. The whole was placed in a silica tube which was evacuated to $(10)^{-2}$ mm. The manganese was then heated inductively to a temperature just above melting. As pure manganese is very volatile, it distilled onto the upper crucible leaving the impurities in the undistilled portion.

To obtain manganese in the beta-crystal form without impurities sufficient to vitiate magnetic measurements, it was found necessary to melt the pure distilled alpha-manganese into a lump in vacuum, then quench it in cold water, so that only the surface became impure. To do this, the manganese in a magnesia crucible was supported inside a tube of Berlin porcelain which was sufficiently nonporous at the melting point of manganese to hold

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[8] M. Gayler, J. Iron and Steel Inst. **115**, 393 (1927).

[9] E. Persson and E. Öhman, Nature **124**, 333 (1929).

[10] G. D. Preston, Phil. Mag. [7] **5**, 1198 (1928).

[11] Y. Shimizu, Sci. Rep. Tohoku Imp. Univ. [1] **19**, 411 (1930).

a vacuum of $(10)^{-6}$ mm. This tube was surrounded by a carbon ring which in turn was surrounded by the coil of the induction furnace. Most of the heat was generated in the carbon ring. Ground joints between the tube and the Pyrex vacuum system were sufficiently distant from the heat to be easily water cooled. At the instant of melting the pressure rose to $(10)^{-4}$ mm, but otherwise kept down to $(10)^{-6}$ mm. When the manganese melted, argon was introduced, and then the manganese lump was quickly driven through the bottom of the tube into cold water. This lump was covered with an oxide film, which was removed by sandblasting.

No chemical analysis can as yet be obtained for this specimen. After consultation with leading authorities on the determination of gaseous impurities in metals, it appears that the errors in nitrogen determinations are as large or larger than the total amount of nitrogen probably present here. The specimen is being retained in the hope that a more precise method may soon be available. However, the susceptibility measurements are a delicate test for ferromagnetic impurities, and others cause only a small percent error. The probable impurities here would be carbon and nitrogen, both of which form ferromagnetic compounds with manganese.

X-RAY ANALYSIS

To determine the crystal structure of these samples, x-ray powder photographs were taken with Mo $K\alpha$ radiation. The value of tan 2θ for Mo $K\alpha$ was calculated from the data given in papers by Sekito[12] and Preston[10] for tan 2θ for Fe $K\alpha$, and compared with tan 2θ from these samples. (Tables I and II.)

TABLE I. *Distilled specimen compared with alpha-manganese.*

Line	Tan 2θ from Sekito	Intensity from Preston	Tan 2θ calculated from film	Estimated intensity
1	0.354	200	0.354	200
2	0.395	200	0.396	100
3	0.416	100		
4	0.435	100	0.433	75
5	0.594	40	0.593	50
6	0.624	100	0.633	50
7	0.644	200		
8	0.675	140	0.678	100
6 lines of lower intensity				
15	0.825	200	0.825	50

TABLE II. *Quenched specimen compared with beta-manganese.*

Line	Tan 2θ from Sekito	Intensity from Preston	Tan 2θ calculated from film	Estimated intensity
1	0.354	strong	0.354	very strong
2	0.374	"	0.374	strong
3	0.395	"	0.395	medium
4	0.451	"	0.454	weak
5	0.525	medium	0.541	weak
6	0.562	"		
7	0.661	very strong	0.668	fairly weak
8	0.675	medium		
9	0.712	very strong	0.710	weak

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[12] R. M. Bozorth, J. Opt. Soc. Amer. **10**, 591 (1925).

In the comparison of the values for alpha-manganese with those from Sekito, it is clear that the prominent lines coincide. Preston and Sekito used cameras with circular film, and so got the lines for larger angles with relatively greater intensities. This explains the absence on our film of lines No. 9 through No. 14. The intensity maximum extending from tan 2θ 0.395 to 0.435 showed practically no structure. This was interpreted as two lines at the distances noted, but another line may have been present in the interval.

For the beta specimen, the lines coincided within the errors of measurement. The lines reflected at larger angles, No. 10 and above, were absent because of the greater distance from powder to film, as on the first film, and lines No. 5 and 6, as well as lines 7 and 8, were not resolved.

No lines which could be attributed to the gamma structure were found on either film.

MAGNETOMETRIC MEASUREMENTS

The magnetometer used was essentially like one described by Bozorth,[12] and was a null-reading instrument. Two small parallel magnets of equal moment were mounted horizontally, one above the other, with north poles in opposite directions, thus forming an astatic system. The specimen was placed so that each end was at the level of one of the magnets; thus each induced pole exerts the same torque on the astatic system. An equal distance from the astatic system but on the side opposite the specimen was placed a coil of proper dimensions, which, when traversed by a suitable electric current, balanced the total torque exerted on the astatic system by the specimen. The specimen was supported in a magnetizing solenoid, and the balancing coil in a similar solenoid, provided to cancel the torque on the magnets due to the magnetizing solnoid. Since the dimensions of the balancing coil and the current passing through it gave its magnetic moment, which was adjusted to be the same as that of the specimen, the magnetic moment and susceptibility of the specimen could be calculated.

The container for the specimen of powdered manganese was a glass tube cut from a 2 cm^3 hypodermic syringe of inside diameter 0.9083 cm, with ends ground flat and plugged with amber so that the inside length was 4.000 cm. The balancing coil used to counteract the torque of the specimen on the astatic system was wound on an amber spool which was so slightly paramagnetic that it deflected the magnetometer zero less than 1 mm, that being about the limit of accuracy in single readings. Two coils were wound identically, for purposes of adjustment, with two layers of 186 turns each. The winding space was 4.000 cm long, and 0.824 cm in diameter. The magnetizing solenoids were wound on brass spools 15 cm long and 1.585 cm in diameter, with 5027 turns in 20 layers. A current of air was kept constantly flowing between the specimen and the spool, and this eliminated much shifting of the wires as they heated, and also kept the specimen within a few degrees of room temperature. The adjustment was carried out as suggested by Bozorth, except that it was not found possible to hold the same adjustment for various high fields.

As the balancing coil was wound in two layers its moment was measured magnetically by the common method of placing it in the center of a long solenoid, and measuring the charge passed through a calibrated ballistic galvanometer in series with the balancing coil and a standard mutual inductance, when a current was passed through the solenoid. From this, the magnetic moment, M, was found to be 21.62 i, with a probable error of $\frac{1}{2}$ percent, where i is the current through the balancing coil in amperes.

The average value of the field, H, in the magnetizing solenoid was calculated to be 0.982 of that of an infinite solenoid of the same number of turns per unit length. Therefore, H in gauss was found to be 413.6 I, where I is the magnetizing current in amperes; and χ, the mass susceptibility, $=M/H\cdot$mass, or $52.27(10)^{-3}\,i/I\cdot$mass.

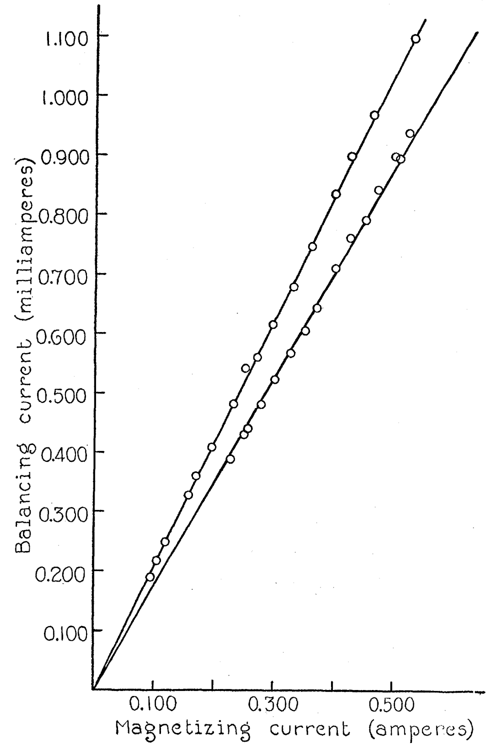

Fig. 1. Upper line, beta-manganese; lower line, alpha-manganese

The total deflection without balancing current was between 5 and 10 cm, and the limit of accuracy in each reading was about 1 mm. Since the volume susceptibility turned out to be of the order of $(10)^{-5}$, the demagnetizing effect of the poles of the specimen was neglected. With the astatic system in its zero position, the resultant field produced by its magnets on the specimen would be small. Experimentally, no change in value was noticed when the zero was changed slightly, or when the suspended system was rotated through 180°. The field on the specimen in the direction of its axis due to the second magnetizing solenoid in which the balancing coil was supported was calculated to be 1/400 that of the first magnetizing solenoid, and was neglected.

The diameter of the container was slightly larger than the average diameter of the balancing coil, but it seemed impossible that this could make a measurable change in the result, especially as the average diameter of the sample of manganese must necessarily be smaller than the container.

It is conceivable that the powdering of the manganese to place it in the container might have changed the susceptibility. Evidence would suggest that if this happened the susceptibility was increased rather than decreased by the powdering. As no change of susceptibility with field was noted, there could have been present no measurable ferromagnetic impurity, and a paramagnetic impurity would cause only a small percent error.

The results are presented in Table III and in Fig. 1 which shows the straight line relations to be expected in the absence of ferromagnetic impurities.

TABLE III. *Susceptibility measurements on alpha- and beta-manganese.*

Mass of sample, 11.307 grams			Mass of sample, 10.420 grams		
I	$i \cdot 10^3$	$(i/I) \cdot 10^3$	I	$i \cdot 10^3$	$(i/I) \cdot 10^3$
0.095	0.189	1.989	0.227	0.390	1.718
0.106	0.216	2.038	0.250	0.430	1.720
0.120	0.248	2.067	0.256	0.441	1.723
0.158	0.327	2.070	0.278	0.482	1.734
0.172	0.360	2.093	0.300	0.524	1.747
0.197	0.409	2.076	0.327	0.568	1.737
0.233	0.482	2.069	0.350	0.606	1.731
0.252	0.543	2.155	0.370	0.645	1.743
0.271	0.562	2.074	0.400	0.712	1.780
0.297	0.617	2.077	0.426	0.763	1.791
0.330	0.680	2.061	0.452	0.793	1.754
0.361	0.749	2.075	0.472	0.844	1.788
0.400	0.836	2.090	0.500	0.900	1.800
0.427	0.900	2.108	0.507	0.897	1.769
0.463	0.970	2.095	0.524	0.940	1.794
0.530	1.10	2.075			
$i/I = (2.076 \pm .006) \cdot 10^{-3}$ $\chi = (9.60 \pm .03) \cdot 10^{-6}$			$i/I = (1.754 \pm .005) \cdot 10^{-3}$ $\chi = (8.80 \pm .02) \cdot 10^{-6}$		

CONCLUSIONS

Thus, it can be concluded that for alpha-manganese the mass susceptibility is $9.60(10)^{-6}$, and for beta-manganese, $8.80(10)^{-6}$. Considering that the specimens previously measured were probably a mixture of these two crystal structures, this result is lower than Honda's first value of $10.6(10)^{-6}$, and agrees better with his second value, $9.70(10)^{-6}$, and with that of Owen, $8.93(10)^{-6}$. The more recent work of Shimizu gave still lower values, as previously noted. For these low values no explanation can here be offered. No trace of the ferromagnetism observed in the specimens of Kuh, Hadfield, and Freese was found.

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