VARIABILITY IN ARTIFICIAL FERROMAGNETIC IRON OXIDES.

LARS A. WELO AND OSKAR BAUDISCH.

Our chief purpose in collecting some and preparing most of the magnetites and ferromagnetic ferric oxides (gamma oxides) described in this paper was to secure a wide variety of material for our biochemical investigations. Both biological activity and magnetic properties are sensitive functions of the method of preparation and we have come to regard the easily determined magnetic properties as reliable indicators of the activity that may be expected from any given oxide. We long ago[1] expressed the opinion that the relation between biological activity, which is catalytic in nature, and magnetic properties is more than a purely empirical one since both are functions of lattice imperfections and internal strains which are determined by the method of preparation. This opinion gains considerable support from the recent work of Eckell[2] who compared the catalytic activities of strained and unstrained nickel.

The reason for presenting the results of our magnetic studies, which were, in a sense, secondary to our main purpose, is that they seem to have a bearing on the great variability found in the magnetic properties of natural magnetites.[3] We find a correspondingly wide range in the artificial oxides of iron. While our studies do not identify the fundamental elements of the problem, we hope that this paper will be a contribution to its solution.

Classification and Preparation of the Oxides.

The methods of preparation will be indicated only in more general terms. Whenever possible we shall give the reference to the paper in which details may be found. We assign a reference number to each oxide or substance that was studied, which is used later to identify the curves of Figs. 1 to 6 and the data of Table I.

---

[1] Baudisch, O., and Welo, L. A., Naturwissenschaften, **14**, 1005, 1926.

[2] Eckell, J., Zeit. f. Elektrochem., **39**, 433, 1933.

[3] Wilson, E., and Herroun, E. F., Proc. Phys. Soc. London, **31**, 299, 1919; **33**, 196, 1921; **41**, 99, 1928; Wilson, E., Jl. Inst. Elect. Eng., **59**, 319, 1921.

Magnetites: Direct Preparation. Fig. 1, Nos. 1 to 4.

1. Precipitation from an equimolar solution of $FeSO_4$ and $Fe_2(SO_4)_3$ with NaOH. J. Lefort's Method, Compt. Rend., 34, 488 (1852); L. A. Welo and O. Baudisch, Phil. Mag., [7], 3, 396 (1927). Lefort's method does not yield a black oxide as it is always over-oxidized. The FeO content is of the order 17% instead of the theoretical 31% for magnetite, $Fe_3O_4 = FeO.Fe_2O_3$.

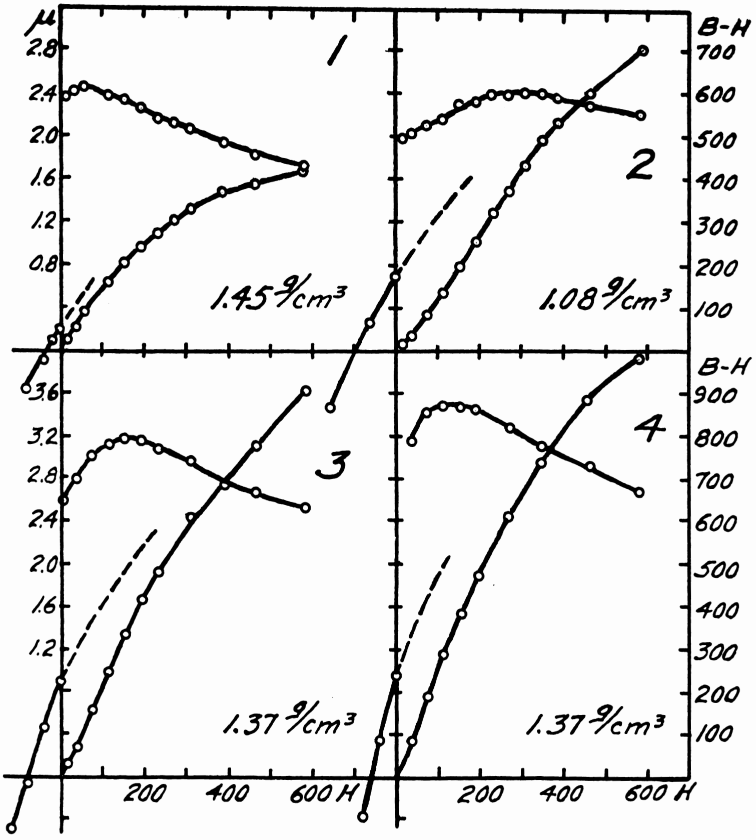

Fig. 1. Magnetites. Direct preparation.

2. A black commercial preparation. D.R.P. No. 463773 (1925) and No. 464561 (1926) to Dr. Julius Laux, Uerdingen.

3. This black magnetite was formed by burning iron carbonyl sprayed into a hot chamber with limited supply of air. Preparation is described by A. Mittasch, Zeit. f. angew. Chem., 41, 827 (1928) and D. R. P., 452, 360 (1926). We regard this as the purest sample of magnetite that we have studied and consider it to be a "standard" sample of magnetite.[4]

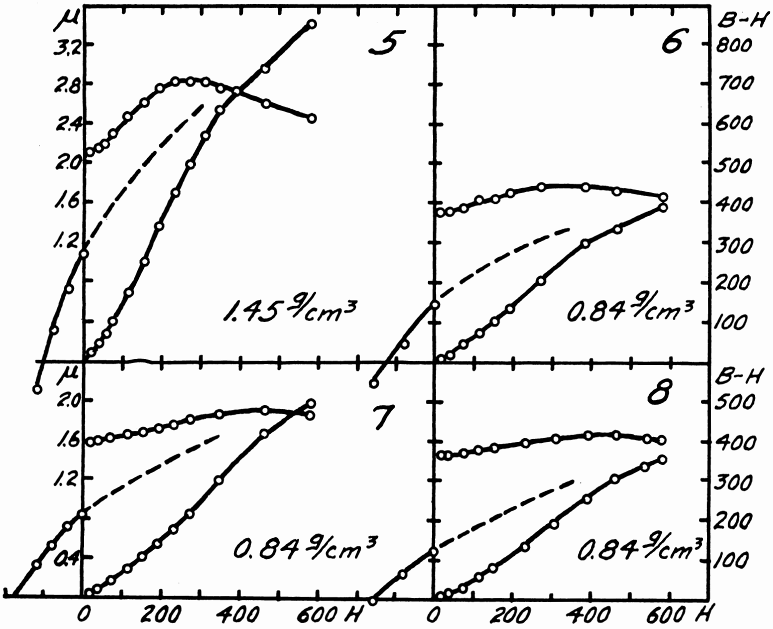

Fig. 2. Magnetites. By reduction of Ferric Oxides.

4. Formed in the same way as No. 3 and subsequently kept in molten sodium acetate at 320° C. for 10 minutes. The hot sodium acetate and the oxide were then poured into water or on an aluminum plate. Either way provides rapid cooling. The oxide was washed until free of acetate and air dried. This is a new way of reducing iron oxides.

Magnetites: By Reduction of Ferric Oxides. Fig. 2, Nos. 5 to 8.

5. Oxide No. 1 was oxidized in oxygen at 200° C. until free of ferrous iron. Then it was reduced as in No. 4.
6. Alpha ferric oxide was made by oxidizing a solution of

---

[4] We thank Professor H. von Euler of Stockholm for providing us with this magnetite.

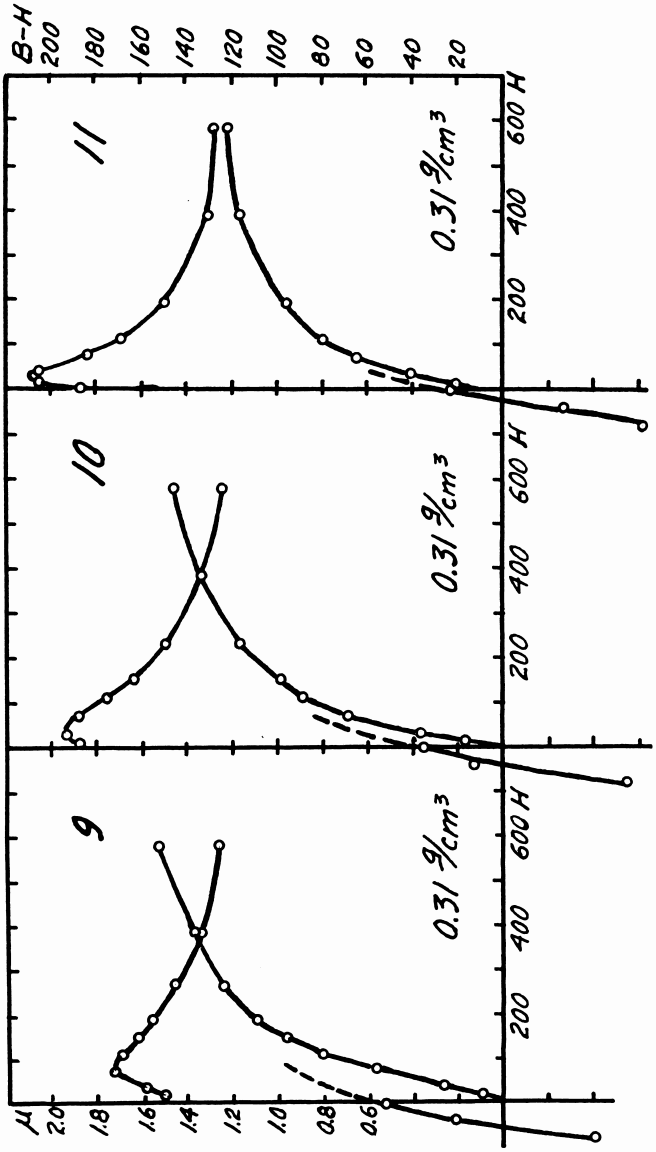

Fig. 3. Ferromagnetic Ferric Oxides (Gamma Oxides). By Dehydration of Gamma Ferric Oxide Hydrates.

ferrous carbonate. This carbonate solution was made by dissolving iron powder from iron carbonyl in carbonated water. The alpha oxide was then reduced to magnetite as in No. 4 except that potassium acetate was used and the temperature was 460° C.

7. Alpha ferric oxide was made by burning iron carbonyl as in No. 3 but with a sufficient supply of air for complete oxidation. The ferric oxide was reduced in sodium acetate as described in No. 4.
8. Prepared in the same way as No. 7.

Ferromagnetic Ferric Oxides: By Dehydration of Gamma Ferric Oxide Hydrates. Fig. 3, Nos. 9 to 11.

9. The preparation of gamma ferric oxide hydrate is described in another paper; L. A. Welo and O. Baudisch, Phil. Mag., in press. Dehydration was carried out by heating, successively, for 5 hours at 180° C., 2 hours at 200° C., 2 hours at 220° C., 2 hours at 240° C., and 2 hours at 260° C. in air.
10. The gamma hydrate was prepared as in No. 9 but NaCl was purposely added to the ferrous chloride to provide an impurity while the crystals were formed. The hydrate was converted to oxide by heating, in air, at 200° C. for 46 hours.
11. Gamma hydrate was made with a solution of FeI_2 instead of $FeCl_2$ and dehydrated at 200° C. for 48 hours.

Ferromagnetic Ferric Oxides: By Oxidation of Magnetites. Fig. 4, Nos. 12 to 15.

12. Lefort's magnetite, No. 1, was oxidized in oxygen at 200° C. until free of ferrous iron.
13. Magnetite No. 1 was oxidized in molten KNO_3 at 395° C. for 10 minutes. The molten nitrate with the oxide were poured on an aluminum plate, washed until free of nitrate, and dried in air.
14. Magnetite No. 2 was oxidized by the method that was used when preparing No. 13.
15. Magnetite No. 7 reoxidized in molten KNO_3 at 360° C. for 10 minutes.

Copper Ferrites. Fig. 5, Nos. 16 and 17.

16. By precipitation of a solution of $FeSO_4$ and $Fe_2(SO_4)_3$ with NaOH in the presence of $CuSO_4$. This ferrite contained 3.9% of copper.
17. The same method was used as in No. 16 but relatively more $CuSO_4$ was present in the solution. The copper content of this ferrite was 9.2%.

Iron Powder from Iron Carbonyl. Fig. 6, Nos. 18 and 19.

18. For method of preparation see A. Mittasch, Zeit. f. angew. Chem. 41, 827 (1928). The carbon content of this sample was stated to be less than 0.001%.
19. Same as No. 18, except that the carbon content was 0.02%.

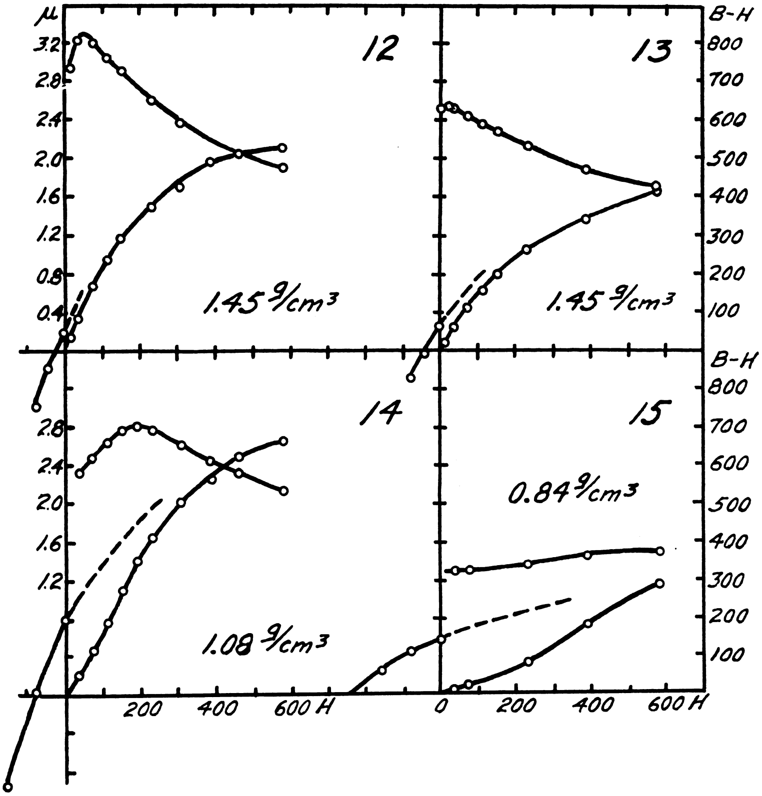

Fig. 4. Ferromagnetic Ferric Oxides (Gamma Oxides) by Oxidation of Magnetites.

Results.

The magnetic data are given in Figs. 1 to 6 and in Table I. The curves were drawn from ballistic data obtained by a method we have already described.[5] For each preparation there is shown a permeability and magnetization curve and a

---

[5] Welo, L. A., and Baudisch, O., Phil. Mag. [6], 50, 399, 1925; [7], 3, 396, 1927.

portion of the hysteresis loop where it crosses the axes. The remanences and coercive forces are therefore also given from the highest magnetizing field that was used, 582 gausses.

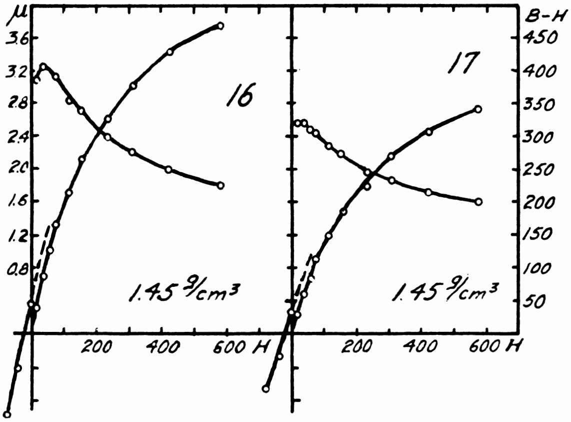

Fig. 5. Copper Ferrites.

Table I contains the specific remanent magnetizations from magnetizing fields of 1790 gausses. The magnetometer method used for these latter measurements is described in another paper.[6]

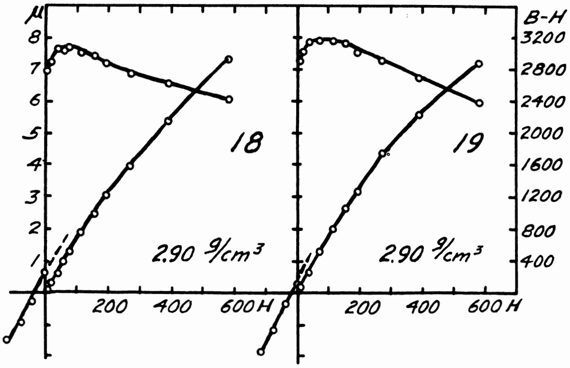

Fig. 6. Iron Powder from Iron Carbonyl.

There was a wide variation in the density of packing. Density of packing could not be accurately controlled and our practice was to adjust the observed values of permeability and

---

[6] Welo, L. A., and Baudisch, O., Phil. Mag., in press.

magnetization to correspond to some standard packing density, provided that the range of adjustment was not too great. Consequently several standard values are recorded in the figures. Density of packing is not involved in the calculation of the specific remanent magnetizations from the magnetometer measurements. But the values obtained do depend on the packing density so that these densities are included in Table I. The latter values are higher than the values shown in the figures. The material was tamped with a rod while being packed in the magnetometer container. The container used for the ballistic measurements was packed by "jarring." Water determinations were not made so that it was not possible to adjust the permeabilities, magnetizations and the remanences to the water free basis.

Discussion of the Results.

Some conclusions of a general nature can be drawn from these magnetic data.

There are no major differences between the magnetic properties of magnetites and those of the ferromagnetic ferric oxides.

The effect of impurities is a minor one as may be seen by an intercomparison between several sets of curves. Oxides No. 9 and No. 11 were pure while No. 10 was purposely precipitated in NaCl solution. The greater hardness in No. 9 is due to the higher temperature used while dehydrating the gamma ferric oxide hydrate from which it was formed. Magnetite No. 4 has the same general magnetic characteristics as the standard sample No. 3 in spite of the fact that it has been heated in molten sodium acetate. A similar conclusion as to the minor rôle of impurities is drawn from a comparison of No. 9 with No. 1. No. 9 is a pure material while No. 1 contains many impurities.[7]

There is consistent evidence among these data that a high temperature at some time during formation yields a material that is magnetically hard; except when a material that is already magnetite is oxidized to ferromagnetic ferric oxide. No. 3 was formed at an elevated temperature and No. 5 and No. 6 were heated during reduction with an alkali acetate. The hardest oxides of all were those which had been heated twice during the course of preparation; first, during the burning of

---

[7] For a complete analysis see Wolf, P. M., and Zeglin, H., Deut. Med. Wochenschrift, No. 24, 1929.

iron carbonyl to form alpha ferric oxide and, subsequently, during reduction with sodium acetate. Examples of this double heating are Nos. 7, 8 and 15. Of these, No. 15 had been heated three times, the last time during oxidation in molten KNO_3. This oxide had by far the highest coercive force that was observed during this study, 240 gausses.

The effect of oxidizing magnetite, either in air at 200° C. or in molten KNO_3, is to soften the material. Compare No. 12 and especially No. 13 with No. 1 and also No. 14 with No. 2. This behavior has been noted by us before.[8] Comparison of No. 15 with No. 7 suggests, however, that this rule is not invariable.

The copper ferrites are extremely soft. We believe that their softness has the same cause as softness in ferromagnetic ferric oxides as compared with the magnetites from which they were made by oxidation. The lattice in ferromagnetic ferric oxide is crowded and strained owing to the presence of more oxygen than corresponds to the magnetite structure which is retained. In the case of the copper ferrites, the lattice is

TABLE I.

Specific Remanent Magnetizations in Ferromagnetic Iron Oxides, Copper Ferrites and Iron Powder. From H = 1790 Gausses.

Number Reference	Material Class of	Density of g./cm. 3 Packing	e.m.u. σ_r
1	Fe_3O_4	1.51	1.97
2	“	1.67	14.5
3	“	2.24	15.8
4	“	...	...
5	“	1.58	16.2
6	“	0.95	12.8
7	“	1.15	17.0
8	“	...	...
9	Fe_2O_3	...	...
10	“	0.69	7.37
11	“	0.67	3.66
12	“	1.69	1.80
13	“	1.51	1.95
14	“	1.77	15.2
15	“	1.57	15.5
16	$CuO.Fe_2O_3$	1.62	0.68
17	“	1.59	0.50
18	Fe	3.52	2.75
19	“	3.04	2.73

---

[8] Welo, L. A., and Baudisch, O., Phil. Mag. [6], 50, 399, 1925; [7], 3, 396, 1927.

strained because the copper ions are larger than the ferrous ions. It may be noted that of the two ferrites, the one containing the most copper is the softer. These ferrites are cubic in structure.

The iron powder is hard, for iron, as it was expected to be because of its powdered form. We notice no effect of the presence of carbon within the small range involved here, 0.001 to 0.02 per cent.

The remanences in either magnetite or ferromagnetic ferric oxide group themselves around three main values according to the data of Table I. Nos. 1, 12 and 13 form a group with specific remanent magnetizations, σ_r, of about 1.90. Nos. 12 and 13 were derived from No. 1 by oxidation. The oxides derived by dehydration of gamma ferric oxide hydrate, Nos. 10 and 11, form another group with intermediate values. A value, $\sigma_r = 11.0$, was reached in other work on ferromagnetic ferric oxide derived in this way when it was heated for a much longer time or at higher temperatures. The rest of the magnetites or the ferromagnetic ferric oxides form a group with specific remanent magnetizations of from 14.5 to 17. No. 6 with $\sigma_r = 12.8$ probably would have fallen within this group if it could have been more densely packed.

If it be granted that the magnetic properties of magnetite and of ferromagnetic ferric oxide are mainly determined by previous history as to temperature it remains to consider the physical changes that may occur at high temperatures. The principal ones are: growth of crystals and coalescence of particles, elimination of lattice irregularities and removal of strains. To identify changes in magnetic properties with any one of these has been difficult because they may all occur on heating, and our point of view has changed from time to time as new experimental facts have appeared.

In a previous paper[9] we showed that Lefort's magnetite, No. 1 of this paper, gave diffuse lines in the X-ray diffraction pattern, proving that the crystals were small. The other magnetites described in that paper were magnetically hard and gave the sharp lines characteristic of large and well formed crystals. However, we could not conclude that magnetic softness is associated with small crystal size. We found that Lefort's magnetite, when it was annealed at 1000° C., became hard with properties approaching those of Nos. 2 and 5 of this paper. There was evidence that the crystals had not

---

[9] Welo, L. A., and Baudisch, O., Phil. Mag. [7], 3, 396, 1927.

grown appreciably during the annealing so we concluded that the change from a soft to a hard condition was due to either perfection of the lattice, or removal of strains, or both, and that magnetic properties are independent of crystal size.

The reader is referred to another paper[10] for a description of our work on ferromagnetic ferric oxide derived by dehydration of gamma ferric oxide hydrate, and on ferromagnetic ferric oxide particles of colloidal dimensions. We have been led anew to the conclusion that magnetic hardness in this class of material is a function of crystal or particle size, at least within the range in which they are very small.

[10] Welo, L. A., and Baudisch, O., Phil. Mag. (In press).

YALE UNIVERSITY,
NEW HAVEN, CONN.