[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Disperse Structure of Paramagnetic Oxides and Hydroxides[1]

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If a base is added to a ferric salt solution, there is formed a familiar reddish-brown gelatinous precipitate. This precipitate is commonly, although almost certainly incorrectly, referred to as "ferric hydroxide." A better name is "hydrous iron sesquioxide." This substance may be partially dried to a powder, or to a fairly hard mass. If it gives any X-ray, or electron, diffraction pattern, the pattern is diffuse and difficult to interpret. The substance is characterized by a high surface area. Electron microscopy yields little information, except that the particles are very small, or appear to be aggregates of very small particles. If the hydrous oxide is heated, it undergoes first a moderate irreversible endothermic change, which seems to be associated with the loss of water. At somewhat higher temperatures there occurs a vigorous irreversible exothermic change, often called the "glow phenomenon." The product which remains after the glow is typical, crystalline, α-iron sesquioxide.

The above description of hydrous iron sesquioxide is characteristic, with minor modifications, of nearly all the oxides and hydroxides of the metals, and of some of the non-metals. Such substances are often called "gels." These substances are of major importance in catalysis and in related fields, but a knowledge of their structure remains in a rudimentary state. Even the nomenclature is unsatisfactory. The name "hydrous oxide" implies the presence of water. But several of these substances may be obtained virtually free from water and still possessing the peculiar degree of attenuation which characterizes all of them and distinguishes them from more perfectly crystallized solids. The name "gel" implies something like a jelly, but some of these substances, such as so-called chromia gel, may be prepared in a state which much more resembles a glass than it does a jelly.

These substances, the study of which forms a branch of colloid chemistry, reveal little about their structure by the usual tools of structural chemistry. Any new method which gives information about them is welcome. The purpose of the present article is to describe the application of magnetic susceptibilities to most of the substances on which the method is useful. This includes oxides and hydroxides of vanadium, chromium, manganese, iron, cobalt, nickel and copper. The method is not applicable to gels of diamagnetic oxides, such as silica or alumina.

Principle of the Method.—It is well known that the susceptibility of magnetically dilute compounds of the paramagnetic metals is generally described by the Curie–Weiss Law, $\chi = C/(T + \Delta)$, where χ is the susceptibility, C and Δ are the Curie and Weiss constants, respectively, and T is the absolute temperature. The Curie constant is related to the oxidation state of the paramagnetic ion through the expression $\mu = 2.84\sqrt{C_A}$ where μ is the moment in Bohr magnetons and C_A is the Curie constant per gram-atom; and through the "spin-only" formula, $\mu = \sqrt{n(n + 2)}$ where n is the number of unpaired electrons. These relations afford for most of the transition group elements a reasonably satisfactory method for determination of oxidation states, without resort to chemical analysis. The Weiss constant similarly affords some measure of information concerning the environment, and especially about the paramagnetic neighborhood surrounding each positive ion. The details of both of these applications to structural chemistry have been described in publications from this Laboratory.[2]

The observation on which the present work is based is that the hydrous oxides and hydroxides of the paramagnetic ions are, in general, magnetically dilute substances.[3] The significance of this observation will be clear if it is considered in relation to the magnetic properties of crystalline oxides which are, almost without exception, magnetically concentrated substances. The distinction will be illustrated by reference to the magnetic susceptibility per gram of chromium in crystalline chromium sesquioxide, and in the corresponding chromia gel.

TABLE I

SUSCEPTIBILITIES ($\times 10^6$) FOR CHROMIA AND CHROMIA-GEL

Oxide	$\chi_{25°}$	$\chi_{-170°}$
Cr_2O_3 crystalline	25	23
Cr_2O_3 gel	37	82
Cr^{+3} in crystalline	37	33
Cr^{+3} in gel	78	174

It will be noted that the susceptibility per gram of chromium in the gel at −170° is over five times greater than that in the crystalline oxide. This observation, illustrated for chromia, makes it possible to study the oxidation state and, to a degree, the atomic environment of the metal ion in many hydrous oxides and hydroxides, and to follow changes which occur *in situ*, so to speak.

The Structure of Hydrous Oxides and Hydroxides.—What little structural information is available on hydrous oxides and hydroxides has nearly all been obtained by phase rule studies involving isobaral and isothermal de-

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[1] This work was performed, in part, under contract with the Signal Corps Engineering Laboratories, Fort Monmouth, N. J.

[2] Eischens and Selwood, THIS JOURNAL, 69, 1590 (1947).

[3] Selwood, Eischens, Ellis and Wethington, *ibid.*, 71, 3039 (1949).

hydration. In a few cases these have been supplemented by X-ray and electron diffraction studies, by structural information obtained from reaction rate studies, and by surface area measurements by such methods as low temperature nitrogen adsorption. The results of investigations in this field have been summarized by several writers, including Hurd,[4] Goodeve,[5] Weiser and Milligan,[6–8] and Tamele.[9] The consensus is that these substances are formed in a complex network of fiber-like particles. The evidence in favor of this hypothesis is far from complete. Such X-ray and electron diffraction data as are available suggest that the relation of one positive ion to the next is the same in the gels as in the crystalline state. For instance, although the electron diffraction lines produced by hydrous iron sesquioxide are quite diffuse, they are said to be in the same position as the sharply defined lines produced by the crystalline α-oxide. The study of pore volume and pore shape by the method of adsorption isotherms is not inconsistent with the view that the gels consist of tenuous filaments separated for the most part by relatively large spaces, which may be partially or completely filled by water.

Magnetic Properties of Crystalline Oxides.—Except for the rare earths, all oxides of the transition elements are typically magnetically concentrated substances. Some hydroxides may likewise belong to this category but most are, through structural accidents, magnetically dilute. The number of known paramagnetic hydroxides is not large.

Some oxides of the transition elements are ferromagnetic, but most are antiferromagnetic. The principal magnetic difference between the crystalline and the gel-like oxides seems to be the virtual absence of such exchange effects in the latter. Ferromagnetism and antiferromagnetism are a consequence of magnetic concentration and the parallel or antiparallel alignment, respectively, of electron spin moments. If the paramagnetic atoms are dispersed, as in magnetically dilute substances, then neither ferromagnetism nor anti-ferromagnetism may appear. For this reason the term "disperse" oxide seems preferable for this class of substances. It is believed that this term is more completely descriptive than either "hydrous" oxide or oxide "gel." The term adopted here to indicate the magnetically concentrated state is "massive." The term "crystalline" is objectionable in this connection because some disperse oxides give definite, though faint, evidence of crystallinity.

Magnetic Properties of Disperse Oxides and Hydroxides

Remarks on Techniques.—The several physical methods employed, which include magnetic susceptibility, surface area by BET adsorption, X-ray and thermal analysis, have all been described in earlier publications. The methods of chemical preparation and analysis are given under each separate substance.

Chromia I.—Interest in so-called chromia gel as a catalyst is such that several different preparative procedures were employed. The first method was the familiar addition of 0.1 *N* ammonium hydroxide to 0.1 *N* chromic nitrate solution. The precipitate was washed, and dried in a vacuum desiccator at room temperature over phosphorus pentoxide. The sample was analyzed for chromium by oxidation of Cr^{+3} to Cr^{+6} with perchloric acid, reduction with excess ferrous ammonium sulfate, and titration with potassium permanganate. The sample contained 44.8% chromium. Magnetic susceptibilities are given in Table II, but derived quantities and other data are summarized in Table V. In Table II the susceptibilities (χ) per gram of sample at several temperatures are followed by the susceptibilities (χ_{Cr}) per gram of chromium at each temperature. For instance, at 25° the susceptibility per gram of gel is 45.2 × 10^{-6}, the susceptibility per gram of chromium is 101 × 10^{-6}.

TABLE II

MAGNETIC SUSCEPTIBILITY OF CHROMIA I

Temp., °C.	$\chi \times 10^6$	$\chi_{Cr} \times 10^6$
25	45.2	101
−44	59.5	133
−58	62.8	140
−73	64.8	145
−89	68.1	152
−125	78.7	175

In Fig. 1 there are compared the suceptibilities per gram of chromium as a function of temperature, for the above disperse system, and for massive chromia as reported by Honda and Soné,[10] whose results are consistent with those from this Laboratory and elsewhere.

Chromia II.—A second sample of chromia was prepared by addition of dilute sodium hydroxide solution to chromic nitrate solution. The gel was dried as for chromia I. It contained 34.6% chromium. Magnetic data are given in Table III.

TABLE III

MAGNETIC SUSCEPTIBILITY OF CHROMIA II

Temp., °C.	$\chi \times 10^5$	$\chi_{Cr} \times 10^6$
25	36.0	103
−44	46.8	135
−73	53.5	154
−106	61.5	178

Chromia III.—A third sample was prepared by addition of dilute sodium carbonate solution to chromic nitrate solution. The gel was dried as above. It contained 24.4% chromium. Magnetic data are given in Table IV.

TABLE IV

MAGNETIC SUSCEPTIBILITY OF CHROMIA III

Temp., °C.	$\chi \times 10^4$	$\chi_{Cr} \times 10^6$
25	24.2	99
−44	31.8	130
−73	37.7	154
−146	51.2	209

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(4) Hurd, *Chem. Revs.*, **22**, 403 (1938).

(5) Goodeve, *Trans. Faraday Soc.*, **35**, 342 (1939).

(6) Weiser and Milligan, *Chem. Revs.*, **25**, 1 (1939).

(7) Weiser and Milligan, *J. Phys. Chem.*, **44**, 1081 (1940).

(8) Weiser and Milligan, "Advances in Colloid Science," Vol. I, edited by E. O. Kraemer, Interscience Publishers, Inc., New York, N. Y., 1942.

(9) Tamele, "Chemical Architecture," edited by R. E. Burk and O. Grummitt, Interscience Publishers, Inc., New York, N. Y., 1948, 175.

(10) Honda and Soné, *Sci. Repts. Imp. Univ. Tohôku*, **25**, 473 (1927).

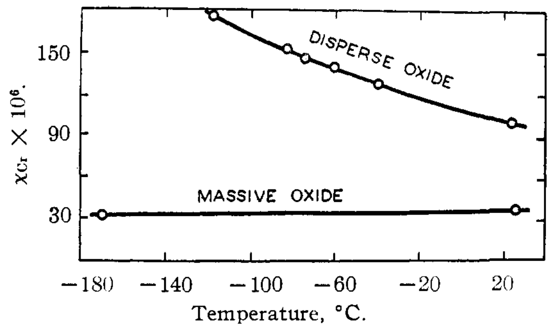

Fig. 1.—Susceptibility per gram of chromium in disperse chromia (gel) and in massive chromia (crystalline).

Table V gives the magnetic moment (μ) in Bohr magnetons, the Weiss constant (Δ) in centigrade degrees, the glow temperature (T_G) in centigrade degrees and the surface area (S) in square meters per gram of sample, as found by low temperature nitrogen adsorption and the BET equation. To these data there are added results on a sample of commercial "Chromia Aerogel."

TABLE V

MAGNETIC MOMENTS AND OTHER DATA FOR CHROMIA GELS

Gel	% Cr	μ	Δ	T_G	S
Chromia I	44.8	4.3	104	~390	2[a]
Chromia II	34.6	3.7	10	~430	146
Chromia III	24.4	3.6	20	~520	56
"Aerogel"	47.8	3.6	114	~515	970[a]

[a] This very low area is almost meaningless because the gel was rather obviously still moist. To have dried it further at this point would have defeated one purpose of the work. The extremely high area for the Aerogel is discussed later.

Figure 2 shows typical thermal analysis curves for two of the chromias. Not one of the above samples showed anything but a diffuse X-ray pattern on the Norelco recording X-ray spectrometer. Similar negative results were reported for electron diffraction studies made on these samples at Squier Signal Laboratories. No X-ray pattern developed after the endothermal change but before the glow.

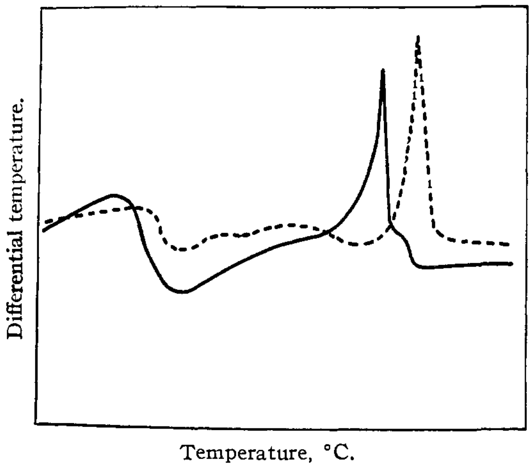

Fig. 2.—Thermal analysis curves for two samples of chromia gel.

Chromia IV.—This sample was similar to Chromia I except that the magnetic and other studies were conducted at intervals during the process of isobaral dehydration. For this study samples of gel were progressively dehydrated in an atmosphere of oxygen-free nitrogen. The temperature was gradually raised, and the time of drying increased, until the glow occurred. From time to time samples were removed for measurement. It was found necessary to exclude air rigidly, to prevent oxidation of the chromia. In Table VI there are given the cumulative hours of dehydration, the highest temperature to which any sample was subjected, the percentage chromium, the susceptibilities per gram of chromium at three temperatures, the magnetic moment, the glow temperature, and the result of attempted X-ray diffraction studies. In Fig. 3 there is given magnetic susceptibility per gram of chromium as a function of percentage chromium during the various stages of dehydration. Susceptibilities given in Fig. 3 are those at 100° K.

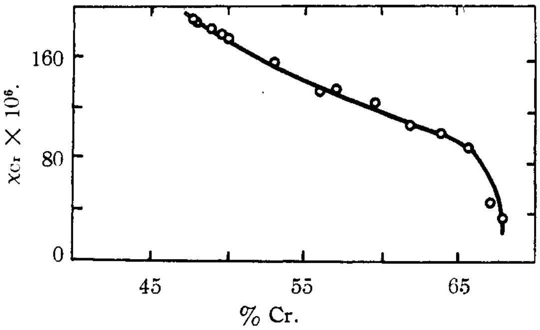

Fig. 3.—Susceptibilities per gram of chromium in chromia gel at various dehydration stages.

Iron Sesquioxide.—Hydrous iron sesquioxide precipitated from old ferric nitrate solutions almost always contains a trace of ferromagnetism. A gel free from ferromagnetism, within the limits of sensitivity of the susceptibility determination, was prepared as follows: about 50 g. of ferrous ammonium sulfate was dissolved in water, and concentrated nitric acid was added. The solution was heated to boiling and more nitric acid was added until oxidation was complete as shown by no further evolution of nitrogen dioxide. The solution was now diluted and cooled, and the hydrous oxide was precipitated by the addition of excess ammonium hydroxide. The gel was washed by decantation until the wash water was neutral to litmus. It was then filtered and dried in air at room temperature. Samples were analyzed for iron by the Zimmermann–Reinhardt method.

It is well known that hydrous iron oxide tends to change somewhat on aging.[11] A sample aged for 101 days increased in susceptibility at room temperature about 11%. This increase was apparently caused by an increase of magnetic moment. But because of the rather subtle influence[12] of ferromagnetic traces on measurements of this kind, the subject of aging was not further pursued, pending construction of a more appropriate apparatus.

A freshly prepared sample of hydrous iron oxide, prepared as described above, contained 40.4% iron. Magnetic data for this sample are shown in Table VII.

From the data of Table VII the magnetic moment was found to be 4.6, and the Weiss constant −20°. The sample gave only a diffuse X-ray pattern, and had a glow temperature of 286°. The susceptibilities were so high that samples were mechanically diluted with alumina, before measurement.

A similar sample of hydrous iron sesquioxide was now subjected to progressive isobaral dehydration. The data are given in Table VIII.

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(11) Evans and Pryor, *J. Chem. Soc.*, S157 (1949).

(12) Knappwost, *Z. physik. Chem.*, **A118**, 246 (1941).

TABLE VI

DEHYDRATION OF CHROMIA GEL

Hours	Temp., °C.	Cr, %	$\chi_{Cr} \times 10^6$ 300°K.	$\chi_{Cr} \times 10^6$ 200°K.	$\chi_{Cr} \times 10^6$ 100°K.	μ	Δ	S, m.²/g.	X-Ray	TG, °C.
17	127	48.0	95.6	128.0	192	4.0	99	...	None	437
3	110	48.1	87.5	119.1	186	3.7	78	...	None	454
16	120	49.2	86.0	117.2	183.5	3.7	79	...	None	442
18	140	49.6	90.6	121.0	181.5	3.9	101	340	None	454
24	170	49.7	82.5	111.8	174.0	3.6	79	...	None	426
24	210	53.4	79.7	107.0	155.2	3.8	123	199	None	475
24	210	56.7	74.2	95.0	132.3	3.8	155	...	None	407
24	210	57.0	72.5	94.2	135	3.7	142	306	None	426
65	210	59.4	70.3	89.6	124.0	3.7	165	...	None	477
55	266	62.6	64.3	80.7	108.6	3.7	196	342	None	429
65	280	64.4	58.8	74.2	100.8	3.5	187	329	None	407
70	308	65.4	55.7	71.1	89.5	3.5	228	290	None	428
..	~350	67.1	46.1	45.8[a]	47.3[b]	...	...	110	Weak Cr_2O_3	None
..	~400	68.5	36.7	....	33.3	...	...	10	Strong Cr_2O_3	None

[a] 184°K. [b] 128°.

TABLE VII

MAGNETIC SUSCEPTIBILITY OF HYDROUS IRON SESQUIOXIDE

Temp., °C.	$\chi \times 10^6$	$\chi_{Fe} \times 10^6$
25	67.7	168
−44	108	267
−89	144	353
−146	216	535

TABLE VIII

DEHYDRATION OF HYDROUS IRON SESQUIOXIDE

Dehydration Hours	Dehydration Temp., °C.	Fe, %	$\chi \times 10^6$ at 25°	$\chi_{Fe} \times 10^6$ at 25°
24	25	54.8	99	180
24	140	66.3	160	241
24	110	67.3	153	228
24	160	68.1	138	203
24	220	70.1	29.5	42
24	270	69.0	19.0	27

It will be noted that at the higher temperatures the oxide was going through the glow phenomenon. In Fig. 4 there are compared the magnetic susceptibilities of iron in the hydrous oxide as in Table VII and of iron in massive α-Fe_2O_3, prepared by igniting the gel above the glow temperature until it showed a sharply defined X-ray pattern for α-Fe_2O_3. The decrease of susceptibility on going through the glow phenomenon is especially striking if the susceptibilities are measured at low temperatures.

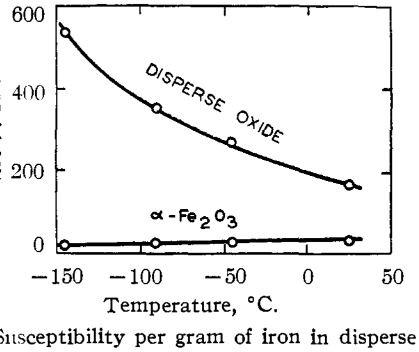

Fig. 4.—Susceptibility per gram of iron in disperse oxide and in massive alpha sesquioxide.

Measurements on iron oxide were pursued no farther, pending elucidation of the effects of traces of ferromagnetism on the apparent results.

Manganese Dioxide.—This gel and its changes on isobaral dehydration have been reported previously.[13]

Manganese Dihydroxide.—The preparation and magnetic properties of this *pure crystalline* compound have also been described.[13]

Copper Hydroxide I.—This substance was prepared by treating 35 g. of filtered copper sulfate hydrate dissolved in 2 l. of water with 20 g. of potassium hydroxide dissolved in 100 cc. of water. The solutions and mixture were cooled by the addition of ice prepared from distilled water. The gelatinous blue precipitate was filtered immediately, and washed with ice-water to remove excess alkali. The precipitate was washed with alcohol and ether, and dried in a vacuum desiccator overnight. A portion of gel so prepared retained its blue color for several days. Analysis for copper by electrolysis showed 53.4% copper. The X-ray pattern was diffuse. Magnetic data are shown in Table IX.

TABLE IX

MAGNETIC SUSCEPTIBILITY OF COPPER HYDROXIDE I

Temp., °C.	$\chi \times 10^6$	$\chi_{Cu} \times 10^6$
25	10.6	19.8
−44	14.2	26.4
−73	15.4	28.6
−106	17.8	33.0

From the data of Table IX the magnetic moment is found to be 1.8, and the Weiss constant is 32°.

Copper Hydroxide II.—This sample was prepared as follows: 35 g. of copper sulfate hydrate was dissolved in 400 cc. of water. The solution was boiled, filtered, and brought to boiling again. The green basic sulfate was precipitated by addition of excess of ammonium hydroxide. The precipitate was washed free from excess sulfate, and then mixed with 200 cc. of 5% sodium hydroxide solution. The precipitate was washed by decantation, filtered and dried. The color was bright blue. Electrolytic analysis showed 63.1% copper. The product gave a good X-ray pattern, as shown in Table X.

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[13] Moore, Ellis and Selwood, THIS JOURNAL, **72**, 856 (1950).

TABLE X

CRYSTAL INTERPLANAR SPACINGS AND RELATIVE INTENSITIES OF REFLECTION FOR COPPER HYDROXIDE II

d, Å.	$I/I_{\max.}$
5.27	0.9
3.72	1.0
2.64	0.7
2.49	.5
2.35	.3
2.26	.7
2.07	.2
1.72	.5
1.47	.2

Magnetic susceptibilities for this sample are shown in Table II.

TABLE XI

MAGNETIC SUSCEPTIBILITY OF COPPER HYDROXIDE II

Temp., °C.	$\chi \times 10^6$	$\chi_{Cu} \times 10^6$
25	11.6	18.4
−44	15.2	24.1
−73	16.7	26.4
−106	19.6	31.2
−146	22.9	36.5

From the data of Table XI the magnetic moment is found to be 1.8, and the Weiss constant 36°.

Copper Oxide.—Hydrous copper oxide was prepared by the addition of excess sodium hydroxide solution to copper nitrate solution. The original light blue precipitate turned gray-black. It was filtered, washed and dried. The product contained 71.5% copper, and gave a good X-ray pattern for CuO. Magnetic susceptibility data are shown in Table XII.

TABLE XII

MAGNETIC SUSCEPTIBILITY OF HYDROUS CUPRIC OXIDE

Temp., °C.	$\chi \times 10^6$	$\chi_{Cu} \times 10^6$
25	3.4	4.7
−44	3.3	4.6
−89	3.4	4.7
−146	3.2	4.5

It is obvious from the above data that no magnetic moment is calculable.

Vanadium Dioxide.—Hydrous vanadium dioxide was prepared according to the method of Crow.[14] Ammonium metavanadate was dissolved in dilute sulfuric acid, and sodium sulfite was added to reduce vanadate to vanadyl. Precipitation of the hydrous oxide must be carried out in a carbon dioxide atmosphere to prevent oxidation. The vanadyl solution was placed in a three-necked flask, carbon dioxide being bubbled through the system and out *via* an aspirator. Sodium carbonate was added dropwise from a dropping funnel until the blue color disappeared. The solution and precipitate were then poured into a sintered glass funnel, washed with boiled water, and then with alcohol and ether. The precipitate was dried in a vacuum desiccator over phosphorus pentoxide. The product was analyzed for V^{+4} by dissolving a sample in dilute sulfuric acid and titrating the vanadyl ion with potassium permanganate. The same sample was then analyzed for total vanadium by reduction with sodium sulfite, followed by boiling to remove excess sulfite, and titration with permanganate. Analysis showed that the gel contained 44.1% total vanadium, and 37.2% V^{+4}. This corresponds to a formula $VO_{2.08}\cdot 1.7\ H_2O$. The color was a purplish-gray. The thermal analysis gave a confused pattern, probably owing to partial oxidation.

Magnetic susceptibility data are shown in Table XIII. The values for χ_V are not corrected for the small content of pentavalent vanadium.

TABLE XIII

MAGNETIC SUSCEPTIBILITY OF HYDROUS VANADIUM DIOXIDE

Temp., °C.	$\chi \times 10^6$	$\chi_V \times 10^6$
25	5.1	12.7
−46	6.1	15.2
−58	6.2	15.4
−73	6.4	15.7
−106	6.9	16.8
−125	7.3	17.9
−146	8.0	19.3

From the data of Table XIII the magnetic moment for tetravalent vanadium is found to be 1.7, and the Weiss constant is 225°.

Nickel Hydroxide.—The hydrous hydroxide was prepared by addition of excess potassium hydroxide solution to a nickel nitrate solution in water. The green precipitate was washed, then dried in a vacuum desiccator. A sample analyzed by the dimethylglyoxime method gave 58% of nickel. The X-ray pattern was that of $Ni(OH)_2$, although moderately diffuse. Susceptibility measurements for this material are given in Table XIV.

TABLE XIV

MAGNETIC SUSCEPTIBILITY OF HYDROUS NICKEL HYDROXIDE

Temp., °C.	$\chi \times 10^6$	$\chi_{Ni} \times 10^6$
25	48.3	83.9
−44	65.6	113.7
−89	91.5	158

From the data of Table XIV the magnetic moment is found to be 2.9, and the Weiss constant is −55°.

Efforts to convert this material to a disperse oxide were unsuccessful, the massive oxide being obtained in every case.

Cobalt Dihydroxide.—The hydrous hydroxide was prepared by the addition of ammonium hydroxide to cobalt nitrate solution. The blue precipitate turned pink on standing; it was washed, filtered and dried. The X-ray pattern was that of $Co(OH)_2$. Analysis by electrolysis showed 63.1% cobalt. Magnetic data shown in Table XV were obtained by the mechanical dilution method.

TABLE XV

MAGNETIC SUSCEPTIBILITY OF HYDROUS COBALT HYDROXIDE

Temp., °C.	$\chi \times 10^6$	$\chi_{Co} \times 10^6$
25	141	224
−44	189	300
−89	237	376
−146	320	508

From the data of Table XV the magnetic moment is found to be 5.4 and the Weiss constant is −22°.

Other Gels.—Attempts were made to prepare disperse sesquioxides of titanium, nickel and cobalt, but in no case was a pure trivalent product obtained.

Discussion of Results

No true hydroxide has been discovered in this work, or elsewhere, to be other than magnetically dilute, although the oxyhydroxide of manganese, MnOOH, (*manganite*) was thus previously reported from this Laboratory.[13] We may then

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[14] Crow, *J. Chem. Soc.*, 453 (1876).

confine our discussion of the effect described here to the hydrous oxides and their crystalline counterparts, or in other words, to the disperse structure as compared with the massive structure of the transition element oxides.

The problem is somewhat further simplified by the fact that all the oxides studied are antiferromagnetic in the massive state. It will be observed that antiferromagnetism is a more common phenomenon than is ferromagnetism.

Susceptibility *versus* temperature for a typical antiferromagnetic is shown in Fig. 5. The effect of a critical temperature, below which the susceptibility falls, is accompanied at the critical point by a specific heat anomaly, and in some cases by a moderate dependence of susceptibility on field strength. The critical point is referred to as the antiferromagnetic Curie point. It is a so-called second order transition.

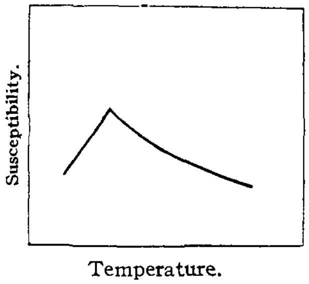

Fig. 5.—Susceptibility for a typical antiferromagnetic.

The theoretical explanation for this effect has been developed by Néel,[15–18] Kramers,[19,20] Hulthén,[21] Bitter[22] and Van Vleck.[23] The theory is based on the Weiss molecular field and on the Heisenberg exchange interaction. It is similar to the corresponding development of the theory of ferromagnetics, except that a negative exchange integral gives rise to an antiparallel spin alignment.

For the present purposes, the most useful development is the expression for the antiferromagnetic Curie point, $T_C = 2JzS(S + 1)/3k$, where J is the exchange integral, z is the number of nearest paramagnetic neighbors possessed by each paramagnetic ion (*i. e.*, the paramagnetic neighborhood), S is the spin vector sum, and k the Boltzmann constant. This is the same as the expression for the ferromagnetic Curie point, except that the sign is changed. T_C may be found experimentally either as the actual critical point in a plot of susceptibility *versus* temperature, or as the Weiss constant from magnetic measurements above T_C.

The results on the disperse oxides will be considered with special reference to chromia. The antiferromagnetic Curie point for this oxide in the massive state is not well defined, but is in the neighborhood of room temperature.[10,24] For a typical chromia in the disperse state the Weiss constant $\Delta \simeq 100^\circ$. For both massive and disperse states the expression given above for T_C may be expected to hold, the only possible differences being in the exchange integral J, and the number of nearest paramagnetic neighbors, z, possessed by each chromium. For reasons to be described below it is believed that J will be the same for both massive and disperse states. Hence, it is possible to write $z' = zT'_C/T_C$, where z', T'_C apply to the disperse state, and z, T_C to the massive state. It is a little difficult in chromia to know what value should be chosen for z. This is because there are actually several neighbors at slightly different distances, but the number *nine* is probably not too much in error. Then the average number of nearest chromium neighbors possessed by each chromium ion in the gel is $z' = 9 \times 100/300 = 3$.

This is, of course, an astonishing degree of attenuation; but it is in agreement with the value previously obtained for supported chromia, by an even more approximate method of calculation.[2] In making this calculation, no consideration has been given to chromiums at distances much greater than the minimum chromium–chromium distance. The reason for this is that exchange effects diminish as the cube of the distance.

The objections to this computation are formidable. Some of them will be described, but comfort will be taken in the statement made above that *any* structural information, no matter how tenuous, is welcome in this field of hydrous oxides. Some of these objections are as follows:

1. Derivations of the formulas for T_C, and for the susceptibility below T_C, are based on a body-centered structure in which, as pointed out by Van Vleck,[23] the effect of paramagnetic neighbors being neighbors to each other is ignored. Not one of the gels described here falls into this class, and precise application of the theory of antiferromagnetics to gel structure must wait for further theoretical developments. It may, however, be pointed out that at such extremes of attenuation, as seem to be the case for these hydrous oxides, the problem may actually be somewhat simpler than in massive oxides. The reason for this is that the number of paramagnetic neighbors which are neighbors of each other in the gels must be a small fraction of the number similarly placed with respect to each other in the massive oxides. A difficulty related to this is how the exchange effects may be expected to operate when the paramagnetic ions are separated by diamagnetic oxide ions. This difficulty has been recognized by Kramers[20] and by Néel,[15–17] who use the concept of "superexchange."

2. The next difficulty is that the Weiss constant does not always equal the Curie point. In ferromagnetics the deviation is seldom very large, but in manganese (mon)oxide, at least, the data

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(15) Néel, *Ann. Phys.*, **18**, 5 (1932).

(16) Néel, *ibid.*, **5**, 256 (1936).

(17) Néel, *ibid.*, **3**, 137 (1948).

(18) Néel, *Bull. soc. franc. elec.*, **9**, 308 (1949).

(19) Kramers, *Physica*, **1**, 182 (1934).

(20) Kramers, "Le Magnetisme," Proc. Strasbourg Conf., Collection Scientifique, Paris. 1940, Vol. III, p. 45.

(21) Hulthén, *Proc. Amsterdam Acad. Sci.*, **39**, 190 (1936).

(22) Bitter, *Phys. Rev.*, **54**, 79 (1938).

(23) Van Vleck, *J. Chem. Phys.*, **9**, 85 (1941).

(24) Foëx and Graff, *Compt. rend.*, **209**, 160 (1939).

reported by Bizette, Squire and Tsai[25] show that Δ is numerically equal to five times T_C. This is perhaps an extreme case, but until more data are available it is idle to insist that Δ and T_C are even approximately equal.

3. It was assumed above that the exchange integral, J, is the same in both disperse and massive states. The alternative is rendered less probable for two reasons. The first is that electron diffraction studies on hydrous iron sesquioxide reported by Weiser and Milligan[7] show that the structure is similar to that in α-Fe_2O_3, and that the iron–iron distance is the same in the two cases. But this situation remains a little confused by the discovery by Fordham and Tyson[26] that freshly precipitated iron oxide gel has a face-centered cubic structure, quite different from that reported by Weiser and Milligan, and also different from goethite, $Fe_2O_3 \cdot H_2O$. A further complicating factor, namely, that the gel changes on aging, has been referred to above.

The second reason lies in the somewhat reduced moment found for plus three iron in both the hydrous oxide reported here, and in iron sesquioxide supported on alumina as previously reported.[27] Assuming that this decreased moment, amounting to about 30% under the spin-only value for five unpaired electrons, is due to covalent bonds[28] between adjacent iron ions, it is difficult to see how this effect could persist in the hydrous oxides if the iron–iron distance in this system is appreciably greater than it is in the massive oxide.

4. It is well known that the Weiss constant depends on several factors besides the exchange interaction. Thus, Δ may often have a substantial value for paramagnetic ions in solution where they are obviously at infinite magnetic dilution. All such effects, other than the exchange effects, have been ignored, for two reasons. These are, first, the fact that Δ approaches zero for nearly all supported paramagnetic oxides as the concentration of the supported oxide diminishes, provided that the support must, of course, be diamagnetic. The second reason for ignoring other possible causes of Δ is that some of the gels, notably hydrous iron sesquioxide, contain the positive ions in an S spectroscopic state, in which, owing to the absence of an orbital contribution, all effects contributing to the Weiss constant are negligible, except, of course, for the exchange effects.

5. In some of the gels the Weiss constant becomes so low that the rough computation given above leads to less than one nearest paramagnetic neighbor. This is true for hydrous iron oxide, for which $T_C \simeq 900$°K., and for some, but not all, of the chromia gel preparations. It is difficult to see how a gel formed of nothing but oxide ions and positive metal ions could retain much mechanical stability and yet have less than two such positive ions near each other in the structure. This evidence suggests that other ions such as hydroxide or hydronium help to stabilize the gels, perhaps with the aid of hydrogen bonding between scattered points where the filamentous structures come in effective contact.

6. It might be thought that the magnetic susceptibility of the gels could be accounted for by assuming that they consist of a mixture of totally dispersed paramagnetic ions plus some massive oxide. Thus, iron oxide gel might consist of a mixture of magnetically dilute Fe^{+3} ions, together with appropriate anions, plus some α-Fe_2O_3. This idea may be shown to be wrong by calculation of the proportion of each kind of iron which would be necessary to fit the magnetic data. The necessary data are given in Table XVI.

TABLE XVI

SUSCEPTIBILITY ($\times 10^6$) PER GRAM OF IRON IONS

Kind of iron	χ at 25°	χ at −146°
Fe^{+3} in gel	168	535
Fe^{+3} in atomic dispersion (calcd.)	269	630
Fe^{+3} in α-Fe_2O_3	27.3	21.2

On the assumption that the susceptibilities of the components of such a mixture would be additive, the proportion p of atomically dispersed iron at 25° is then given from the relation $269\,p + 27.3(1 - p) = 168$, from whence $p = 58\%$. Similarly, at −146°, $p = 84\%$. The obvious disagreement between these two results establishes the fallacy involved, namely, that the gel cannot be considered a mixture of dilute and concentrated forms of iron. Furthermore, if 42% of α-Fe_2O_3 were present in the gel, it would give a very clear X-ray diffraction pattern.

With the above reservations in mind, it may be said that the magnetic method described yields useful qualitative information concerning the gel structure of hydrous paramagnetic oxides. The method is valuable in the study of structural changes occurring in such systems as a function of time or of dehydration. The method may be expected to yield quantitative structural information as the theory of exchange interaction in oxide systems becomes better developed. It may be pointed out that to some degree the disperse oxide state is related to the massive state as a super-cooled liquid is to a normal liquid. This will be clear from Fig. 6, in which it is shown how the magnetic susceptibility of the

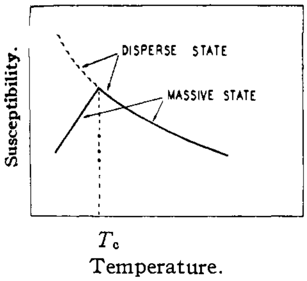

Fig. 6.—Susceptibility as a function of temperature for a paramagnetic substance in the disperse (gel) state and in the massive (crystalline) state.

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(25) Bizette, Squire and Tsai, *Compt. rend.*, **207**, 449 (1938).

(26) Fordham and Tyson, *J. Chem. Soc.*, 483 (1937).

(27) Selwood, Ellis and Wethington, THIS JOURNAL, **71**, 2181 (1949).

(28) Hill and Selwood, *ibid.*, **71**, 2522 (1949).

ions in the disperse state are related to those in the massive state. It will, of course, be clear that Fig. 6 represents a partially idealized condition, because the magnitude of the Weiss constant for the massive state above the Curie point is often much larger than that found for the disperse state. Furthermore, for gels such as iron sesquioxide, the glow temperature is reached long before the Curie point could ever be attained.

The method does not apply to diamagnetic oxides. To oxides such as molybdenum dioxide, in which strong valence bonds occur between adjacent molybdenums, the method is of restricted applicability. The method is also restricted in its application to substances such as the hydroxides of manganese, cobalt, nickel and copper, in which the paramagnetic ions remain magnetically dilute in the pure crystalline solid. But even in these cases the information obtained from magnetic measurements is interesting and confirmatory of X-ray structural determinations.

The structural information obtained by the magnetic method is not inconsistent with earlier speculations concerning gel structure. The astonishing degrees of attenuation found by the magnetic method could be achieved only by particles or threads of little more than one atom diameter in cross-section. It would seem that sheets or honeycomb structures containing only one oxide ion layer would, in some cases at least, be insufficiently attenuated to account for the magnetic results. Figure 7 shows a possible model of filamentous chromia, extended along the hexagonal axis. This model, which possesses an average of three chromium ion neighbors for each chromium, illustrates the difficulty in filling the magnetic requirements and yet giving the model sufficient mechanical stability. Some chromiums are represented as on the surface of the thread, or to express it another way, of having less than octahedral coördination. But the very small value of the Weiss constant makes this configuration unlikely. Vanadium dioxide, on the other hand, with its fairly large value for the Weiss constant, behaves in more the manner which might, on the basis of earlier studies, have been expected for all the gels.

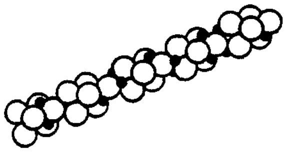
Fig. 7.—Model of filamentous chromia extended along the hexagonal axis.

There seems to be little relation between degree of attenuation revealed by the magnetic method, and surface area. A highly attenuated gel will naturally tend to have a high area, but this area may be greatly reduced by included molecules such as water. This is shown by the results on chromia gel. The aerogel has a much higher area, but a slightly lower degree of attenuation, than have some of the other chromia preparations. Similarly, during dehydration the chromia gel increases in surface area, owing to removal of water; but during this process the chromia groups are actually moving, on the average, a little closer together. This is probably not to say that the minimum chromium–chromium distance ever decreases, but rather that the average number of chromium neighbors to be found at this minimum distance is gradually increasing. The phenomenon of the glow simply means that thermal vibrations have become sufficiently violent so that the structure surmounts the energy barrier toward formation of the more stable massive solid.

It was thought that perhaps the glow phenomenon might be related to the formation of intercationic valence bonds. This would explain the vigorous glow found for hydrous ferric oxide, and the partial or complete absence of the effect in hydrous manganese dioxide and in hydrous alumina. But further search of the literature and thermal analysis of a few diamagnetic oxide gels showed that there is no relation between paramagnetism and the glow phenomenon. In fact, the large amount of heat liberated during this transition seems easily explained on the basis of the large entropy change associated with the great diminution of surface area.[29] This diminution of area frequently exceeds 250 sq. m. per g.

This article will be concluded with a few remarks concerning the specific data reported above.

Chromia.—The magnetic moments derived from the several gels are consistent with the spin-only formula for Cr^{+3}. The Weiss constants indicate considerable difference in attenuation, depending on mode of preparation. Slow isobaral dehydration results in a moderate decrease of attenuation, accompanied in some cases with a moderate increase in surface area. But at the glow point the area and magnetic susceptibility both decrease precipitously as the X-ray pattern develops. There is no obvious relation between glow temperature and any other property, although some of the evidence indicates that low initial water content may be related to the high glow point. In this connection it should perhaps be pointed out that just as massive oxides may possess structural defects in which the positive ions are somewhat more dispersed than normal, so a disperse oxide may possess structural defects in which the positive ions are somewhat more closely aggregated. It would appear probable that the presence of such defects in the disperse structure would promote the transition to the massive form.

An earlier report on chromia gel indicated that it was ferromagnetic.[30] This observation was probably the result of contamination with some higher oxide of chromium, possibly CrO_2, which is well known to be ferromagnetic.

It has often been remarked that the extremely high surface area sometimes found for chromia

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(29) Rodebush, *J. Chem. Phys.*, **9**, 284 (1941).

(30) Selwood, Hill and Boardman, THIS JOURNAL, **68**, 2055 (1946).

gel and similar substances could only be explained by layers of gel no more than one atom layer thick. These observations have even tended to throw some doubt on the reliability of surface area determinations at these great degrees of attenuation. But it will be noted that such results are entirely consistent with inferences drawn from the magnetic data.

Iron Sesquioxide.—All samples of hydrous iron oxide gave the anomalous low magnetic moment which was previously[27] reported for supported iron oxide on alumina.

The high susceptibility of iron sesquioxide gels has been observed several times previously. Courty[31] gives a good review of this topic. In particular, Blanc,[32] who also studied chromia, observed the diminution of susceptibility when the gel passes through the glow phenomenon.

Manganese Dioxide.—This substance fails to show a well developed glow effect for the rather obvious reason that it decomposes before the glow temperature is reached. In this substance, as in those described above, there is a definite tendency toward aggregation long before dehydration approaches completion. The moment is normal, and rises only as the concentration of Mn^{+3} ions becomes appreciable.

As mentioned already, there have been numerous magnetic studies on manganese dioxide, at least some of which have given anomalous results because the compound studied tended to be gel-like rather than crystalline. However, Amiel, Rodier and Brenet[33] have noted the high susceptibility of catalytically active samples of both natural and artificial origin. It will be worth while to mention the theoretical explanation offered by the French workers. Their theory, supported by X-ray studies, is that the increased activity and susceptibility is due to a relaxation of the Mn–O bonds, with consequent increase in the average number of unpaired electrons. This idea is not inconsistent with current views expressed by Néel, Bizette, and others with respect to the nature of antiferromagnetism. The fact that the magnetic moment is normal both for disperse manganese dioxide and for crystalline pyrolusite above the antiferromagnetic Curie point argues against the French view. Actually, however, their view and that expressed here are not very different. In the present work there has been emphasized the effects of exchange and nearest paramagnetic neighbors, while Amiel, Rodier and Brenet have interpreted these effects in terms of actual covalent bonds between manganese and oxygen.

Manganese Dihydroxide.—This substance, together with the other true hydroxides studied, remains magnetically dilute even though the composition approaches $Mn(OH)_2$. This is due to the particular structure, which prevents close approach of manganese ions to each other.

Copper Oxide.—The familiar transition from blue copper hydroxide to black cupric oxide is seen to be accompanied by a very large diminution of magnetic susceptibility. This is one of the most striking magnetic transitions observed. It had previously been noted by Chaumeton.[34]

Cobalt Hydroxide.—It will be noted that the Co^{+2} ion shows the familiar enhancement of moment, probably due to some orbital contribution.

Vanadium Dioxide.—This gel shows a normal moment for one unpaired electron, but the Weiss constant indicates a less attenuated structure than for several of the other gels.

Table XVII gives antiferromagnetic Curie points for the several massive oxides studied, and the literature source from which each is obtained.

TABLE XVII

ANTIFERROMAGNETIC CURIE POINTS

Oxide	T_C	
Cr_2O_3	55°	Foëx and Graff[24]
α-Fe_2O_3	675	Néel[35,36]
MnO_2	−189	Bizette and Tsaï[37]
Mn_2O_3	< −189	Honda and Soné[38]
MnO	−151	Bizette, Squire and Tsaï[25]
CuO	~150	Bizette and Tsaï[37]
VO_2	68	Hoschek and Klemm[39]
NiO	~374	Foëx and La Blanchetais[40]
CoO	−2	Bizette[41]

Almost without exception these substances give a normal moment above T_C, but the difficulty of locating T_C is often enhanced by the difficulty in preparing stoichiometric samples of the oxides.

Summary

Paramagnetic oxides of the transition group elements may exist in either a gel-like, disperse state; or in a crystalline, massive state. The magnetic properties of the disperse state differ greatly from those of the massive state. This difference may be used to gain structural information concerning the so-called gels.

EVANSTON, ILL. RECEIVED JANUARY 14, 1950

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(31) Courty, Thesis, Faculty of Sciences, University of Paris, 1935.

(32) Blanc, *Ann. chim.*, **6**, 18 (1926).

(33) Amiel, Rodier and Brenet, Proc. Conf. on the Polarization of Matter, Paris, April 4-9, 1949.

(34) Chaumeton, *Compt. rend.*, **206**, 1104 (1938).

(35) Néel, *ibid.*, **206**, 1104 (1938).

(36) Néel, *Ann. Phys.*, **4**, 249 (1949).

(37) Bizette and Tsaï, Proc. Conf. on the Polarization of Matter, Paris, April 4-9, 1949.

(38) Honda and Soné, *Sci. Repts. Imp. Univ. Tohôku*, **3**, 139 (1914).

(39) Hoschek and Klemm, *Z. anorg. allgem. Chem.*, **242**, 63 (1939).

(40) Foëx and La Blanchetais, *ibid.*, **228**, 1579 (1949).

(41) Bizette, *Ann. Phys.*, **1**, 233 (1946).