negative. Similar observations made at several diferent values of  $V$  from 3 to 1000 volts are shown in Fig. 2. Evidently both the magnitude and direction of  $\Delta I$ depend on  $V$ . The fractional change in reflected primary current expressed as  $\Delta I/I$  was sometimes rather large, lying between  $+20$  and  $-45$  percent.

The time required following a target flash, for  $I$  to return to its pre-Gash value, was always roughly proportional to the monolayer adsorption time. This can be seen in all the curves of Fig. 1, including the last two, (f) and (g), where a lower pressure resulted in a measurement interval of 400 seconds.

These observations serve to point out the necessity of providing an atomically clean surface for measurements of electron reflection coefficient and of making



FIG. 2. A plot of the fractional change in reflected primary current, expressed as  $\Delta I/I$  in percent, as a function of electron voltage V.

such measurements in a relatively short time and under good vacuum conditions.

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# Magnetic Properties of Colloidal Nickelous Oxide

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Magnetic susceptibility measurements by the Faraday method have been made in the temperature range 4-550'K for a series of iron-free nickelous oxide samples prepared by the heat-treatment of hydrous nickelous hydroxide in a current of nitrogen at temperatures of 250—1300'C, the crystal size as given by electron diffraction methods varying from 80—2000 A. Samples (crystal size  $\sim$ 2000 A) prepared at 1200–1300°C exhibit susceptibilities typical of an antiferromagnetic material, the observed Neel point of 523'K agreeing with the results of earlier investigators. In samples (crystal size  $\sim$ 100-200 A) prepared at 300-500°C the susceptibility agrees with that for the larger crystals above the Néel point, but exhibit maxima at lower temperatures. The temperatures,  $T_c$ , at which the maxima appear, decrease regularly and the amplitudes of the maxima increase regularly, with decreasing crystal size. In the range studied, linear plots  $\lceil 10^{-4}T_c=1.090f-1.037\rceil$ are obtained for  $T_c$  as a function of f, the ratio of the average number of next nearest magnetic neighbors per nickel atom to the number of next nearest magnetic neighbors in an infinite crystal, as computed from the observed crystal sizes. Neutron diffraction patterns demonstrate that the magnetic structure is antiferromagnetic at temperatures both above and below  $T_c$ , and hence the maxima do not correspond to shifted Néel points.

The magnetic susceptibility curves for the colloidal crystals of nickelous oxide resemble those obtained by others for certain iron

### INTRODUCTION

ICKELOUS oxide, as normally prepared, consist of crystals larger than the colloidal range of particle size, and exhibits a transformation at approximately  $523^{\circ}K$ , detectable by back reflection x-ray diffraction,<sup>1,2</sup> magnetic peaks in neutron diffraction patterns,<sup>3</sup> and the appearance of a Néel point in magand chromium sulfides. In iron sulfide,  $\text{FeS}_x$ , the susceptibility increase to the maximum is attributed by Néel and others to a ferrimagnetic structure, analogous to certain ferrites. In view of the "active" oxygen (Bunsen test) contents of the nickelous oxide samples which vary from 0.36 to  $0.00\%$  as the crystal size increases from 80 to 2000 A, it is possible to attribute the ferrimagnetic behavior to the ordering of a sublattice of defects, as Néel does for  $FeS<sub>x</sub>$ . However, the subsequent decrease in susceptibility at temperatures below  $T_c$  cannot be readily explained for either  $\text{FeS}_x$  or NiO.

In view of the linear relationship between  $T_c$  and f, it is concluded that the unusual magnetic properties of colloidal nickelous oxide is attributable to the small size of the crystals and the accompanying enhanced specific surface and the decreased number of next nearest magnetic neighbors which results in an altered magnetic environment.

Nickelous oxide prepared at 250'C contains a small amount of undecomposed nickelous hydroxide detectable by electron diffraction methods. The magnetic susceptibility of pure nickelous<br>hydroxide follows a Curie-Weiss law  $\left[\chi_m=1.07/(T-36)\right]$  from about 300' to 90'K. Below 90'K, the susceptibility increases more slowly to a value of  $\sim 2000 \times 10^{-6}$  emu at  $4^{\circ}$ K, and some field dependence was observed, suggesting the desirability of additional studies concerning possible ferromagnetism.

netic susceptibility measurements.<sup>4</sup> Below 523°K nickelous oxide is rhombohedral and antiferromagnetic, whereas above  $523^{\circ}K$  it is cubic and paramagnetic.<sup>5</sup> The rhombohedral structure results from only very small distortions from the cubic form. In the antiferromagnetic form, Shull  $et al.^3$  found that of the 12 nearest neighbors surrounding any Ni ion, 6 are oriented parallel to the central ion and 6 are antiparallel. However, the number of next nearest neighbors for an infinite

<sup>\*</sup>Humble Oil and Re6ning Company Fellow, 1952-1955. ' H. P. Rooksby, Nature 152, 304 (1943); Acta Cryst. I, 226 (1948).

 $2^{2}$  Y. Shimomura, Bull. Namiwa Univ. A3, 175, 185 (1955).

<sup>&#</sup>x27;Shull, Strauser, and Woilan, Phys. Rev. 83, 333 (1951).

**<sup>&#</sup>x27; M. Foex, Bull. soc. chim. France 19, 373 (1952).** ' M. Foex, Bull. soc. chim. France 19, 373 (1952). ' J. S. Smart and S. Greenwald, Phys. Rev. **82,** 113 (1951).

crystal of nickelous oxide is 6, all coupled antiparallel to the central ion. According to the concepts of Anderson,<sup>6</sup> the dominant exchange forces are produced by the phenomenon of superexchange, in which the electronic wave functions of the magnetic nickel ions overlap those of the intermediate oxygen ions, and thus the next nearest neighbors are especially significant in controlling the alignment of the magnetic moments, thereby determining the type of magnetic lattice.

In a previous report from this laboratory<sup>7</sup> concerned with magnetic susceptibility studies on dual hydrous oxide gels in the system  $NiO-Al<sub>2</sub>O<sub>3</sub>$ , it was found that very finely-divided nickelous oxide exhibited a remarkable enhancement in its room temperature magnetic susceptibility, the susceptibility increasing regularly as the temperature of heat-treatment decreased. These results suggested the desirability of obtaining magnetic susceptibility data for nickelous oxide of widely varying crystal size over a wide range of temperature, and the purpose of this paper is to report the findings of such a study.

#### EXPERIMENTAL

#### Preparation of Samples

Hydrous nickelous hydroxide gel was prepared in a manner already described,<sup>7</sup> care being taken to minimize sodium and silica contamination by employing polythene containers. The nickelous oxide samples were prepared by heat-treatment of the nickel hydroxide for two-hour periods in a stream of dry nitrogen at temperatures in the range of 100—1300'C. Spectrographic analyses were obtained, and the samples were subjected to the Bunsen test for "active" oxygen.

### Magnetic Susceptibility Measurements

The magnetic susceptibilities were determined by the Faraday method, employing an apparatus similar to one described previously.<sup>8</sup> The cryostat employed for temperatures from 4° to 300°K consisted of an especially designed Dewar flask, containing various liquids boiling at the desired series of temperatures. At temperatures above 300'K, an electric heater took the place of the coolant.

#### Diffraction Measurements

The series of samples of nickelous oxide derived from the several temperature levels of heat-treatment were examined by electron diffraction methods, and the samples heat-treated at 400° and 1200°C were examined by neutron diffraction techniques through the kindness of Dr. C. G. Shull. The electron diffraction patterns were obtained by dispersing the powdered oxide in distilled water with the aid of an ultrasonic apparatus. A drop of the suspension was allowed to dry on a

collodion membrane supported on an Athene grid. The electron diffraction patterns were obtained with a Philips type EM-100 instrument, at an accelerating potential of approximately 100 kv. Neutron diffraction patterns were obtained at both room temperature and the temperature of liquid nitrogen.

#### RESULTS AND CONCLUSIONS

## Chemical Analysis

Spectrographic analysis indicated only the presence of nickel, together with a minute trace of cobalt. Special attention was given to the presence of iron, but no trace could be detected. The results of the "active" oxygen analysis are given in Table I. The active oxygen contents reported here are very slightly higher than those reported by Le Blanc and Sachse. '

#### Electron Diffraction

The electron diffraction patterns for samples heattreated from 300—1300'C corresponded to the standard interplanar spacings observed in x-ray diffraction patterns. No indication was observed of the splitting of certain diffraction lines which is indicative of the rhombohedral form, and observable by high-resolution, back-reflection x-ray techniques. The sample heattreated at 200'C yielded the diffraction pattern of the undecomposed nickel hydroxide. The sample heattreated at 250'C gave an electron diffraction pattern characteristic of nickelous oxide plus a trace of nickelous hydroxide. No trace of nickel hydroxide was observed at the higher heat-treatments. These data are in agreement with x-ray diffraction studies reported by Merlin<br>and Teichner.10 and Teichner.

The observed electron diffraction lines were very broad for the samples prepared at the lower temperatures, and increased in sharpness as the temperature of heat-treatment was increased. For heat-treatments of about 700'C and higher the lines became spotty, indicating the presence of relatively large crystals above the colloidal range of particle size. The electron diffraction lines for the nickelous hydroxide were likewise very broad, in agreement with electron micrographic observations of Feitknecht and Studer<sup>11</sup> who found the gel to consists of very thin plate-like crystals only a few hundred A in diameter, the exact size depending on the extent of aging.

#### Crystal Sizes

In order to obtain an estimate of the size of the crystals in the nickelous oxide samples, the electron



Temperature of heat treatment. °C Active oxygen, %	250 0.36	300 0.37	350 0.32	400 0.33	500 0.15	600 0.11	700 0.03	1300 0.00

<sup>&</sup>lt;sup>8</sup> P. W. Anderson, Phys. Rev. 79, 350, 705 (1950).

<sup>&#</sup>x27;W. 0. Milligan and J. T. Richardson, J. Phys. Chem. S9,

<sup>831</sup> (1955). W. 0, Milligan and H. 3. Whitehurst, Rev. Sci. Instr. 23, 618 (1952).

<sup>&</sup>lt;sup>9</sup> M. Le Blanc and H. Sachse, Z. Elektrochem. **32**, 58 (1926).<br><sup>10</sup> A. Merlin and S. Teichner, Compt. rend. 2**36**, 1892 (1953).<br><sup>11</sup> W. Feitknecht and H. Studer, Kolloid-Z. 115, 13 (1949).

diffraction negatives were measured in a special recording microphotometer constructed in this laboratory. After converting the measured blackening to intensities, and substracting the incoherent scattering, the widths of the  $(220)$  line were measured at half-intensity in the usual manner.<sup>12,13</sup> The resulting half-widths were conusual manner.<sup>12,13</sup> The resulting half-widths were converted to cube edges,  $d$ , employing the formula<sup>13</sup>:  $d=0.95\lambda/b \cos\theta$ , where  $\lambda$  is the wavelength; and b is defined by  $b=B-b_0$ , where B is the observed halfwidth and  $b_0$  is the limiting (12) half-width observed for powders consisting of crystals just large enough to no longer give broadening. In the samples under consideration  $B$  decreased from a value of 0.0414 radian, for the smallest crystals, to a limiting value of 0.0236 radian, which is taken as the value of  $b_0$ . The calculated crystal sizes are given in Table II and are included in Fig. 4. Electron micrographs of the samples heattreated above  $500-600^{\circ}\text{C}$  show that the crystals are actually cubic, and the observed sizes are consistent with the data in Table II. The exact morphology of the samples, prepared at heat treatments below 500°C, has not been determined by electron microscopic methods, because of extremely small crystal size.

The smallest particles considered here are the limiting size attainable by the method of preparation employed. Possibly, smaller particles could be produced by decomposing the hydroxide at lower temperatures under a high vacuum. In this connection, Teichner and Morrison<sup>14</sup> recently observed that pure nickelous hydroxide heated above 250 $\degree$ C at a pressure of the order of 10<sup>-6</sup> mm Hg, becomes black in color, exhibits ferromagnetic properties, and gives x-ray diffraction lines characteristic of metallic nickel in addition to those of nickel oxide. In view of these unexpected results, attempts to prepare more minute crystals of nickelous oxide from the hydroxide by the method mentioned above, must be limited to temperatures below about 200'C to avoid possible formation of metallic nickel.

#### Magnetic Susceptibility

The magnetization,  $M$ , of a substance exhibiting a small spontaneous magnetization,  $M_0$ , is given by:  $M=\chi H+M_0$ , where  $\chi$  is the usual paramagnetic susceptibility. In the calculations, it is assumed that saturation does not occur, and that  $H$ , the internal magnetic field, may be taken to be the applied field. The maximum applied field employed in the experi-

TABLE II. Crystal sizes of nickelous oxide samples.

Temperature of heat treatment. °C Particle size. A	250 80	300 104	350 117	400 140	500 170	600	700 664 > 1000	1300 >2000

<sup>&</sup>lt;sup>12</sup> C. R. Adams and W. O. Milligan, J. Phys. Chem. 58, 817 (1954). <sup>13</sup> G. G. Libowitz and S. N. Bauer, J. Phys. Chem. 59, 214

300  $250^{\circ}$ C 4 O **ann**  $\boldsymbol{\mathsf{x}}$ **¥**<br>ው 200 ۴Ã ่จรก่ IlQ I-0. LU V f00 V  $400^{\circ}$ C بیا<br>ب  $500^{\circ}$ C S°006 C- $1300^{\circ}$ C  $\Omega$ 200 300 400 500 600 IOO  $\mathbf{o}$ TEMPERATURE , <sup>o</sup>K

FIG. 1. Magnetic susceptibilities of nickelous oxide samples, prepared at temperature levels of heat-treatment from 250- 1300'C, as a function of temperature.

ments reported here was 3500 gauss. Graphs of the observed susceptibility as a function of  $1/H$  were linear at all temperatures, indicating that magnetic saturation did not occur. The slopes of the linear plots give the spontaneous magnetization, and the intercepts give the true paramagnetic susceptibility.

The corrected magnetic susceptibilities for nickelous oxide samples, heat-treated at 250, 300, 350, 400, 500, 700, and 1300'C, are given in Fig. 1 as a function of temperature. Other susceptibility curves for samples heat-treated in the temperature range 600—1200'C are omitted from the figure to avoid confusion. The susceptibility data for samples heat-treated at 1200' and  $1300^{\circ}$ C are given in greater detail in Fig. 2, in which (a) the open circles correspond to nickelous oxide prepared from the hydroxide at 1300'C, (b) the closed circles correspond to the oxide prepared by heating the nitrate to 1200'C, and (c) the curve corresponds to mitrate to  $1200^{\circ}\text{C}$ , and (c) the curve corresponds to<br>the data of Foex and La Blanchetais.<sup>15</sup> It will be noted that the characteristic Néel point occurs at the normal temperature of about  $523^{\circ}\overline{\text{K}}$ . The agreement between the present data and that of Foex and La Blanchetais is very satisfactory.

It will be noted in Fig. 1, that at temperatures just <sup>15</sup> M. Foex and H. La Blanchetais, Compt. rend. 228, 1579 (1949).

<sup>(1955).</sup> '4 S.J. Teichner and J. A. Morrison, Trans. Faraday Soc. Sl, 961 (1955).



FIG. 2. Magnetic susceptibility of nickelous oxide as a function of temperature for samples prepared by heating the hydroxide at 1300'C (open circles), and by heating the nitrate at 1200'C (closed circles), compared with the results of Foex and La Blanchetais (curve).

below the normal Néel point, the susceptibility increases rapidly as the temperature is decreased, and passes through a maximum at a transition temperature. The temperature,  $T_c$ , at which the maxima appears, decreases regularly as the temperature of heat-treatment and the size of the crystals decrease. Likewise, the amplitude of the maxima increases regularly as the size of the crystals is decreased. The susceptibility data do not follow a simple Curie-Weiss law, as the maxima are approached. The field dependence of the measured susceptibilities is more pronounced for the samples prepared by heat-treatment in the range of 250—500'C. These results suggest that the spontaneous magnetization is greater for the smaller crystals. The spontaneous magnetization increases with decreasing temperature, passing through a maximum at the same temperature,  $T$ , as the susceptibility. The spontaneous magnetization effects will not be discussed in detail here.

The appearance of maxima in the susceptibility data for nickelous oxides has not been observed previously. However, very similar susceptibility data have been reported for iron<sup>16,17</sup> and chromium sulfides.<sup>18</sup> The observed susceptibility maxima possibly could be attributed to factors such as (a) the formation of metallic nickel by decomposition of the oxide, (b) a shifting of the normal Néel point resulting from an altered magnetic environment, (c) the presence of defects resulting from the enhanced oxygen content, (d) the presence of undecomposed nickelous hydroxide to which is attributed unusual magnetic properties, or (e) the effect of very small crystal size in altering the magnetic environment.

X-ray and electron diffraction patterns show no indication of the presence of metallic nickel, nor does the magnetic behavior suggest ferromagnetism, and hence possibility (a) may be rejected. The neutron diffraction patterns obtained for samples heat-treated at  $400^{\circ}$ C and  $1200^{\circ}$ C at both  $78^{\circ}$ K and  $295^{\circ}$ K exhibit (111) magnetic spacings, characteristic of the double unit cell. In the sample heat-treated at 1200'C, the intensities of the magnetic spacings at 78'K and 295'K, normalized to the (200) nuclear spacing, were plotted against temperature. A smooth curve was drawn through the experimental points, which extrapolated to zero intensity at the normal Néel temperature of 523'K. Similar results were obtained for the sample heat-treated at 400'C, the resulting intensity curve for the (111) magnetic spacing falling slightly below that of the former sample. The results clearly demonstrate that the sample heat-treated at 400'C is antiferromagnetic both above and below its transition temperature of about  $200^{\circ}$ K, and that the true Néel temperature is unchanged, and that hence the magnetic susceptibility data cannot be explained in terms of shifted Néel points, in accordance with possibility (b). The presence of "active" oxygen (Table II) is considered significant, and possibility (c) will be discussed in the next section of this report. A trace of nickelous hydroxide was detected by electron diffraction methods in the sample prepared at the lowest temperature  $(250^{\circ}$ C), but none was found at higher temperatures of heat-treatment. The magnetic susceptibility of pure nickelous hydroxide (Fig. 3) is too small at the higher temperatures (above  $100^{\circ}$ K) to account for the magnitude of the suscepti-



FIG. 3. Magnetic susceptibility of nickelous hydroxide gel as a function of temperature.

<sup>&#</sup>x27;6 H. Haroldsen, Z. anorg. allgem. Chem. 246, 169, 195 (1941). ' Hirone, Maeda, and Tsuya, J. Phys. Soc. Japan 9, 736 (1954).  $s$  K. Yosida, Physica 17, 794 (1951); Progr. Theoret. Phys. 6,

<sup>691</sup> (1951).

$n = 1000$	500	100	50	25	10			
0.999	0.998	0.990	0.980	0.961	0.905	0.818	0.603	0.357
0.866	0.865	0.860	0.854	0.841	0.803	0.746	0.603	0.435
${0.777}$	0.776	0.771	0.768	0.752	0.715	0.658	0.518	0.357
								0.518
0.556	0.555	0.553	0.549	0.543	0.527	0.500	0.435	0.357
	0.734	0.733	0.730	0.726	0.719	0.702	0.674	0.603

TABLE III. Examples of the effect of crystal size and shape on the average number of next nearest neighbors.<sup>8</sup>

 $\phi$ ,  $q$ , and  $r$  are the number of unit cells per edge, of a parallelopiped. *n* is the number of unit cells per edge, for the edges being varied. *f* is defined as<br>the ratio of the number of next nearest neighbors per

 $2 \left[12pqr+2(pq+qr+pr)-(p+q+r)\right]$ /6 $\left[4pqr+2(pq+qr+pr)+(p+q+r)+1\right]$ .

bilities near or above the maxima or for the existence of the maxima, and hence possibility (d) cannot receive serious consideration. All of the available data suggest that possibility (e) and to some extent (c) is of special significance.

## Effect of Crystal Size

The size of the crystals increase regularly as the temperature of heat treatment is increased, as shown in Fig. 4. Likewise, the transition temperatures,  $T_c$ , increase regularly with the crystal size, as shown in Fig. 5, in which the crystal size is expressed in terms of  $n$ , the number of unit cells per cube edge. In Fig. 5, the experimental points are given as open circles, and the curve represents the relation between  $n$  and  $f$ , where  $f$  is the ratio of the average number of next nearest magnetic neighbors per nickel atom to the number of next nearest neighbors in an infinite crystal (i.e., 6). The value of  $f$  is computed from the following formula:  $f = \frac{4n^3 + 2n^2 - n}{4n^3 + 6n^2 + 3n + 1}$ . The value of f depends also on the exact morphology of the crystals, and in Table III there is given results of calculations where various crystal shapes have been assumed. The close connection between the magnetic properties and the size of the crystals is apparent from the linear plot of the transition temperatures,  $T_c$ , and f as shown in Fig. 6. In the range studied, the linear curve is represented accurately by  $\lceil 10^{-4}T_c = 1.090f - 1.037 \rceil$ . Obviously, the curve must depart from linearity, for smaller crystal sizes if such crystals were available for study.



FIG. 4. Crystal size of nickelous oxide samples as a function of heat-treatment.

In view of the linear relationship between the transition temperatures and the average number of next nearest magnetic neighbors, it is concluded that the observed magnetic properties of nickel oxide depend primarily on an alteration in the magnetic environment resulting from the decreased average number of next nearest magnetic neighbors, which is a consequence of the reduced size of the crystals. It is difficult to account for the exact form of the susceptibility curves, but the increase in susceptibility, as the temperature is reduced to  $T_c$  to form the maxima, is considered to be associated with the ferrimagnetic state.

# Ferrimagnetism

**THE FETTIMIZE CONSERVANCE FOR SUFFERIOR**<br>The magnetic behavior of iron sulfide,<sup>18</sup> FeS<sub>z</sub>, has been attributed to a ferrimagnetic structure similar to been attributed to a ferrimagnetic structure similar that existing in the ferrites.<sup>19,20</sup> The basic ferrimagnet structure is antiferromagnetic (detectable by neutron diffraction), with two ferromagnetic sublattices, aligned with net magnetic moments antiparallel, but with a different magnetization for each sublattice, thereby giving a net magnetization or ferromagnetic effect detectable by magnetic measurements. The concept of ferrimagnetism has been generalized<sup>21</sup> over the original ferrimagnetic behavior of the ferrites, and the phenomenon is characterized by large numerical values of the susceptibility which increase with decreasing temperature, and show a field dependence. In  $\text{FeS}_x$  and  $CrS<sub>x</sub>$  the ferrimagnetism has been explained by Yasida<sup>18</sup> on the basis of two sublattices, one with  $Fe^{++}$  ions, and the other with  $Fe^{+++}$  ions, resulting in a net magand the other with Fe<sup>+++</sup> ions, resulting in a net mag<br>netization. Néel,22 however, favors the view that defect: or vacancies assume an ordered state below a certain critical temperature, resulting in an unequal number of ions for each sublattice, thereby producing ferrimagnetism. '7 The theory of ferrimagnetism resulting from ordered vacancies in nonstoichiometric compounds has ordered vacancies in nonstoichiometric compounds ha<br>also been discussed recently by Elcock.<sup>23</sup> In the sample of nickelous oxide studied here, excess "active" oxygen is present. Adsorption of oxygen on the surface could lead to migration of  $Ni^{++}$  ions to the surface, thereby

<sup>&</sup>lt;sup>19</sup> L. Néel, Ann. phys. 3, 137 (1948).<br><sup>20</sup> L. Néel, Ann. phys. 4, 249 (1949).<br><sup>21</sup> J. S. Smart, Am. J. Phys. 23, 356 (1955).<br><sup>22</sup> L. Néel, Revs. Modern Phys. 25, 58 (1953).

<sup>~</sup> E.W. Elcock, Proc. Roy. Soc. (London) A227, <sup>102</sup> (1954).



FIG. 5. Transition temperatures of nickelous oxide samples prepared at temperature levels of 250–600°C as a function of particle size, expressed as  $n$ , the number of unit cells along a cube edge. The curve represents the relationship between f, the ratio of the average number of next nearest neighbors per nickel atom and the number of next nearest neighbors in an infinite crystal (i.e., 6), and the crystal cube edge,  $n$ .

creating Ni+++ ions and vacancies in the surface layer or layers. Such an effect would increase with increasing surface area and with decreasing particle size. Inasmuch as the present nickel oxide samples were prepared in a stream of nitrogen gas, they should not exhibit an enhanced oxygen content arising from surface oxidation. However, it is conceivable that nickelous oxide may react with water vapor during heat-treatment according to the following formal mechanism:  $2NiO + H<sub>2</sub>O \rightarrow$  $Ni<sub>2</sub>O<sub>3</sub>+H<sub>2</sub>$ . This effect has been observed in the thermal decomposition of  $Fe(OH)_2$  and  $Mn(OH)_2$ .<sup>24</sup> The observed amounts of "active" oxygen decrease as the particle size increases as one would expect. The color of the samples, likewise, vary from almost black (250'C heat-treatment) to yellowish-green (1300<sup>o</sup>C heat treatment), in agreement with the observation of others.<sup>9</sup> It is significant that the amount of extra oxygen present is not large enough to result in a change in lattice parameters detectable by x-ray and electron diffraction methods. In view of the similarity in the magnetic effects observed for nickelous oxide and the active oxygen contents, it is believed that the magnetic behavior of the nickelous oxide is analogous to the ferrimagnetic character of  $\text{FeS}_x$  and  $\text{CrS}_x$ .

Although the increased susceptibility to the maxima at  $T_c$  can be explained on the basis of ferrimagnetism, the subsequent decrease at lower temperatures requires the subsequent decrease at lower temperatures requires<br>further consideration. In the case of  $\text{FeS}_{x}$ ,<sup>17</sup> the suggestion has been made that the alignments of the two sublattices possess a different temperature dependence, and that below  $T_{e}$ , the vacancies are realigned to form a different arrangement of sublattices in which the net magnetization is small or absent. It will be noted that the amplitudes of the susceptibility maxima vary regularly with the size of the crystals and hence with  $f$ , the quantitative significance not being clear, but this information has not been employed as yet in attempting to explain the magnetic behavior of the nickel oxides. Further work will be required to elucidate this phenomenon.

#### Susceptibility of Nickelous Hydroxide

In connection with the above work on nickelous oxide, a complete magnetic susceptibility curve (Fig. 3) was obtained for pure nickelous hydroxide in the temperature range  $4^{\circ}-300^{\circ}$ K. It will be noted in Fig. 3 that the susceptibility increases to very high values at 4<sup>o</sup>K, and that the data follows a Curie-Weiss law in the analytical form of  $\chi_m = 1.07/(T - 36)$  from room temperature to well below  $100^{\circ}$ K. Below  $90^{\circ}$ -100 $^{\circ}$ K, the



Frc. 6. Transition temperatures of nickelous oxide samples prepared at temperature levels of 250–600°C as a function<br>of f.

susceptibility increases more slowly to a value of about  $2000\times10^{-6}$  emu at  $4^{\circ}\text{K}$ , and some field dependence was observed. The high susceptibility and the field dependence suggest the possibility of ferromagnetism, and further studies on the magnetic properties of nickelous hydroxide are in progress in this laboratory.

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<sup>&#</sup>x27;4 W. Feitknecht, private communication.