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Magnetic Susceptibility Studies in the
Dual Hydrous Oxide System; $\text{NiO} - \text{Al}_2\text{O}_3$

by

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PART I

MAGNETIC SUSCEPTIBILITY STUDIES ON NICKEL OXIDE

ABSTRACT

Nickelous oxide, NiO, as normally prepared, consists of crystals larger than the colloidal range of particle size, and exhibits a transformation at about 250°C, detectable by back reflection x-ray diffraction, magnetic peaks in neutron diffraction patterns, and the appearance of a Néel point in magnetic susceptibility measurements. Below 250°C, NiO is rhombohedral and antiferromagnetic, whereas above 250°C, it is cubic and paramagnetic. In samples of NiO consisting of extremely finely-divided crystals, or consisting of aggregates of small crystallites existing in a plate-like or rod-like type of morphology, the reduction in the average number of next nearest magnetic neighbors would result in an attenuated magnetic interaction, thereby preventing the occurrence of antiferromagnetism, and such crystals would exhibit a typical paramagnetic behavior. Crystals of NiO of extremely small size have been prepared by the heat-treatment of hydrous nickelous hydroxide gel at temperature levels in the range 300-1300°C. A sample prepared at 300°C, exhibits a paramagnetic type of susceptibility-temperature curve. As the heat-treatment temperature level is increased, the crystal size increases, the average number of magnetic neighbors increase, and the magnetic properties change from strong paramagnetism (300°C), through temperature independent paramagnetism (1200°C), to antiferromagnetism (1300°C). The NiO samples prepared from the hydroxide below 1300°C are all cubic and paramagnetic. The cubic structure is stabilized at the temperatures below the normal Néel point (250°C) by the presence of adsorbed trace amounts of sodium, or possibly silica. Heating to 1300°C expells the impurity, and the sample becomes rhombohedral and antiferromagnetic. Samples prepared by the heating of hydrated nickelous nitrate crystals do not contain the stabilizing impurities, and were found to consist of rhombohedral crystals at room temperature, and exhibit a normal Néel point at 250°C, in agreement with the results of other investigators.

INTRODUCTION

Nickelous oxide, NiO , exhibits a transformation at about 250°C which has been detected by several methods. Rooksby (1) observed from precise x-ray diffraction patterns that the structure is rhombohedral below about 275°C and cubic above about 275°C .

The antiferromagnetic properties are associated with the low-temperature rhombohedral crystal form, whereas the high-temperature cubic form is paramagnetic. Shull, Strauser, and Wollan (2) detected magnetic peaks in neutron diffraction patterns, the results demonstrating that nickelous oxide is antiferromagnetic at room temperature, analogous to the isomorphous cobaltous and ferrous oxides, which exhibit Néel points at lower temperatures. Foex (3) has discussed in detail the nickelous oxide transformation from the viewpoint of irregularities in the expansion coefficients, specific heats, electrical conductivity, chemical activity, and the appearance of the antiferromagnetic Néel point at a temperature of about 250°C . Foex (3) found that samples of NiO , prepared by heating nickelous nitrate, exhibited at room temperature a susceptibility varying from 8.73 to 10.10×10^{-6} , depending on the exact treatment.

In particular, Foex and Blanchetais (4) found that slight differences in the susceptibility resulted from heat treatments at temperatures from 505° to 1400°C . However, Foex (3) reports no important differences in the x-ray patterns, and suggested that all of the samples

consist of well-formed crystals of considerable dimensions, without any striking structural defects. Evidently, most of the previously studied samples of nickelous oxide (a) have been prepared by the decomposition of nickelous nitrate, (b) exhibit a characteristic antiferromagnetic Néel point, and (c) consist of crystals well above a size where surface effects should play an important role.

In the well-known Curie-Weiss Law for paramagnetism,

$$\chi = C/(T - \theta),$$

the Curie constant, C , may be related to the magnetic moment, and the Weiss constant, θ , to the paramagnetic environment. The Weiss constant reflects the amount of interaction between neighboring atoms, and is a measure of the departure from the ideal Curie Law. This deviation increases as θ becomes large. The interaction may become so strong that the magnetic moments align themselves parallel (ferromagnetism) or antiparallel (antiferromagnetism) and the Curie-Weiss relationship is then only valid above the Curie and Néel points, respectively.

The antiferromagnetic properties thus depend upon an ordered antiparallel arrangement of electron spins, the exchange forces being transmitted from one nickel atom to its next nearest magnetic neighbor, through the intermediate oxygen atoms. According to the concepts of Anderson (5), the phenomenon of superexchange, in which the electronic wave functions of the magnetic nickel ions overlap those of

the intermediate oxygen ions, is responsible for these exchange forces. The net effect of exchange between the nearest neighbors, is small, since, according to the magnetic structure of NiO found by Shull et al (2), of the 12 nearest neighbors, surrounding any Ni ion, 6 are oriented parallel to the central ion and 6 antiparallel. However, the number of next nearest neighbors for an infinite crystal of NiO is 6, all coupled antiparallel to the central ion.

One would expect that a reduction of the average number of these second nearest neighbors would reduce the antiferromagnetic properties. In relatively large finite crystals of NiO, the number of surface atoms may be neglected, and the number of next nearest magnetic neighbors remains identical with the preceding case. As the crystal size is decreased, the number of surface atoms increases rapidly. When the size of the crystals approaches colloidal dimensions, the average number of next nearest neighbors also decreases, and such crystals should exhibit a less pronounced Néel point.

Methods of computing the susceptibility from the average number of next nearest neighbors are not developed as yet, but it is to be expected that a reduction in the number of neighbors will markedly attenuate the antiferromagnetic effect. Indeed, for crystals of a size near the lower limit of the colloidal range of particle size, the Néel point may vanish, and the crystals may be expected to exhibit a typical paramagnetic behavior.

In these considerations of crystal size, it has been assumed that the crystals are reduced in size in three dimensions. Very small crystals having the crystal habit of thin plates or rods (fibers), or aggregates of very small crystallites exhibiting a plate-like or rod-like morphology, would likewise be expected to possess enhanced paramagnetism.

Furthermore, if the paramagnetic cubic crystal form could be stabilized at temperatures below the normal Néel point, such samples would not be expected to exhibit antiferromagnetic properties.

Samples of nickelous oxide consisting of extremely small crystals may be prepared by decomposition of nickelous hydroxide at controlled temperatures. It is the purpose of this paper to report the results of magnetic susceptibility measurements on such crystals.

EXPERIMENTAL

Preparation of Samples.

Hydrous nickelous hydroxide gel was prepared by precipitation from 0.5 M nickelous nitrate solution using 3.77 M NaOH solution, free of carbonate. The amount of NaOH solution necessary to complete the precipitation and maintain the pH value at 7.50 throughout was determined by preliminary titration. A rapid mixing device, described elsewhere (6) was employed to insure uniform mixing.

The gel was first washed with distilled water by decantation in a five gallon container, and then washed ten times in a centrifuge. The final supernatant liquid showed no trace of nitrate with the diphenylamine test.

After washing, the gel was filtered, air-dried, and ground to a uniform powder. Samples of nickelous oxide were prepared by heat treatment at the desired temperature for two hours in a stream of dry nitrogen. Samples heated from 300°C to 1000°C, at intervals of 100°C, were obtained in this manner. Further samples at 1200°C and 1300°C were prepared by heating the original air-dried gel in air, rather than in nitrogen.

For comparison purposes, samples of NiO were also prepared by heating hydrated nickelous nitrate crystals in air at 1000°C, 1200°C, and 1300°C.

Magnetic Susceptibility Measurements.

Magnetic susceptibility measurements were made in an apparatus described elsewhere in detail (7). The Faraday method was used, with the force on the sample, due to the inhomogeneous field, determined with a vitreous silica spring of a sensitivity of $1.072 \pm .001$ mg/mm. The spring extension was measured with a traveling microscope capable of an accuracy of 0.001 mm.

A small spherical vitreous silica bucket, weighing approximately $\frac{3}{4}$ mg, contained from 50 to 75 mg of sample. The bucket was small enough so that HdH/dx remained constant over the range of the extension. The whole spring assembly supporting the bucket could be positioned with a sylphon bellows arrangement so that the sample always occupied the same place in the magnetic field.

The magnetic field was calibrated with Mohr's salt of 99.95% purity. The susceptibility of this salt at a temperature, T , is given by $\chi = 9500 \times 10^{-6} / (T + 1)$ cgs units per gram (8). The geometry of the polepieces was arranged to give the greatest force on the ferrous salt at the point of maximum HdH/dx , without causing lateral deflections.

After the heat-treatment of the gels, they were allowed to come to equilibrium with the water vapor in the atmosphere. This procedure made it possible to load samples into the magnetic susceptibility apparatus, and to weigh aliquots for subsequent chemical analysis for

water and nickel. The water analyses were obtained from the loss in weight on prolonged ignition to constant weight at 1000°C. The percentage of nickel in the samples was determined by the standard dimethylglyoxime gravimetric method. A loss of adsorbed water occurs during magnetic susceptibility measurements made at elevated temperatures. These losses can be followed on the silica spring balance, and the necessary corrections may be applied.

The susceptibilities of the samples were measured as a function of temperature from 25°C to 400°C. In instances where the susceptibility values were high, the susceptibility field dependence was measured in order to detect any ferromagnetic impurity. Measurements were taken with increasing and decreasing temperatures to insure that the results were reproducible. Corrections were made for the diamagnetic susceptibility of the adsorbed water on each sample, assuming that the susceptibilities of the "dry" sample and water are additive.

X-Ray Diffraction Patterns.

Standard x-ray diffraction powder techniques were employed, using a Norelco X-Ray Diffraction Unit with a cylindrical camera. In some instances, for more precise measurements, a back reflection camera, with a sample to plate distance of 12.0 cm, was used, with copper radiation and a nickel foil beta filter.

RESULTS AND CONCLUSIONS

The magnetic susceptibility as a function of temperature is given in Fig. 1 for samples of nickel oxide prepared from hydrous nickelous hydroxide at several temperatures of heat-treatment. The sample heat-treated at 300°C exhibits a typical paramagnetic behavior, without any indication of a Néel point in the temperature range examined. Samples heat-treated at successively higher temperatures approach temperature independent paramagnetism, and finally the sample heated at 1300°C becomes antiferromagnetic with a Néel point at approximately 250°C .

In the inset of Fig. 1, the magnetic data for certain samples are given on an enlarged scale. The curve represents the data of Foex (4), the open circles represent the present data for a sample prepared by heat-treatment of the hydroxide at 1300°C in air, and the closed circles represent a sample prepared by heat-treatment of nickel nitrate at 1200°C in air. This agreement between the data of this investigation and those of Foex appears to be satisfactory.

The change in the magnetic properties of the samples from strong paramagnetism, through temperature independent paramagnetism, to antiferromagnetism, as the temperature of heat-treatment is increased, may be explained qualitatively on the basis of the size and structure of the crystals of nickel oxide.

The original hydrous nickelous hydroxide gel consists of very thin plate-like crystals only a few hundred Å units in diameter (9). Heat-treatment of the hydroxide at temperatures above approximately 250°C yields very small crystals of NiO which may remain distributed in a plate-like aggregate, which is a pseudomorph of the original hydroxide crystal.

Heat-treatment at high temperatures such as 800-1200°C yields crystals of NiO large enough to give powder diffraction lines which are slightly spotty, and thus do not exhibit pronounced surface properties. At lower temperatures of heat-treatment the x-ray diffraction lines become successively broader and more diffuse. Samples heat-treated at 300°C exhibit extremely broad and diffuse x-ray diffraction lines. The interplanar spacings measured at room temperature show no deviation as the temperature level of heat-treatment is changed. However, it is recognized that slight shifts in the lattice parameters could not be detected in samples exhibiting extremely broad and diffuse lines.

It is well known that line broadening may be caused by deformation or strain or by a decrease in the crystal size. It is assumed in this discussion, that the broadening is principally attributable to a decrease in crystal size, or that the strains and distortions are not materially removed by heat-treatment. No quantitative measurements on crystal size have been carried out, but a qualitative exam-

ination of the x-ray negatives suggests that the size of the crystals formed at 300°C is approximately 25 to 50 Å. It is not feasible to consider NiO crystals formed at 250°C, inasmuch as this is the approximate decomposition temperature of nickelous hydroxide, and such samples might be contaminated with undecomposed hydroxide.

Precision back-reflection x-ray diffraction patterns obtained at room temperature with a sample-film distance of 12.0 cm for the samples heat-treated at 1200°C do not display a splitting of the cubic (422) line, the results indicating that the cubic structure is stabilized well below its normal transformation point. This stabilization phenomenon is attributed to traces of sodium, or perhaps, silica, which became adsorbed or entrained within the gel structure when the hydrous nickelous hydroxide was precipitated. It is well known that traces of non-volatile adsorbed impurities cannot be removed entirely from such gels, even on prolonged washing. It is also well recognized that such trace impurities may stabilize a crystal phase in its less stable form.

Heat-treatment of the hydroxide gel at 1300°C results in a slight growth of the crystals, as indicated by more spotty x-ray diffraction lines, and the precision back reflection x-ray patterns display a splitting of the cubic (422) line, in confirmation of the results of Rooksby (1). It will be noted in Fig. 1, that the cubic sample prepared at 1200°C exhibits temperature independent paramagnetism,

whereas the rhombohedral sample prepared at 1300°C possesses its characteristic Néel point. It is believed that the trace impurities are expelled from the cubic lattice at 1300°C, thus permitting the occurrence of the normal transformation to the rhombohedral structure when the temperature is reduced below 250°C.

The increased temperature-dependent paramagnetic properties of the samples prepared at successively decreasing temperatures result from the decreased average number of next nearest magnetic neighbors, as a consequence of the reduction in crystal size, the plate-like morphology of the aggregates, and perhaps, of the enhanced imperfection of the crystals. These views are consistent with the concepts of Selwood (10) who has carried out excellent investigations of "magnetically dilute" or "dispersed" hydrous oxides.

It is not considered possible that the enhanced paramagnetism of the small crystals, prepared at the lower temperature levels, results from the presence of ferromagnetic impurities, inasmuch as measurements did not show typical ferromagnetic field dependence. In instances where very slight field dependence occurred, the susceptibilities were extrapolated to infinite field strength, in order to give the correct paramagnetic value. Furthermore, there is no indication of the presence of possible higher oxides of nickel.

In order to test further the hypothesis that the traces of impurities could stabilize the cubic crystal form of NiO, a special sample

of hydrous nickelous hydroxide was prepared as described above, except that all reactions and washings were carried out in a polythene bottle, in which silica contamination (from glass apparatus) would be obviated. Heat-treatment of this material at 1200°C gave a sample exhibiting typical antiferromagnetic properties. This result demonstrates that the stabilization of the paramagnetic cubic form of NiO can be influenced by the amount and kind of impurities. It will be noted that the susceptibility-temperature curve for this special sample is just an extrapolation of the curve for the antiferromagnetic sample prepared at 1300°C from the hydroxide.

In addition to the samples prepared from the hydroxide, the inset in Fig. 1 includes the result from one of several samples prepared by heat-treatment of nickelous nitrate. In all instances these samples exhibit a characteristic Néel point, in complete confirmation of the work of earlier observers.

The effect of the addition of alumina to these nickel oxide gels has been systematically investigated at compositions of every 5 mole per cent. In this work, reported in Part II, it has been found that the crystal sizes and the morphology, and hence the magnetic properties, may be drastically altered, as a function of the composition of these dual hydrous oxide gels.

PART II

MAGNETIC SUSCEPTIBILITY STUDIES IN THE DUAL

HYDROUS OXIDE SYSTEM: $\text{NiO-Al}_2\text{O}_3$

ABSTRACT

A comprehensive investigation of the magnetic susceptibility of the system: $\text{NiO-Al}_2\text{O}_3$, has been conducted on 105 samples, prepared at every 5 mole per cent, and heat-treated at temperature levels of 300°, 400°, 500°, 600°, and 700°C. The magnetic measurements were made at room temperature. The resulting susceptibility-composition curve for the 300°C temperature level exhibits three regions of interest. In region (a) from 100-80 mole per cent NiO, the susceptibility curve drops rapidly as the alumina content increases; in region (b) the curve exhibits a broad maximum at a composition of 60 to 80 mole per cent NiO; and in region (c) the susceptibility increases regularly as the amount of alumina is increased. The following somewhat speculative explanation is offered. In region (a), the initial higher susceptibility of the pure NiO is attributed to the decreased magnetic interaction, resulting from a decrease in the number of next nearest magnetic neighbors, as a consequence of the very small crystallite size, and the plate-like morphology of the aggregates of crystallites. In region (b), the maximum in the susceptibility curve results from the existence of a marked change in the structure of the alumina gel, previously known from x-ray studies to occur in the zone of mutual protection against crystallization. Such zones are likewise detectable in numerous multiple hydrous oxide systems by means of x-ray and electron diffraction studies (amorphous-like zone), and adsorption measurements (enhanced differential and integral isothermic heats of adsorption and enhanced specific adsorptive capacity.) In region (c) the regularly increasing magnetic susceptibility results from the increase in degree of dispersion of the NiO within the alumina gel structure.

At higher temperatures of heat-treatment, the susceptibility of the NiO increases regularly throughout the entire composition range. Here the composition zone of mutual protection has narrowed or vanished. At the low concentrations of nickel, the susceptibility curves and the magnetic moments for NiO increase towards a limiting value of 3.2 bohr magnetons, in accordance with the previous work of Selwood.

INTRODUCTION

In a previous report (11) from this laboratory, it was found that dual hydrous oxide gels in the system: $\text{NiO-Al}_2\text{O}_3$ exhibit a mutual protective action against crystallization. The observed composition zone of mutual protection occurred at about 50-70 mole per cent of nickelous oxide, in samples heat-treated at a temperature of 500°C . The zone of protection narrows and finally vanishes as the temperature of heat-treatment is increased, as do multiple zones of protection which have been observed in numerous other multiple hydrous oxide systems (12). At the 100°C temperature level, x-ray evidence demonstrated the formation of nickel spinel, $\text{NiO} \cdot \text{Al}_2\text{O}_3$.

The magnetic properties of the system: $\text{NiO-Al}_2\text{O}_3$ has been studied recently by Selwood and Hill (13) in the region of low nickel oxide concentrations. The paramagnetism of the nickel increased markedly when small amounts of nickel oxide were dispersed over a large excess of alumina. Investigations, reported in Part I, show that very small crystals of pure nickel oxide, prepared by the controlled thermal decomposition of hydrous nickelous hydroxide, do not exhibit an anti-ferromagnetic Néel point, as do massive crystals previously studied by others.

Traces of sodium, or possibly silica, irreversibly adsorbed at the time of precipitation of the gel, stabilize the cubic, paramag-

netic form of NiO, whereas the unstabilized oxide is antiferromagnetic and rhombohedral below the Néel point (about 250°).

Inasmuch as Selwood's careful investigations did not include the high concentration range of nickel oxide, and in view of the results obtained for highly dispersed nickel oxide free of alumina, it was considered desirable to extend the previous magnetic studies to the entire system: NiO-Al₂O₃. It is the purpose of this paper to report the results of a systematic magnetic susceptibility investigation of this system for samples heat-treated at several temperature levels.

EXPERIMENTAL

Preparation of Samples.

Dual hydrous oxide gels were prepared by precipitation from varying volumes of 0.5 M nickelous nitrate and 0.5 M (with respect to Al_2O_3) aluminum nitrate solutions, using as the precipitant an amount of 3.77 M sodium hydroxide solution (carbonate-free) such that the final pH value was 7.50. The required amounts of alkali were determined by preliminary titration on aliquots of the metal ion solution mixtures. The compositions of the gels were adjusted to give a series of twenty-one hydrous oxide gels at every 5 mole per cent.

The gels were washed with distilled water by decantation in five gallon containers, followed by ten washings in a centrifuge, until the supernatant liquid was free of nitrate ions. The samples were filtered, air-dried, and ground to a uniform powder.

Separate portions of the air-dried samples were heated for two hours in a stream of dry nitrogen at 300°, 400°, 500°, 600°, and 700°C. These samples were then allowed to come to equilibrium with the moisture in the atmosphere, in order that the subsequent transfers could be made without detectable loss or gain of adsorbed water.

The series of twenty-one gels heated at 500°C was analyzed for nickel content, using the standard gravimetric dimethylglyoxime method. The water content was determined from the loss in weight on prolonged

ignition to constant weight at 1000°C. The alumina content was determined by difference, and the mole per cents of NiO and Al₂O₃ were calculated on the dry basis. The series of samples derived from the original air-dried gels at the remaining 4 temperatures of heat-treatment were analyzed for water content, as just described, but the mole ratios of NiO to Al₂O₃ were assumed to be independent of the temperature of heat-treatment. The results of these analyses are given in Table II.

Magnetic Susceptibility Measurements.

Magnetic susceptibility measurements were conducted in an apparatus already described (7), employing techniques reported in Part I. The samples were loaded into the magnetic apparatus concurrently with the weighing of the aliquots for chemical analysis, in order that the water contents of the samples would be accurately known. The measured magnetic susceptibilities were converted to a basis of one gram of dry sample, assuming that the diamagnetic susceptibilities of adsorbed water, alumina, and the diamagnetic contribution of the nickel were all additive. These data are presented in the upper portion of Fig.II. In the lower portion of Fig.II, there is given an interpretation of the data, in which the susceptibility of the NiO alone is calculated on the assumption that the susceptibility of the alumina is independent of the concentration.

In the inset in the lower portion of Fig.II, there is given the

magnetic moment in bohr magnetons of the nickel ion as a function of concentration. The magnetic moment, μ_{eff} , was computed for concentrations of nickel below 15 weight per cent, from the relationship,

$$\mu_{\text{eff}} = 2.83 \sqrt{\chi_m T} ,$$

where χ_m is the molar susceptibility, and T is the absolute temperature. This expression is assumed to be valid at the low concentrations, where the nickel ions are sufficiently dispersed so that the ideal Curie law holds, in accordance with the views of Selwood (13).

X-Ray Diffraction Patterns.

X-ray diffraction patterns were obtained for many of the samples, employing standard powder methods. These results will not be reported in detail here, inasmuch as they agree with previous work in this laboratory (11).

DISCUSSION

It will be noted in the lower portion of Fig. II, where the magnetic susceptibility of the nickel oxide is plotted as a function of composition, that the curve corresponding to the 300°C heat-treatment level exhibits three regions of interest. In the first region at high concentrations of nickel oxide, the susceptibility decreases rapidly as the amount of alumina in the gels increase. In previous work (see Part I) the high susceptibility of the pure nickel oxide was attributed to extremely small size of the crystallites, and to the plate-like morphology of the aggregates (secondary particle) of the crystallites. The effect of reduction in crystal size and the morphology of the aggregates on the ratio of specific surface to specific volume (and hence the average number of next nearest magnetic neighbors) on the magnetic interaction is detailed in Part I. The observed reduction in the susceptibility as a consequence of the addition of alumina could be explained on the basis of an increase in crystal size, or to change in the plate-like morphology. X-ray diffraction studies show that the addition of small amounts of alumina retards the development of the original hexagonal nickelous hydroxide plates, and the samples of gels containing alumina consist of spheroidal particles. Detailed x-ray diffraction, electron diffraction, and electron microscopic studies have not been made on the structure and

morphology of the original air-dried hydrous oxides or hydroxides, but it is evident that the plate-like form of the nickelous hydroxide is modified. As a hypothesis, on the basis of the presently known information, the reduction of the susceptibility of the nickel oxide on addition of alumina is attributed to change in the morphology of the original nickelous hydroxide, which is reflected in the samples heat-treated at 300°C, so as to give spheroidal, rather than plate-like, aggregates. Inasmuch as the size of the crystallites in the pure NiO, at a heat-treatment level of 300°C, is of the order of 25-50 Å, one would expect little further reduction in size as the alumina is added.

The second region of interest is the maximum in the susceptibility curve in the composition range 60 to 80 mole per cent nickel oxide. This composition region corresponds to the zone of mutual protection already reported (11) for the system, wherein the samples are essentially amorphous to x-rays. The maximum in the susceptibility curve for NiO in this composition region is considered to reflect the enhanced dispersion of the NiO within the gel structure of the alumina.

In the third region of interest, the susceptibility of the NiO increases in a regular manner, because of the increasing dispersion as the amount of alumina increases. This regular change would have continued towards the higher concentrations of NiO, had not the zone of protection occurred, wherein the properties of the alumina gels were markedly changed.

The one or more zones of mutual protection encountered in numerous multiple hydrous oxide systems were first detected by x-ray diffraction methods (12). In 1948 it was predicted (14) that such zones of protection may correspond to regions of maximum surface, and which, therefore, may exhibit enhanced adsorptive and other surface properties. Enhanced differential and integral isotheric heats of adsorption (15), enhanced specific adsorptive capacity (15) and a marked increase in the number of crystallites per aggregate (16,17) have been found in the zones of mutual protection occurring in the system: $\text{BeO-In}_2\text{O}_3$. In view of these results, it is not surprising that magnetic susceptibility measurements can detect in a zone of protection an enhanced dispersion of NiO in alumina, the increased dispersion making the Ni ions more magnetically dilute, thereby decreasing the average number of next nearest magnetic neighbors, and thus the magnetic interaction.

In the samples heat-treated at successively higher temperatures, the zone of mutual protection as indicated by x-ray studies (11) narrows and vanishes, and inspection of Fig. II shows that the magnetic susceptibility of the NiO does not show any irregularity in this region.

In an earlier investigation (11), x-ray diffraction patterns established the existence of a definite nickel spinel, $\text{NiO} \cdot \text{Al}_2\text{O}_3$, after heat-treatment of the original air-dried gel at 1000°C , the

new crystalline phase not being detectable at lower heat-treatments. It was considered possible that magnetic susceptibility measurements might be able to detect the formation or incipient formation of the spinel at lower temperatures of heat-treatment. However, no indication has been found of any irregularity in the susceptibility at a mole ratio of NiO to Al_2O_3 of unity.

In the inset of Fig. II, for very low nickel concentrations, the magnetic moment approaches a limiting value of 3.2 bohr magnetons. These results agree almost exactly with the previous results of Selwood (13), and hence will not be discussed in detail here.

TABLES

TABLE I

Magnetic Susceptibility of NiO Samples Prepared at Different

Temperatures

Temp. of Prep	Temp °C	$\chi \times 10^6$ (dry sample)				
		4.0 amp	6.0 amp	8.0 amp	10.0 amp	∞
300°C	25	83.11	79.83	79.67	78.16	74.97
	75	55.28	53.04	51.96	51.39	48.71
	125	36.28	31.12	29.39	28.20	23.94
	200	field independent			16.27	16.27
	250	"			15.92	15.92
	300	"			14.94	14.94
400°C	25	37.86	35.77	35.14	34.06	32.01
	75	32.24	29.39	28.58	27.11	24.44
	150	19.97	18.60	17.51	16.62	16.50
	200	field independent			15.43	15.43
	250	"			14.66	14.66
	300	"			14.48	14.48
500°C	25	31.25	30.12	29.77	28.80	27.39
	90	field independent			24.09	24.09
	160	"			17.14	17.14
	205	"			13.58	13.58
	260	"			13.70	13.70
	300	"			13.30	13.30
	350	"			13.73	13.73
600°C	25	"			15.70	15.70
	75	"			15.77	14.77
	160	"			13.65	13.65
	260	"			13.33	13.33
	300	"			13.21	13.21
	350	"			13.21	13.21
700°C	25	"			15.20	15.20
	100	"			14.14	14.14
	150	"			13.50	13.50
	200	"			12.84	12.84
	225	"			12.82	12.82
	250	"			12.82	12.82
	260	"			13.45	13.45
	275	"			12.93	12.93
	300	"			12.67	12.67
	350	"			12.65	12.65

TABLE I. (Contd.)

Temp. of Prep	Temp °C	$\chi \times 10^6$ (dry sample)				
		4.0 amp	6.0 amp	8.0 amp	10.0 amp	∞
1000°C	25	field independent			13.06	13.06
	100		"		12.55	12.55
	200		"		12.61	12.61
	225		"		12.40	12.40
	250		"		12.63	12.63
	260		"		12.67	12.67
	275		"		12.50	12.50
	300		"		12.65	12.65
	350		"		12.58	12.58
1200°C	25		"		12.10	12.10
	70		"		11.95	11.95
	120		"		11.81	11.81
	175		"		11.94	11.94
	200		"		12.04	12.04
	230		"		12.12	12.12
	240		"		12.19	12.19
	250		"		12.19	12.19
	260		"		12.22	12.22
	270		"		12.20	12.20
	300		"		12.38	12.38
	325		"		12.34	12.34
	350		"		12.27	12.27
	400		"		12.19	12.19
1300°C	25		"		9.10	9.10
	100		"		9.77	9.77
	150		"		10.35	10.35
	200		"		10.98	10.98
	220		"		11.39	11.39
	240		"		11.73	11.73
	250		"		12.27	12.27
	260		"		12.24	12.24
	280		"		12.27	12.27
	300		"		12.20	12.20
	320		"		12.27	12.27
	340		"		12.27	12.27
	400		"		12.27	12.27

TABLE II
Water and Nickel Analyses of NiO-Al₂O₃ Samples

NiO Synth Mole %	NiO Anal		Wt. % H ₂ O						NiO Composition	
	Wt. %		300°C	400°C	500°C	600°C	700°C		Wt. %	Mole %
0	0.00		28.45	24.25	20.36	17.66	17.26		0.00	0.00
5	2.21		29.46	25.71	22.40	19.95	17.77		2.85	3.85
10	4.77		24.20	23.83	21.20	16.83	13.90		6.05	8.08
15	5.52		26.56	23.54	19.13	16.22	15.64		6.83	9.10
20	9.43		27.20	26.40	23.05	18.33	15.99		12.25	16.00
25	12.37		27.50	23.03	20.20	18.43	16.94		15.50	20.50
30	15.22		24.20	23.09	20.55	18.15	15.77		19.16	26.00
35	19.67		26.00	22.89	19.60	16.70	14.75		24.47	30.66
40	23.67		26.43	21.98	21.00	20.03	16.64		29.96	36.86
45	23.96		27.30	23.23	21.60	19.58	15.71		30.56	37.53
50	31.05		27.24	21.54	21.05	18.24	16.07		39.33	46.94
55	35.26		26.03	21.03	19.10	16.84	13.62		43.58	51.32
60	37.13		28.95	21.44	19.70	17.73	14.87		46.24	54.00
65	45.94		29.45	20.02	17.65	15.76	15.15		55.79	63.27
70	48.48		30.56	21.63	18.50	16.03	15.33		59.48	66.71
75	55.43		30.07	21.65	17.75	15.17	14.69		67.39	73.83
80	59.55		28.47	18.38	16.83	15.29	13.83		71.60	77.48
85	68.08		25.49	15.79	13.60	12.06	11.86		78.80	83.53
90	72.69		23.18	18.76	15.00	12.19	11.13		85.52	88.96
95	82.78		22.85	14.41	11.55	9.28	8.03		93.59	95.22
100	94.79		15.45	9.08	5.65	4.71	3.65		100.00	100.00

TABLE III

Magnetic Susceptibilities of $\text{NiO-Al}_2\text{O}_3$ Samples - Corrected for Water Content

NiO Comp Mole %	$\chi_{\text{Sample}} \times 10^6$					$\chi_{\text{NiO}} \times 10^6$				
	300°C	400°C	500°C	600°C	700°C	300°C	400°C	500°C	600°C	700°C
0.00	-0.54	-0.50	-0.50	-0.47	-0.41	-	-	-	-	-
2.85	1.04	1.26	1.11	1.03	1.25	64.02	61.26	61.26	58.13	57.84
6.05	3.30	3.36	3.26	3.18	3.03	69.93	59.00	61.64	56.89	56.45
6.83	3.87	4.20	4.00	3.91	3.96	64.03	59.53	60.99	56.19	55.37
12.25	6.75	6.79	6.74	6.33	6.54	61.83	58.23	58.60	55.04	54.37
15.50	10.44	8.40	8.44	8.54	8.13	63.59	58.85	58.85	55.47	54.69
19.16	11.71	11.31	10.90	10.40	10.45	62.18	58.02	56.52	54.39	53.91
24.47	14.92	13.40	12.66	12.59	12.65	60.11	56.30	53.28	52.90	50.71
29.96	17.64	14.44	13.66	13.16	13.26	59.01	52.57	49.90	48.50	47.35
30.56	17.07	15.37	14.97	14.41	13.79	59.15	51.86	49.89	48.22	46.74
39.33	22.19	18.91	17.49	16.38	16.20	56.52	46.23	44.00	41.41	40.81
43.58	22.55	16.79	15.83	15.02	15.27	55.08	43.33	40.80	38.24	37.24
46.24	25.74	18.59	17.91	16.72	16.11	54.69	42.10	39.08	36.66	35.08
55.79	27.67	20.27	18.21	16.67	15.83	52.41	37.14	33.20	31.20	29.36
59.48	30.21	21.14	19.01	17.39	16.44	52.15	35.82	31.95	29.56	27.68
67.39	36.06	22.11	19.72	17.88	16.14	51.60	32.59	29.33	26.34	24.68
71.60	36.83	21.95	20.26	17.91	16.69	51.65	30.78	28.09	24.91	23.21
78.80	32.46	21.89	19.72	17.74	16.44	41.34	29.07	26.91	22.64	21.43
85.52	30.24	25.88	22.30	18.77	18.82	36.45	29.79	26.39	22.03	22.08
93.59	47.29	29.90	24.67	20.28	18.66	50.57	31.45	26.10	21.70	19.97
100.00	74.97	32.41	27.39	15.65	15.20	74.97	32.41	27.39	15.65	15.20

FIGURES

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APPENDIX

Number of Next Nearest Neighbors for a Face Centered Cubic Crystal

The atoms of a face centered cubic structure, such as NiO, may be divided into two types; the A atoms at the corner of the unit cell, and the B atoms on the faces. An isolated unit cell of NiO will contain 8 atoms of type A and 6 atoms of type B. The next nearest neighbors of a given nickel atom are at a distance of a_0 along cubic axes passing through the intermediate oxygen atoms. In an isolated unit cell, the A atoms have 3 next nearest neighbors and the B atoms have one. If the crystal is in the form of a parallelepiped of dimensions m , n , and p unit cells, the number of next nearest neighbors possessed by each atom will depend on its position in the crystal. Atoms at the corners, on the edges and faces, in the interior, and at distances of $a_0/2$ from the edges or faces all have different number of neighbors.

In Table A, the number of next nearest neighbors is computed for each of the different types of atoms. In Table B, the ratio of the number of next nearest neighbors per atom for the crystal to the ideal number for an infinite lattice, is computed for crystals of different morphology. It is apparent that the effect of the surface atoms in reducing the number of next nearest neighbors becomes greater as the crystal morphology approaches plates, rods and cubes of small dimensions.

TABLE A

<u>Type of Atom</u>	<u>No. of A Atoms</u>	<u>No. of B Atoms</u>	<u>No. of Next Nearest Neighbors</u>
Corner	8		3
Edge	$4[(\ell-1)+(m-1)+(n-1)]$		4
First line, $a_0/2$ from edge			
corner		2^4	3
edge		$8[(\ell-2)+(m-2)+(n-2)]$	4
Face	$2[(\ell-1)(m-1)+(m-1)(n-1)+(\ell-1)]+2[(\ell-2)(m-2)+(m-2)(n-2)+(\ell-2)]^*$		5
First layer, $a_0/2$ from face			
edge	$4[(\ell-1)+(m-1)+(n-1)]$		4
face	$2[(\ell-2)(m-1)+(m-1)(n-2)+(\ell-2)(n-1)]+2[(\ell-1)(m-2)+(m-2)(n-1)+(\ell-1)(n-2)]^*$		5
Interior	$[(\ell-1)(m-1)(n-1)]$	$[(\ell-1)(m-2)(n-2)+$ $(\ell-2)(m-1)(n-2)+$ $(\ell-2)(m-2)(n-1)]$	6

* Denotes combined number of A and B atoms.

TABLE B
EXAMPLES OF THE EFFECT OF CRYSTAL SIZE AND SHAPE ON THE AVERAGE NUMBER
OF NEXT NEAREST NEIGHBORS

Morphology	f									
	q = 1000	500	100	50	25	10	5	2	1	
cube, $\ell=m=n=q$	.999	.998	.990	.980	.961	.905	.818	.603	.357	
sheet, $\ell=2; m=n=q$	.866	.865	.860	.854	.841	.803	.746	.603	.435	
sheet, $\ell=1; m=n=q$	.777	.776	.771	.768	.752	.715	.658	.518	.357	
rod, $\ell=m=2; n=q$	.734	.733	.730	.726	.719	.702	.674	.603	.518	
rod, $\ell=m=1; n=q$	.556	.555	.553	.549	.543	.527	.500	.435	.357	

q is the number of unit cells per edge, for the edges being varied.

f is defined as the ratio of the number of next nearest neighbors per atom for a specific value of q to the ideal number of next nearest neighbors per atom for an infinite face-centered cubic lattice, and is computed from:

$$\frac{2[12\ell_{mn} + 2(\ell_m + mn + n\ell) - (\ell + m + n)]}{6[4\ell_{mn} + 2(\ell_m + mn + n\ell) + (\ell + m + n) + 1]}$$

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