times without incident with smaller quantities (ca. 3–5 g) of the phosphine. *The use of appropriate safety shields is essential.*

Materials and General Procedures. The (silylamino)phosphine reagents were prepared according to the published procedures.[2] *tert*-Butyl trimethylsilyl peroxide was purchased from Petrarch Systems, Inc., and used without further purification. Dichloromethane was distilled from P_2O_5 and stored over molecular sieves. Proton, ^{13}C, and ^{31}P NMR spectra were recorded on JEOL MH-100 and FX-60 spectrometers. Infrared spectra were obtained on a Perkin-Elmer 297 or Beckman IR-4250 spectrophotometer. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen. The following procedures are typical of those used in the oxidation of (silylamino)phosphines with O_2 or $t\text{-BuO}_2\text{SiMe}_3$. Preparative, analytical, and NMR spectroscopic data for all of the new compounds are summarized in Table I.

Preparation of *P*-Methyl-*P*-phenyl-*P*-(trimethylsiloxy)-*N*-(trimethylsilyl)phosphinimine (2). Oxygen, dried by passing slowly through a trap cooled to −78 °C, was bubbled through a solution of $(\text{Me}_3\text{Si})_2\text{NP(Ph)Me}$ (16.1 mmol) in CH_2Cl_2 (25 mL) at room temperature. As determined by ^1H NMR spectroscopy, the reaction was complete in about 2.5 h. After removal of solvent under vacuum, distillation afforded **2** as a colorless liquid (2.81 g, 59% yield; bp 90–93 °C (0.5 torr)).

Preparation of [(*tert*-Butyldimethylsilyl)methylamino]dimethylphosphine Oxide (6). *tert*-Butyl trimethylsilyl peroxide (23.0 mmol) was added to a stirred solution of $t\text{-BuMe}_2\text{SiN(Me)PMe}_2$ (23.0 mmol) in CH_2Cl_2 (25 mL) under a nitrogen atmosphere. The flask was tightly stoppered, and the mixture was allowed to stir at room temperature for 12 days during which time the progress of the reaction was periodically checked by ^1H NMR. After removal of the solvent and $t\text{-BuOSiMe}_3$ under reduced pressure, distillation afforded **6** as a colorless liquid (4.41 g, 87% yield, bp 59–64 °C (0.01 torr)) which partially solidified to needlelike crystals (mp ca. 25 °C). IR spectrum (neat liquid): 2950 (s), 2920 (s), 2890 (sh), 2850 (s), 1555 (m), 1410 (m), 1390 (sh), 1355 (w), 1290 (s), 1250 (s), 1190 (s, br), 1070 (s), 1050 (br, sh), 925 (s), 890 (s), 850 (s), 825 (s), 785 (s), 730 (s), 670 (m), 580 (w), 475 (w), 410 (m) cm^{-1}.

Silyl Peroxide Oxidation of $t\text{-BuMe}_2\text{Si(Me}_3\text{Si)NPMe}_2$. In a manner similar to that described above for the synthesis of **6**, equimolar quantities (29.0 mmol) of the reactants were allowed to stir in CH_2Cl_2 (25 mL) for 5 days at room temperature. Solvent removal left a colorless liquid residue which was tentatively characterized as mainly $t\text{-BuMe}_2\text{SiN}{=}\text{PMe}_2\text{OSiMe}_3$ by its ^1H NMR spectrum (20% v/v in CH_2Cl_2): Me_2Si singlet (δ 0.00), Me_3Si singlet (δ 0.33), *t*-Bu singlet (δ 0.90), and Me_2P doublet (δ 1.42, J_{PCH} = 13.5 Hz). Distillation gave three major fractions: (A) bp 34–43 °C (1.25 torr), 1.25 g, identified as $\text{Me}_3\text{SiN}{=}\text{PMe}_2\text{OSiMe}_3$ (**1**); (B) bp 62–66 °C (1.25 torr), 2.92 g, identified as mainly a mixture of fractions A and C along with some $t\text{-BuMe}_2\text{SiN}{=}\text{PMe}_2\text{OSiMe}_3$; (C) bp 67–90 °C (1.25 torr), 2.90 g, identified as $t\text{-BuMe}_2\text{SiN}{=}\text{PMe}_2\text{OSiMe}_2(t\text{-Bu})$ (**7**). The last portion of the distillate solidified in the condenser. This portion was combined with fraction C, and the mixture was redistilled to afford an analytically pure sample of **7** (bp 87–90 °C (1.25 torr)) as a low-melting slushy solid. After standing for 2 weeks, fraction B was shown by ^1H NMR to contain increased amounts of the disproportionation products **1** and **7**.

Acknowledgment. The authors thank the United States Army Research Office, the TCU Research Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support. The initial phase[1] of this research was conducted at Duke University and the support of the Duke Research Council is acknowledged.

Registry No. **1**, 63744-07-0; **2**, 72049-27-5; **3**, 72049-28-6; **4**, 72049-29-7; **5**, 72049-30-0; **6**, 72049-31-1; **7**, 72049-32-2; **7a**, 72049-33-3; $t\text{-BuMe}_2\text{SiN(Me)PMe}_2$, 68437-93-4; $t\text{-BuMe}_2\text{Si(Me}_3\text{Si)NPMe}_2$, 68437-90-1; $t\text{-BuO}_2\text{SiMe}_3$, 3965-63-7; $(\text{Me}_3\text{Si})_2\text{NP(Ph)Me}$, 68437-87-6.

Contribution from the School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

Polymer-Anchored Metal Oxide Particles. 1. Superparamagnetic Magnetite Microcrystals Stabilized by Lignosulfonate

KAREN L. HASSETT, LINDA C. STECHER, and DAVID N. HENDRICKSON*[1]

Received June 11, 1979

Physical data are used to show that microcrystals (ca. 100 Å diameters) of magnetite can be stabilized by polymeric lignosulfonate. X-ray powder patterns indicate Fe_3O_4; line broadening in the patterns reflects the small size of the microcrystals. Magnetic susceptibility and ^{57}Fe Mössbauer results indicate that these materials are superparamagnetic and that the size of the magnetite microcrystals can be readily varied. Dissolution of these water-soluble magnetite–lignosulfonate solids gives ferrofluids and the magnetization of one of these ferrofluids has been measured.

Introduction

Ferrofluids consist of ca. 100 Å diameter particles of a magnetic solid (usually magnetite, Fe_3O_4) colloidally suspended in a carrier fluid.[2-4] Typical carrier fluids include hydrocarbons, water, fluorocarbons, esters, diesters, organometallics, polyphenyl ethers, and silicones. Surfactants such as oleic acid and other small molecules as well as a few polymers have been used to coat the surface of microcrystalline Fe_3O_4 to help prevent particle flocculation. At present, the only general approach used to synthesize ferrofluids involves placing the *bulk* magnetic compound, surfactant, and carrier liquid in a ball mill half-filled with steel balls and *grinding for 1–6 months*. It is of considerable interest, thus, to develop better synthetic approaches for ferrofluids, particularly since their unusual magnetic properties are finding applications in loudspeakers, zero-leakage seals, damping liquids, nonwearing electrical switches, artificial muscles,[2] magnetic inks,[5] ore separation,[6,7] and energy converters.[8]

In view of the desirability of identifying simple syntheses of ferrofluids, our interest was drawn to reports[9,10] that highly

---

(1) A. P. Sloan Foundation Fellow, 1976–1978.

(2) Kaiser, R.; Rosensweig, R. E. Report CR-1407; NASA: Washington, DC, 1969; p 1.

(3) Moskowitz, R. *IEEE Spectrum* **1975**, *12* (3), 53.

(4) Khalafalla, S. E. *CHEMTECH* **1975**, 540.

(5) Kuhl, L.; Myers, R. A. *Sci. Am.* **1979**, April, 162.

(6) Andres, U. T. *Mater. Sci. Eng.* **1976**, *26*, 269.

(7) Khalafalla, S. E.; Reimers, G. W. *AIME Trans.* **1973**, *254*, 193.

(8) Rosensweig, R. E. *Int. Sci. Technol.* **1966**, 48.

(9) Briggs, W. S.; Kjargaard, N. J. U.S. Patent 4 019 995, April 26, 1977.

0020-1669/80/1319-0416$01.00/0

magnetic materials could be formed from aqueous iron ions in the presence of either lignosulfonate or polymeric arylsulfonates. Lignin, a component of the cell walls in woody and vascular plants, is a byproduct of wood processing and is converted to water-soluble lignosulfonate in the bisulfite pulping process. Lignosulfonate is a three-dimensional network polymer. Briggs and Kjargaard[9] found that treatment with OH^- and O_2 of a water solution containing iron ions and lignosulfonate produced a water solution (actually a colloidal suspension) that was highly magnetic. A dark brown magnetic solid can be isolated by freeze-drying the solutions. These iron oxide lignosulfonate materials could be easily prepared with variable iron content and were found to remain intact during various treatments such as dialysis and gel permeation chromatography.

It was the goal of this work to determine if, in fact, the iron oxide lignosulfonate materials do contain magnetite, if the magnetite is present as microcrystals (ca. 100 Å diameters needed to exhibit superparamagnetism), and if the diameter of the microcrystals reflects the iron content in a given sample.

Experimental Section

Sample Preparation. Preparation of the lignosulfonate iron materials is detailed in the patent by Briggs and Kjargaard.[9] The lignosulfonate has to be purified initially. It must be essentially free of the low molecular weight, potentially iron-coordinating impurities that are normally present in the residual pulping liquor. The lignosulfonate should contain more than 3% sulfonate sulfur and 4.5–6% is common. The lignosulfonate used in this study had an average molecular weight of 35 000. The specific iron compound used to initiate the reaction is not important, as long as it can be dissolved in water at about pH 5.5. The amount of iron which can be added should be at least twice the molar number of sulfonate groups in the lignin but can be increased substantially over that. As in the preparation of bulk magnetite, base must be added to the reaction mixture. The addition of 1.1–1.25 equiv of base to 1 equiv of iron is preferred. For the most effective reaction temperature (90–140 °C), the reaction time may be from 15 min to 4 h, depending on the exact temperature, concentration, and pH. After reaction, the mixture must be freed of the inorganic salts (calcium sulfate, for example) and any other impurities. A physical separation such as dialysis should be used.

The preparation of a given lignosulfonate sample simply involves, thus, the controlled addition of O_2 and OH^- to a water solution containing iron ions and lignosulfonate. By the variation of the ratio of iron to lignosulfonate in solution the amount of iron contained in the freeze-dried material can be changed. Addition of nickel or manganese salts to the iron–lignosulfonate solution resulted in materials which contain those ions. It should be noted here that the lignosulfonate iron materials are slightly hygroscopic, so care was taken to prevent excessive exposure to the atmosphere.

Physical Measurements. All physical characterizations were carried out on the dried powder, except for Evans technique magnetic susceptibility measurements on the solution. The analytical data were determined by the University of Illinois microanalytical lab. The magnetic data were measured on a PAR Model 150A vibrating-sample magnetometer equipped with either a 50-kG superconducting magnet or an electromagnet. The Mössbauer data were collected on two different instruments. One is equipped to cool the sample to liquid-nitrogen temperature and to store the collected data with a Texas Instruments Model 960 minicomputer. The other has a Hewlett-Packard multichannel analyzer and Janis Dewar which could maintain the sample at liquid-helium temperature. Both instruments used constant acceleration drives, with ^{57}Co in Rh sources. Chemical shifts are reported in reference to iron metal at room temperature. The X-ray line-broadening study was done by using a Norelco X-ray diffractometer with unfiltered Mo radiation. An instrumental broadening of 0.20° was measured by using a silicon pellet, and the measured peak widths were corrected for this according to standard procedures.[11] Powder patterns used to fingerprint the Fe_3O_4 were taken on a Debye-Scherrer camera, using filtered Mo radiation. The Evans measurements were made on a Varian E-M 390 NMR spectrometer at a frequency of 90 MHz and a field of 21.14 kG.

Table I. Analytical Data

sample	% Fe	% C	% H	% S	% M
A	6.51	39.28	5.39	4.51	
B	7.89	40.70	5.22	4.35	
C	9.31	39.76	4.55	3.92	
D	13.84	35.10	3.85	3.05	
E	15.58	34.93	4.59	2.34	
F	17.10	35.36	3.77	3.69	
G	24.17	29.53	3.53	2.92	
H	6.53	33.90	4.93	2.59	Ni 6.68
I	10.66	32.95	4.42	1.54	Mn 4.29

Table II. X-ray Powder Diffraction Data

Fe–lignosulfonate			Fe_3O_4[b]		
d, Å 24.17%	d, Å 13.84%	rel intens[a]	d, Å	I/I_{100}	hkl
			4.85	8	111
2.963	2.97	4	2.967	30	220
2.54	2.53	1	2.532	100	311
			2.424	8	222
2.096	2.09	4	2.099	20	400
1.71			1.715	10	422
1.61	1.62	3	1.616	30	511
1.48	1.48	2	1.485	40	440
1.28	1.28		1.281	10	533
1.09	1.09		1.093	12	731
1.05			1.050	6	800
0.967			0.9695	6	751
			0.8802	6	931
0.854			0.8569	8	844
			0.8117	6	951

[a] 1 = most intense. [b] JCPDS powder diffraction files, file 19-629.

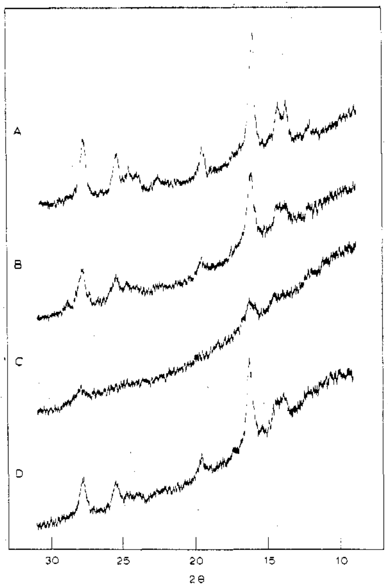

Figure 1. X-ray powder patterns for magnetite–lignosulfonate samples: 24.17% Fe (A); 13.84% Fe (B); 9.31% Fe (C). Tracing D is for a sample of the 24.17% Fe–lignosulfonate material diluted with lignosulfonate to give an iron content of 10% for the mixture.

Results and Discussion

Sample Identification. Nine different lignosulfonate–iron samples were supplied by Georgia-Pacific Corp. Two of these samples contain either manganese or nickel as well as iron. Analytical data for all samples are given in Table I. The majority of the work reported in this paper was carried out on three of the samples, sample B with 7.89% Fe, sample D

---

(10) Neal, J. A. U.S. Patent 4018691, April 19, 1977.

(11) Klug, H. P.; Alexander, L. E. "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials"; Wiley: New York, 1954; p 491.

with 13.84% Fe, and sample G with 24.17% Fe.

X-ray powder patterns were measured for many of the samples. The data for samples D and G are given in Table II, together with literature values for magnetite, Fe_3O_4. Figure 1 illustrates the powder patterns obtained for these same two samples, as well as for sample C. It is clear that these lignosulfonate–iron samples contain crystalline magnetite.

Particle Size Determination via X-ray Line Broadening. As per the Bragg equation, relatively sharp diffraction lines result for crystallites with diameters in the range of 10^{-3} to 2×10^{-5} cm. Crystallites with diameters less than approximately 2×10^{-5} cm show broadened X-ray diffraction lines. This broadening is described by the Scherrer equation:[11,12]

$$\beta = K\lambda/(D \cos \theta)$$

In this equation, λ is the X-ray wavelength, K is the shape factor, D is the average diameter of the crystallite in angstroms, θ is the Bragg angle in degrees, and β is the line broadening measured at half-height and expressed in units of 2θ. The value of K is dependent on several factors, including the Miller index of the reflecting planes and the shape of the crystallites. If the shape is unknown, K is often assigned a value of 0.89. This approximation prevents absolute size measurements with accuracy better than 25–50%; however, it provides a good means of comparing crystallite diameters in related samples.[13]

In this work, K was assumed to be 0.89 and the variation of relative crystallite diameter with % Fe content was determined from the 311 reflection. Measured peak widths were corrected for instrumental broadening by use of the correction curve in Figure 9-8 of ref 11. Examination of the powder patterns illustrated in Figure 1 shows that as the iron content is decreased from 24.17 to 13.84%, and finally to 9.31%, the Fe_3O_4 diffraction lines are broadened. In tracing D is given the powder pattern for the 24.17% Fe sample diluted with pure lignosulfonate to an iron content of 10%. The fact that the lines are sharper in this pattern than the corresponding lines in tracing C for the 9.31% Fe sample shows that the effect is not simply the result of dilution. It is clear, then, that the magnetite particle size decreases as the percentage of Fe is lowered. Along a direction perpendicular to the 311 planes, the average crystallite size of the 24.17% Fe sample was found to be increased by a factor of 1.2–1.4 compared to the average crystallite size of the 13.84% Fe sample.

Magnetic Susceptibility. If the crystallites of magnetite that are anchored to the lignosulfonate are small (i.e., diameters in the range of ca. 100 Å), then single domain crystallites would be present and would exhibit unusual magnetic properties. Single domain crystallites of magnetite have been studied for more than 40 years. They have been used in colloidal suspensions as early as 1937 to delineate the domain structure of ferromagnetic compounds.[14]

Magnetite, Fe_3O_4, crystallizes as an inverse spinel. There are two types of sites for the iron ions to occupy, tetrahedral and octahedral. These are usually called the A and B sites, respectively. The Fe(III) ions are distributed equally between the A and B sites, with the Fe(II) ions filling the remaining octahedral positions. Magnetite exhibits a phase transition at 119 K, the Verwey transition (T_v).[15] The two types of iron ions are distributed randomly in the B sites above T_v. Below this temperature, the ions are presumed to become ordered, which accounts for the sharp decrease in electrical conductivity. Other physical properties also change at this point, such as the heat capacity and the magnetic susceptibility. The crystal structure below T_v has been assumed to be orthorhombic,[16,17] although recent X-ray work concludes that it is actually rhombohedral.[18] Other recent work indicates that this transition does not occur as abruptly as was originally thought but could include up to six smaller transitions.[19] Magnetite exhibits ferrimagnetism.

Ferromagnetism results when there is a magnetic exchange interaction between neighboring ions and this interaction tends to align the individual moments. There does exist a temperature for each ferromagnetic material above which the energy exceeds the magnetic exchange energy, and the compound behaves as a normal paramagnet above the Curie temperature, T_c. The external manifestations of ferromagnetism are well-defined. The compound will exhibit hysteresis. This means that when a magnetic field is applied and then removed, the magnetization does not immediately drop back to zero. Also, unlike paramagnetic substances, the susceptibility is highly field dependent. The magnetization is also much higher in ferromagnetic substances since the effect of the exchange interaction of the moments is to increase the number which are aligned with the field.

Ferromagnetic substances have what is called domain structure. When a ferromagnetic substance is not saturated, parallel moments are grouped together into small areas which are called domains. There are thin areas of changing moment (called Bloch walls) between the domains. When the magnetization of a ferromagnetic substance increases because of an increasing external magnetic field, what actually happens is that the number of domains aligned parallel to the field increases or that the size of those domains increases. When the external field is removed, the magnetization does not immediately return to zero since the domains are stable structures.

Ferrimagnetism is a subdivision of ferromagnetism. Ferrites, such as magnetite, exhibit ferrimagnetism. These compounds have two sublattices within their crystal structure. The magnetic moments on one sublattice tend to align antiparallel to the moments on the other lattice. However, there are more ions on one lattice than on the other, so a net magnetic moment can result.

When the Fe_3O_4 crystallites are small enough (estimated to be on the order of 150 Å),[20] each ferromagnetic crystallite may form a single domain with all moments aligned. If the net magnetization of the single domain crystallites relaxes rapidly, then the particles are said to be superparamagnetic. An exact relaxation time has not been proposed. Approximately 100 s was taken to be adequate for some of the earlier researchers. Nêel was the first to postulate that the direction of magnetization of a small enough single domain particle might fluctuate thermally.[21] His equation describing the thermal relaxation is

$$1/\tau = f \exp(-VK/kT)$$

K is the magnetic anisotropy, V the volume of the particle, τ the relaxation time, and f a frequency factor on the order of 10^9. It follows from this that the size and anisotropy of a particle are both important in determining whether it can be classified as superparamagnetic. In short, a superparamagnet is a material that exhibits the large magnetization of a fer-

---

(12) Azaroff, L. V.; Buerger, M. J. "The Powder Method in X-Ray Crystallography"; McGraw-Hill: New York, 1958; p 254.

(13) Azaroff, L. V.; Buerger, M. J. "The Powder Method in X-Ray Crystallography"; McGraw-Hill: New York, 1958; p 512.

(14) Carey, R.; Isaac, E. D. "Magnetic Domains and Techniques for Their Observations"; Academic Press: New York, 1966.

(15) Verwey, E. J. W. *Nature (London)* **1939**, *144*, 327.

(16) McNab, T. K.; Fox, R. A.; Boyle, A. J. F. *J. Appl. Phys.* **1968**, *39*, 5703.

(17) Kündig, W.; Hargrove, R. S. *Solid State Commun.* **1969**, *7*, 223.

(18) Vieland, L. J. *Acta Crystallogr., Sect. A* **1975**, *31*, 753.

(19) Buckwald, R. A.; Hirsch, A. A.; Calib, D.; Callen, E. *Phys. Rev. Lett.* **1975**, *35*, 878.

(20) Jacobs, I. S.; Bean, C. P. In "Magnetism"; G. T. Rado and H. Suhl, Ed.; Academic Press: New York, 1963; Vol. III, Chapter 6.

(21) Nêel, L. *C. R. Hebd. Seances Acad. Sci.* **1949**, *228*, 664.

Table III. Magnetization as a Function of Temperature[a]

T, K	*M*, emu/g of Fe 7.89%	13.84%	24.17%
285.5	3.00	69.1	87.5
244.6	3.50		95.5
224.2	3.76	78.1	
203.7	4.03		102.0
191.4	4.28		
183.3			106.2
162.8		88.0	110.7
142.7			116.1
122.5			121.7
102.8		95.9	118.6
86.1			115.4
76.9		94.4	
67.0			113.2
55.9			113.4
50.2			114.4
44.1		94.9	115.2
38.2			116.2
31.5			117.2
30.0			117.2
26.6			117.9
24.7			118.1
22.6		98.0	118.2
21.5		98.4	118.5
20.3		98.6	118.8
19.1		98.6	118.6
17.7		99.2	119.4
16.4		99.2	119.1
14.9		99.4	119.4
13.1		101.5	121.6
11.1		103.7	124.0
9.1		106.0	126.6
7.0		104.4	124.5
5.9		99.2	118.2
4.2		94.8	112.3

[a] Measured at a field of 14 020 G.

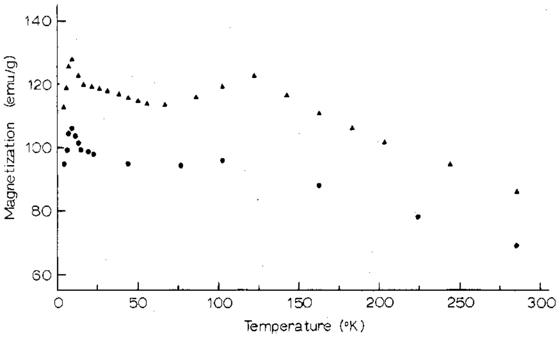

Figure 2. Magnetization vs. temperature plot for the 24.17% Fe sample (upper tracing) and the 13.84% Fe sample.

Table IV. Magnetization as a Function of a Field for 13.84% Fe-Lignosulfonate Sample

increasing field, Oe	*M*, emu/g 203.7 K	285.5 K	decreasing field, Oe	*M*, emu/g 203.7 K	285.5 K
275	32.4	24.9			
295	34.8		3770		55.0
320	37.1	28.1	2770		53.3
345	38.3		1870	63.9	
370	40.3	30.8	1770		50.4
395	41.4		1570	62.4	
420	43.0	33.4	1270	60.2	47.7
470	45.3	35.2	1120	58.7	
520	47.4	36.5	970	56.7	
570	48.3	38.1	820	54.3	
620	50.1	39.3	770		42.2
670	51.3	40.4	720	52.4	
720	52.8	41.4	620	49.5	
770	53.6	42.3	520	46.1	36.4
820	54.7	43.1	420	41.5	
870	55.7	43.9	370	38.5	
920	56.4	44.5	320	33.8	
970	56.9	44.9	295	31.8	
1020	57.7	45.6	275	28.8	23.6
1070	58.3				
1120	58.9	46.4			
1170	59.4				
1270	60.2	47.6			
1370	61.0				
1420		48.6			
1470	61.8				
1570	62.3	49.4			
1720	63.1	50.2			
1870	63.9	50.8			
2020	64.5	51.3			
2170	65.1				
2270		52.1			
2520		52.8			
2770		53.3			
3270		54.3			
3770		55.0			
4270		55.6			
4770		56.1			

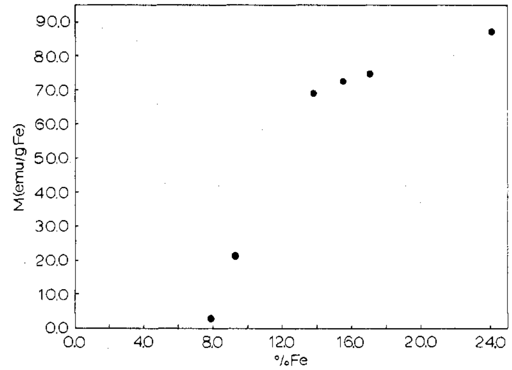

Figure 3. Magnetization as a function of percentage of iron in a given magnetite–lignosulfonate sample.

romagnetic material, but at the same time its magnetization vector is rapidly relaxing as with a simple paramagnet.

Several criteria are in common use to decide whether a particle is superparamagnetic or not. One is the absence of hysteresis in the magnetization. The second criterion stems from the fact that since each single domain is now equivalent to an individual particle in a paramagnetic substance (except that, of course, the moments involved are much larger), the magnetic behavior should be able to be described by using the Langevin equation.[22] If this is true for all the particles present, the ratio of magnetization (M) to saturation magnetization (M_s) vs. H/T at different temperatures will be superimposable for the same sample.[23] The first verification of this superimposability for single domain particles came in the work of Bean and Jacobs,[24] who studied a 2% iron amalgam. Aharoni and Litt studied superparamagnetic magnetite particles in an "inert carbonaceous matrix"[25] formed by the thermal degradation of ferricenium nitrate.

Magnetization data were measured for the magnetite–lignosulfonate samples and are listed in Tables III and IV and illustrated in Figures 2–4. The specific magnetization data are given in terms of grams of iron present in a given sample. As can be seen, the magnetization values for the various magnetite–lignosulfonate samples are large in keeping with

---

(22) Cullity, B. D. "Introduction to Magnetic Materials"; Addison-Wesley: Reading, MA, 1972.

(23) Selwood, P. W. "Chemisorption and Magnetization"; Academic Press: New York, 1975.

(24) Bean, C. P.; Jacobs, I. S. *J. Appl. Phys.* **1956**, *27*, 1448.

(25) Aharoni, S. M.; Litt, M. H. *J. Appl. Phys.* **1971**, *42*, 352.

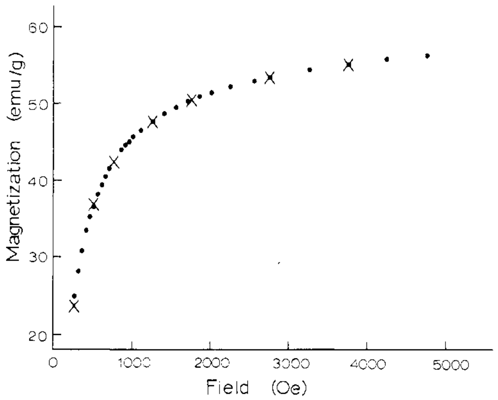

Figure 4. Magnetization vs. applied magnetic field plot for 13.84% Fe sample maintained at 285.5 K. The filled circles are for data collected while increasing the magnetic field. The crosses are for data collected as the field was decreased.

the presence of magnetite. The saturation magnetization for bulk magnetite is 97.4 G at 0 K and 91.6 G at room temperature.[26] This corresponds to 136 emu/g of iron at 0 K and 128 emu/g of iron at room temperature.

A plot of magnetization vs. temperature for the 13.84% Fe and 24.17% Fe samples is shown in Figure 3. There is a bump in the curve at ca. 120 K for the latter compound; this feature is not as apparent in the data for the other sample and even less visible in the data for samples with lower iron content. This bump corresponds, of course, to the Verwey transition and provides further confirmation of the presence of magnetite.

A plot of the magnetization per gram of iron vs. the percent of iron present in a given magnetite–lignosulfonate sample is illustrated in Figure 3. Each sample was maintained at 285.5 K. The four samples with the greatest iron content, running from 24.17 to 13.84%, have magnetization values that vary linearly with the amount of iron present. This results from the fact that the average magnetite particle size is decreasing as the iron content is varied from 24.17% Fe to 13.84% Fe. The low magnetization value for the 7.89% Fe sample shows that at 285.5 K it is composed of particles that are small enough to be considered as simple paramagnets. When the particle size decreases below a certain value at a given temperature, thermal energy exceeds the magnetic exchange interaction of the particle and the individual moments are not aligned. The 9.31% Fe sample has a particle size distribution such that at 285 K approximately half of the sample consists of simple paramagnets.

As mentioned above, two criteria are commonly used to ascertain whether a material is superparamagnetic. Hysteresis was checked for by measuring magnetization vs. applied magnetic field for the 24.17% Fe, 13.84% Fe, and 7.89% Fe samples. In each case, the sample was maintained at 298 K and introduced into the magnet at zero field. The magnetic field was increased in increments and a reading taken at each setting. Approximately 2 min of time were spent at each reading. After the magnetic field was brought to its highest value, the field was decreased in increments to check for hysteresis. None of the three samples showed any effects of hysteresis. The data for the 13.84% Fe samples are illustrated in Figure 4.

The second criterion for superparamagnetism is that plots of magnetization vs. H/T superimpose for measurements carried out at different temperatures for a given sample. The magnetization was measured as a function of magnetic field for the 13.84% Fe sample at 285.5 and 203.7 K. It was found that the plots of M/M_s vs. H/T do not superimpose for this sample. This situation has been seen in previous studies of microcrystalline magnetite. It could result from the presence of a large range in particle size for a given sample or a variation in shape of a magnetite crystallite as the size is changed. Despite the lack of superimposability of M/M_s vs. H/T curves for these samples, it does appear that many of the samples consist of microcrystalline magnetite particles that are superparamagnetic, a fact that is clearly indicated by the ^{57}Fe Mössbauer data for these materials.

In the view of the potential use of magnetite–lignosulfonates as ferrofluids, it is of interest to observe their magnetic properties in the fluid state. If the magnetite particles remain intact in solution, forming the colloidal suspension characteristic of ferrofluids, then the magnetic behavior of the fluid should parallel that of the solid. The magnetization of a fluid can be measured by using the Evans method.[27] In this technique an indicator such as acetone is dissolved in D_2O and placed in two concentric NMR tubes. The inner tube also contains the paramagnetic material for which the magnetization is to be measured. In the presence of a magnetic field the paramagnetic substance changes the magnetic environment for the indicator molecules in the inner tube compared to those in the outer tube. This results in a shifting and broadening of the NMR signal for the inner tube indicator molecules relative to the signal for the indicator molecules in the outer tube. The gram susceptibility of the paramagnetic substance is calculated from the shift, with the equation

$$\chi_g = \frac{3\Delta\nu}{2\pi\nu_0 m} + \chi_g^{\text{solvent}} + \frac{1}{m}(\rho^{\text{outer}} - \rho^{\text{inner}})\chi_g^{\text{outer}}$$

Here $\Delta\nu$ is the frequency shift between the indicator signals, ν_0 is the spectrometer frequency, χ_g^{solvent} is the gram susceptibility of the solvent, m is the mass of paramagnetic species per milliliter of solution, and ρ is the density of each solution. The last term is often ignored, as the solutions usually have similar densities. Multiplying the susceptibility by the magnetic field yields the magnetization. The magnetization of the fluid 13.84% Fe sample was measured at 307 K and compared to that of the corresponding solid. The two samples studied contained 0.00032 g/mL and 0.000224 g/mL of Fe_3O_4–lignosulfonate, while each mixture contained ~3% acetone. Pure lignosulfonate was added to each outer tube in order to minimize any magnetic effects due to the polymer. A magnetization of 70 ± 2 emu/g of Fe was found for the fluid at 307 K. This is in reasonable agreement with the value of 66 emu/g of Fe extrapolated from a $1/M$ vs. T plot for the solid. This confirms that the magnetite particles remain intact in solution, forming a ferrofluid.

Mössbauer Spectroscopy. The Mössbauer spectrum of a superparamagnetic material such as Fe_3O_4 is diagnostic. The theory related to Mössbauer studies on microcrystalline magnetite has been reported.[28,29] With ^{57}Fe Mössbauer experiments on Fe_3O_4 it is possible to readily tell whether the magnetization of the sample is relaxing faster than or slower than ca. 10^7 s^{-1} as set by the lifetime of the ^{57}Fe nuclear excited state.

The unpaired electrons in a ferromagnetic iron compound lead to a large internal magnetic field in the sample. This internal field causes a Zeeman splitting in the ^{57}Fe excited and ground nuclear states. If the internal magnetic field varies slowly in direction compared to the inverse of the lifetime of the ^{57}Fe nuclear excited state, then a six-line magnetic hyperfine pattern will be seen in the Mössbauer spectrum for each

---

(26) Smit, J.; Wyn, H. P. J. "Ferrites"; Cleaver-Hume Press, Ltd.: London, 1959.

(27) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(28) Gager, H. M.; Hobson, M. C., Jr. *Catal. Rev.—Sci. Eng.* **1975**, *11*, 1.

(29) Berry, F. J. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 255.

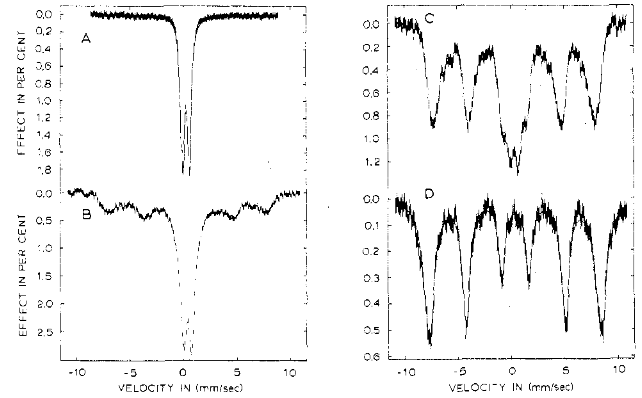

Figure 5. ^{57}Fe Mössbauer spectra for the 7.89% Fe sample at four different temperatures: 96 K (A); 30 K (B); 20 K (C); 4.2 K (D).

different type of iron ion in the sample. The components of a six-line pattern vary in intensity in the ratio of 3:2:1:1:2:3. If, on the other hand, the internal magnetic field varies in direction faster than ca. 10^7 s^{-1}, then each different type of iron ion will only generally show a quadrupole-split doublet. A superparamagnetic material would, thus, simultaneously exhibit a large magnetization and a simple quadrupole-split doublet in the Mössbauer spectrum due to the fact that the magnetization is rapidly relaxing in these single domain particles.

Each of the magnetite–lignosulfonate samples consists of microcrystals with a distribution of sizes. In general, then, a particular material will give a Mössbauer spectrum at a given temperature that shows both a six-line magnetic pattern and a quadrupole-split doublet. The temperature at which there are equal amounts of the two types of signals will vary with average microcrystal size in a sample, such that a sample with smaller sized microcrystals will exhibit equal amounts of the two signals at a lower temperature than the sample with a larger particle size. The internal magnetic field at the nucleus is also particle-size dependent. In order to simulate the spectra for these materials, it is necessary to properly account for the particle size distribution. McNab and co-workers[16] did this for microcrystalline Fe_3O_4 samples which varied in average diameter in the range of 100–160 Å.

Bulk magnetite exhibits *two* six-line magnetic hyperfine patterns, resulting from the A and B sites of the iron ions. None of the magnetite–lignosulfonate samples studied in this work gave a spectrum wherein two six-line patterns could be resolved. This has been observed before in studies of very small particles of magnetite.[16,25,29]

Mössbauer spectra recorded at several temperatures for the 7.89% Fe sample are shown in Figure 5. The magnetite microcrystals are relatively small in this sample, and between room temperature and 96 K no magnetic hyperfine is observed. At 30 K (tracing B), approximately half of the microcrystals exhibit magnetic hyperfine, as judged by the relative areas of the doublet and six-line patterns. The signal at 4.2 K consists of only the six-line type and fitting the spectrum gives a hyperfine field of $H_{(0)}$ = 501 kOe. The behavior that is seen here for the 7.89% Fe sample is similar to the characteristics reported by Aharoni and Litt[25] for magnetite particles of 35 Å average diameter. As was discussed above, most of the microcrystals in the 7.89% Fe sample are so small that they are probably simple paramagnets. The quadrupole-split doublet which results from the superparamagnetic particles would be expected to be identical with the doublet for the paramagnetic particles.

Figure 6 shows that in the case of the 13.84% Fe sample ca. 40% of the particles are superparamagnetic at 293 K on the Mössbauer time scale. The internal magnetic hyperfine field is 521 kOe at 4.2 K. It is clear, then, that the average magnetite particle size is larger in the case of the 13.84% Fe sample compared to the 7.89% Fe sample.

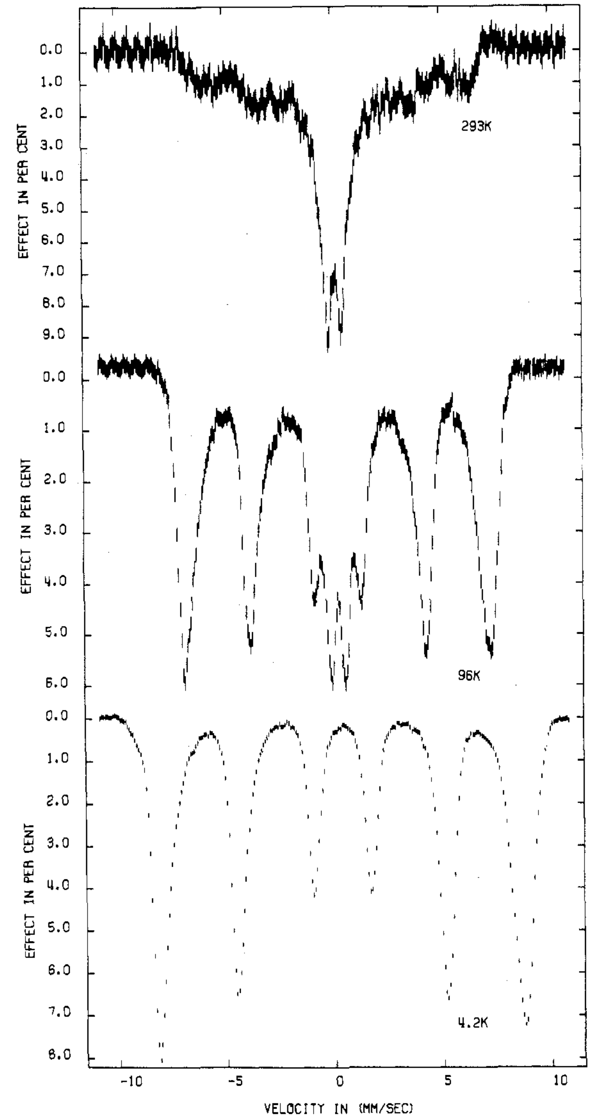

Figure 6. ^{57}Fe Mössbauer spectra for the 13.84% Fe sample at three different temperatures.

The 24.17% Fe sample has the largest average magnetite particle size as evidenced by the Mössbauer spectra summarized in Figure 7. Only ca. 10% of the particles are relaxing rapidly enough at 293 K to give a simple quadrupole-split doublet. This is predicted by Néel's equation given above, an equation which shows that the thermal relaxation of a single domain particle will decrease as the particle size is increased.

Mixed-Metal Ferrites. Two mixed-metal lignosulfonate samples, one with 10.66% Fe and 4.29% Mn and the other with 6.53% Fe and 6.68% Ni were also studied. Several Mössbauer studies have recently been carried out on mixed-metal ferrites. For instance, $Fe_{3-x}Cr_xO_4$ was studied[30] with Mössbauer spectroscopy to determine the cation site distribution of iron and chromium in the A and B sites. $Ca_xFe_{3-x}O_4$[31] and $Fe_{3-x}Al_xO_4$[32] were similarly studied, with emphasis on the mechanism of electron conduction. Although it was not confirmed for our samples, $NiFe_2O_4$ is known to form with

---

(30) Ok, H. N.; Pan, L. S.; Evans, B. J. *Phys. Rev. B* **1978**, *17*, 85.

(31) DeSitter, J.; Govaert, A.; DeGrave, E.; Chambaere, D.; Robbrecht, G. *Phys. Status Solidi* **1977**, *43*, 619.

(32) Dehe, G.; Deidel, B. *Phys. Status Solidi* **1975**, *29*, k47.

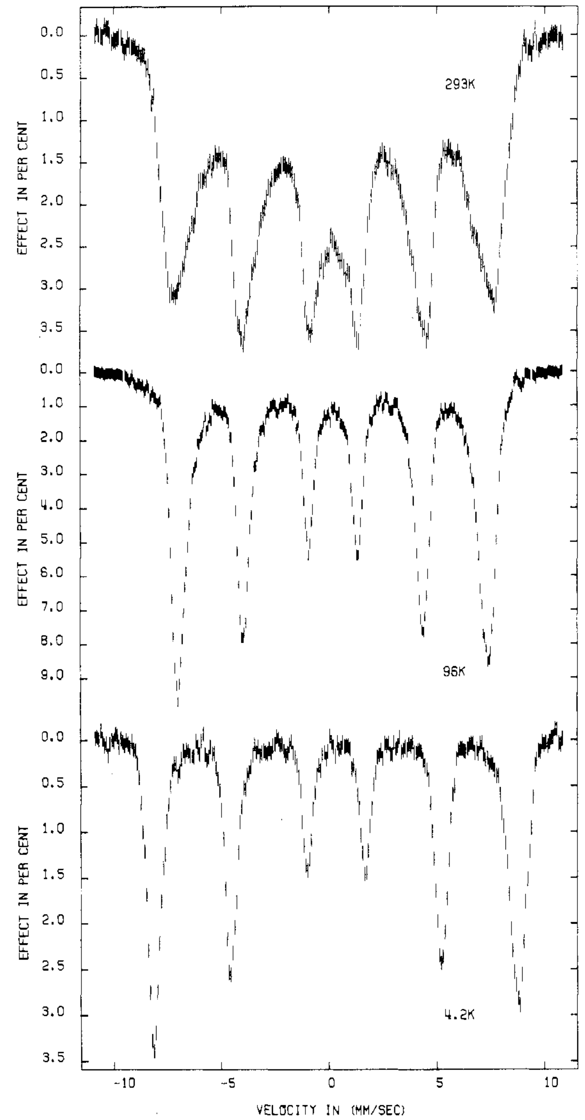

Figure 7. ^{57}Fe Mössbauer spectra for the 24.17% Fe sample at three different temperatures.

the Ni almost exclusively in the octahedral sites,[26] and $MnFe_2O_4$ forms with the Mn primarily in the tetrahedral sites (only 20% of the Mn in the octahedral sites), according to a study by Hastings and Corliss.[33]

Table V. Magnetization as a Function of Temperature for 10.66% Fe, 4.29% Mn-Lignosulfonate Sample

T, K	M, emu/g of metal	T, K	M, emu/g of metal
285.5	58.9	31.5	95.3
244.6	65.7	30.0	95.3
203.7	72.9	28.4	95.8
183.2	76.7	24.7	96.8
162.8	80.8	22.6	97.1
142.6	86.0	21.5	97.5
122.5	91.3	20.3	98.0
102.8	90.7	19.1	98.2
86.1	89.5	17.7	99.0
67.0	89.0	16.4	99.2
55.9	90.0	14.9	98.7
50.2	91.4	13.1	102.1
44.1	92.4	11.1	104.9
38.2	93.8	9.1	108.4
		7.0	108.5
		6.6	106.8
		4.9	104.5

In the Mn–Fe–lignosulfonate sample, there are stoichiometrically 0.9 manganese ions for every 2.1 irons. This compound can thus be assumed to consist of approximately 90% $MnFe_2O_4$. The magnetic data as a function of temperature are listed in Table V. The saturation magnetization of $MnFe_2O_4$ is only 83% as large as that for Fe_3O_4 at room temperature.[33] This explains why the value of 58.9 emu/g for the Mn–Fe–lignosulfonate sample, which contains a total of 14.95% metal, is actually less than that (69.1 emu/g) measured for the 13.84% Fe–lignosulfonate sample.

The magnetization of the Ni–Fe–lignosulfonate sample was only measured at two temperatures. At 285.5 K, the magnetization was 20.7 emu/g, while it was found to be 23.0 emu/g at 244.6 K. This sample has stoichiometrically 0.97 Ni for every 1.00 Fe. This means that the structure has the potential for being very disordered. However, the Mössbauer spectrum at room temperature indicates that the distribution of ions is probably well-defined. This spectrum is similar to the room-temperature spectrum of the 13.84% Fe–lignosulfonate sample. There is a total of 13.21% metal by weight in the nickel-substituted sample. Since the molecular weight of nickel is so close to that of iron, this means that the molar amounts of metal in these two samples are very similar.

Acknowledgment. We thank Dr. John A. Neal of Georgia-Pacific Corp. for the samples studied in this work and for helpful discussions. We are also grateful to Professor Peter Debrunner for help with the Mössbauer work.

Registry No. Fe_3O_4, 1317-61-9; $MnFe_2O_4$, 12063-10-4; $NiFe_2O_4$, 12168-54-6; lignosulfonate, 8062-15-5; magnetite, 1309-38-2.

---

(33) Hastings, J. M.; Corliss, L. M. *Phys. Rev.* **1956**, *104*, 328.