Thermal Stability and Magnetic Properties of Fe−Polyoxocation Intercalated Montmorillonite

Laura V. Govea and Hugo Steinfink*

Materials Science and Engineering Program, The University of Texas at Austin, Austin, Texas 78712

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Iron polyoxocation montmorillonite complexes were prepared by ion exchange. The thermal stabilities of the complexes were determined to 750 °C. Their magnetic behavior was investigated between 2 K and room temperature. The complexes were stable when heated to 500 °C for as long as 60 h although the magnetic behavior for that specimen differs from those heated for shorter periods. At 750 °C the pillared sample collapsed but could be reexpanded with additional Fe−polycation. A dried specimen of the Fe−polycation exhibits spin glass behavior. Intercalated specimens heated in the range 200−500 °C for 1−2 days exhibit complex magnetic behavior when susceptibilities are measured for zero-field-cooled samples. An initial asperomagnetic spin arrangement at 2 K undergoes a transition at 4.4 K to a new asperomagnetic state that then relaxes to a speromagnet. The freezing temperature is about 15 K.

Introduction

The crystal structures of clay minerals consist of negatively charged hydrous aluminosilicate layers that are weakly bonded by interlayer cations. These are easily exchangeable in the smectite mineral group.[1,2] The dioctahedral clay mineral montmorillonite has been extensively investigated for decades because the variability of the *c*-axis dimension permits the intercalation of a large variety of inorganic and organic interlayer cations and desirable physical properties can be engineered into the material.[3] Metal oxide pillared smectites derived from the intercalation of polyoxocations of Al,[4−6] Zr,[7] Cr[8,9] and other metals as well as mixed pillared materials have been studied for their utility as selective catalysts. Attempts to intercalate iron polymeric cations into montmorillonite yielded products with relatively low gallery heights and limited thermal stabilities.[10−13] Rightor et al.[14] described a procedure that expanded montmorillonite to about 25 Å. Bradley and Kydd[15] report the possible existence of $[FeO_4Fe_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, but attempts to intercalate this ion into montmorillonite were not successful. Because the primary focus was on the use of these materials as catalysts, the magnetic properties received less attention. Magnetic transition-metal ions and a Fe hydroxoacetate ion have been introduced into micas, vermiculites, and smectites and their magnetic properties reported.[16−20] We have reported preliminary results of our work on the magnetic behavior of a Fe−polyoxocation intercalated montmorillonite complex[21] and report here the detailed results of such an investigation.

Experimental Section

Montmorillonite. The montmorillonite used in all experiments was labeled “mineral colloid BP” with an approximate exchange capacity of 85 mequiv/100 g of clay and was obtained through the courtesy of Southern Clay Products, Inc. Gonzalez, TX. The mineral was extracted from a Wyoming bentonite deposit and refined to remove accessory minerals. The chemical analysis supplied with the sample showed that about 0.2 Fe was present in the octahedral sites and the calculated formula was consistent with that reported previously for an Upton, Wyoming bentonite, $(Al_{1.56}Fe_{0.19}Mg_{0.26})(Si_{3.89}Al_{0.11})O_{10}(OH)_2{\cdot}xH_2O$.[22] The supplied material was suspended in dis-

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tilled water and the suspension was stirred with a magnetic stirrer. It was observed that a few particles adhered to the magnet. They were removed and the solution was stirred until no further particles adhered. These particles were identified by powder X-ray diffraction as metallic iron and originated from the processing of the raw material. Since the montmorillonite contained Na, Ca, Mg, and a small amount of K as exchangeable ions, the purified material was repeatedly dispersed in 1.0 M $CaCl_2$ solution to produce a single-cation-exchanged montmorillonite. Finally the suspension was washed free of Cl^- as tested with $AgNO_3$ solution. The Ca^{2+}-montmorillonite was expanded with ethylene glycol prior to the intercalation of iron polycation in order to provide an initially greatly expanded gallery space. The powder X-ray diffraction pattern showed an expansion of the *c*-axis from 15 Å to the characteristic 17 Å basal spacing.

Fe−Polycation. The hydrolysis of an aqueous solution of a transition metal salt by a base produces a metal−polyhydroxy oligomer. The process has been studied extensively but the structures of the polynuclear complexes are not known with certainty.[15,23−25] The polycation solution was prepared by hydrolyzing a 0.2 M iron chloride hexahydrate solution with sodium carbonate. The amount of sodium carbonate added to the iron chloride solution was 2.0 equiv/mol of iron. The solution was stirred vigorously for 18−20 h and simultaneously flushed with argon to facilitate the removal of carbon dioxide that evolved during the hydrolysis.[14] A fibrous cationic exchange resin (P11, cellulose phosphate) was added to the polycation solution in order to capture the excess sodium ions produced by the hydrolysis reaction and to minimize their reintroduction into the gallery space. The resin was removed from the polycation solution by vacuum filtration. The ethylene glycol expanded montmorillonite was then added to a beaker of polycation solution and stirred for 2 h. The hydrolysis condition produces a pH = 1.8 which is not affected by the addition of the clay. The product was repeatedly washed with distilled water to remove any excess chloride ions. Washing and centrifugation were continued with constant monitoring of the pH until flocculation, at which point the pH remained constant at 4.3.[14] At this pH highly condensed species of polynuclear Fe-oxohydroxide complexes are present[15,26] for incorporation into the gallery space.

Colorimetry. The total Fe content of every specimen was determined by colorimetry using the standard addition method.[27,28] Approximately 20−30 mg of air-dried samples were dissolved in a small amount of HF and diluted to 100 mL with distilled water. Exactly measured volumes of a Fe^{3+} standard solution were added to aliquot portions of the unknown and an excess of KSCN was added to develop the red complex $(FeSCN)^{2+}$ The absorbances to determine Fe^{3+} were obtained with a 4050 UV/visible LKB Biochrom ULTROSPEC II spectrophotometer at 410 nm. A similar procedure was used to determine Fe^{2+} using a solution of hydroxylamine hydrochloride, sodium acetate, and *o*-phenanthroline to develop the orange-red ferrous complex. The absorbances of these solutions were obtained at 508 nm. Total Fe content is approximately 26 wt %; about 4 wt % is Fe^{2+}. The montmorillonite used in these experiments contains about 2.9% Fe^{3+} and 0.3% Fe^{2+}; 23% Fe represents the complexed Fe−polycation radical. The increase in the Fe^{2+} concentration is due to the presence of ethylene glycol in solution, some of which is oxidized by Fe^{3+} during the exchange process. A sample that had been heated at 750 °C for 72 h and reexpanded with polycation contained 35 wt % Fe.

X-ray Diffraction. X-ray powder diffraction patterns were obtained with Cu Kα radiation using a diffractometer equipped with a graphite crystal diffracted-beam monochromator and a continuously variable divergence slit. Oriented aggregates of the montmorillonite−Fe−polycation complex were prepared by evaporating the suspensions on glass plates or off-axis cut quartz plates. Heated samples were obtained by placing the plates into furnaces at the appropriate temperatures. The specimens were cooled in air and thereafter stored in a desiccator until needed. Runs were started at 1° 2θ and terminated at about 60° 2θ.

Density. Density measurements were carried out with a fully automated gas displacement pycnometer using helium gas. A steel sphere of known volume was used to calibrate the instrument before measurements were made. A specially designed 1 cm^3 sample cup was used to measure the densities of small amounts of very finely powdered samples. To check the technique the density of a powdered sample of Fe_2O_3 was measured. It was 5.3 g/cm^3 as compared to the theoretical value of 5.27 g/cm^3. After an automated purge cycle, each sample was subjected to a run that involved five separate volume determinations. Two different samples of the same preparation were measured to monitor reproducibility. Densities were determined for Na and Ca montmorillonite and for all iron-pillared montmorillonites.

Magnetic Susceptibility. Magnetic susceptibilities were measured with a Quantum Design DC SQUID magnetometer over the range 2−300 K for zero-field-cooled (ZFC) samples and over the range 300−3 K for field-cooled (FC) samples. The ZFC measurements were taken by equilibrating the sample at 2 K, switching on a magnetic field of 1 kOe, and recording the magnetization as a function of temperature to 300 K. With the applied field on, measurements of susceptibility were then continued while the sample was cooled to 3 K to obtain FC data. The samples weighed about 30−45 mg; they were pressed into pellets of about 0.4 cm diameter and 0.2−0.3 cm high and introduced into gelatin capsules. The free space above the pellet was filled with cotton. The capsule was introduced into a drinking straw, which was attached to the sample holder and lowered into the SQUID magnetometer. Diamagnetic susceptibilities of ions and molecules were subtracted from the susceptibility measurements using values given by Selwood.[29] Measurements of thermoremanent magnetization (TRM) versus time were done by lowering the temperature to the desired value in the presence of an applied field of 1 kOe. The field was then switched off and the magnetization was recorded as a function of time.

Surface Area. Measurements were carried out on an iron-pillared sample prepared at room temperature and on a sample heated at 500 °C for 48 h. The measurements were made in a Perkin-Elmer Shell sorptometer using N_2 as the adsorbate at liquid N_2 temperature.

Thermogravimetric Analysis. Measurements were performed with a Perkin-Elmer series 7 thermogravimetric analyzer. The heating protocol was 1 °C/min from room temperature to 900 °C in air.

Mössbauer Spectroscopy. A room-temperature spectrum was obtained on a sample heated at 500 °C for 22 h with a constant acceleration spectrometer and a ^{57}Co source. The sample was mixed with sucrose and pressed into a hole in a plastic holder.

Results and Discussion

Approximately 100 mL of polycation solution was evaporated on an off-axis cut quartz plate; the X-ray diffraction powder pattern showed that the solid was amorphous. Unlike the powder X-ray diffraction patterns of the Ca and ethylene glycol intercalated montmorillonite that showed a series of intense 00*l* diffraction spectra, the X-ray diffraction intensities from a

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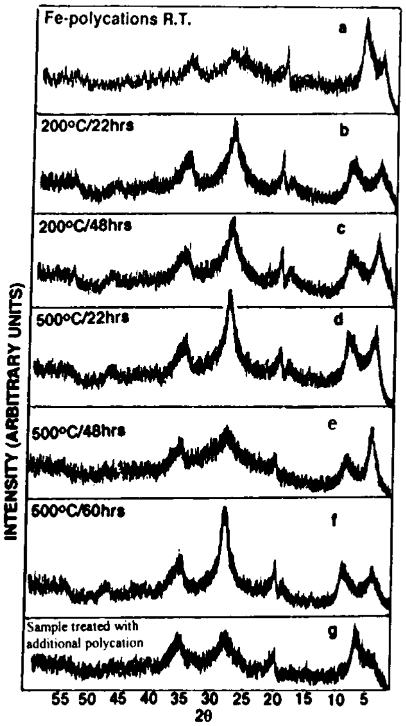

Figure 1. X-ray diffraction powder diagrams of Fe−polycation intercalated montmorillonite.

flake of the pillared material exceeded background by only 50−75 cps; the lines are broad and the preferred orientation has degraded so that the 021 and 201 bands become visible (Figure 1). The diffraction pattern is similar to that obtained by Rightor et al.[14] The first, second, and eighth orders of a 25 Å periodicity are present in Figure 1a; the tenth order overlaps the 201 band. The 00*l* reflections are asymmetric toward higher 2θ values indicative of a random distribution of intercalated layer spacings, but the primary intercalated periodicity is 25 Å. The gallery space is occupied by the polycations and most likely water molecules. The 25 Å intercalate was heated at various temperatures for different time intervals to study the thermal stability of the complex. Heating at 200 °C for 22 h (Figure 1b) produced nonintegral orders of 00*l*, with $d(001) \sim 23$ Å. The symmetric line shape of the $d = 3.16$ Å ($2\theta = 28.2°$) line may indicate that the primary layer periodicities could be 19 and 25 Å so that the sixth order of the former and the eighth order of the latter periodicity overlap. Using Méring's *d* spacing calculation for a 50% random mixture of these two periodicities yields spacings 22, 10.8, 4.8, and 3.16 Å, in good agreement with observed values.[30] The *d* spacing around 10 Å, near 9° 2θ (Figure 1b−f) may also be due to a partially collapsed phase.

A freshly prepared intercalate was heated at 500 °C for 22 h, and its diffraction pattern was essentially the same as for the specimen heated at 200 °C for 48 h (Figure 1c,d). A 23 Å periodicity is visible and the peak at about 2° 2θ (44 Å, Figure 1c) may be indicative of a doubled *c* axis. Further heating for 48 and 60 h at 500 °C leaves the diffraction pattern unchanged (Figure 1e,f). Apparently the 23 Å phase represents a stable form. It is known that heating montmorillonite to 700 °C or above degrades the silicate structure by the removal of structural OH^-. The samples that were heated at 500 °C for 48 and 60 h were heated at 750 °C for 72 h (Figure 2). A collapsed silicate structure, $d = 9.9$ Å, is discernible in addition to some weak, broad lines that were identified as Fe_2O_3. Since the silicate framework appeared to be still present, the sample was treated with a fresh solution of the polycation at room temperature following the previous procedure. The diffraction diagram (Figure 1g) shows that the 25 Å phase is recovered. The diffraction intensities are low and the lines from Fe_2O_3, if still present, are lost in the background.

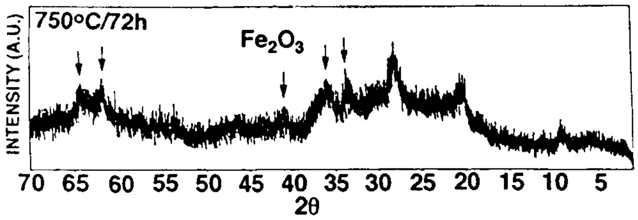

Figure 2. Powder X-ray diffraction diagram of the intercalated material heated at 750 °C showing the formation of Fe_2O_3.

Table 1. Physical Properties of Na and Ca Montmorllonite and Iron-Pillared Montmorillonites[a]

sample	density[a] (g cm^{-3})	calculated mol wt (g/mol)	mass of intercalate in gallery space *g*
Na-montmorillonite	2.41	887	
Ca-montmorillonite	2.16	954	
Fe−polycations, room temp	2.27	1672	950
200 °C/22 h	2.59	1754	1033
200 °C/48 h	2.68	1815	1094
500 °C/22 h	2.95	1998	1277
500 °C/48 h	2.95	1998	1277
500 °C/60 h	2.95	1998	1277
750 °C/72 h	2.95		
750 °C treated with additional polycations	3.27		

[a] Esd's are ±0.05.

The crystal structure of a collapsed montmorillonite is monoclinic with approximate lattice parameters $a = 5.3$ Å, $b = 9.3$ Å, $c = 9.6$ Å, $\beta = 97°$.[1,2] It was assumed that *a* and *b* remain constant as the content of the gallery space is changed so that the volume of the unit cell varies with the *c*-axis dimension. The measured densities of the samples are shown in Table 1. The silicate portion of the unit cell content was calculated based on the idealized formula $Si_8Al_4O_{20}(OH)_4$, 721 g/formula weight. The mass content of the gallery space can be calculated from

$$M = \rho N V - 721$$

where ρ is the measured density of the clay sample, N the Avogadro number, and V the volume of the unit cell. An exchange capacity of 85 mequiv/100 g of clay and $d(001) = 12.5$ Å for Na-montmorillonite yields 8 H_2O molecules/unit cell and $d = 15.5$ Å for Ca-montmorillonite yields 12 H_2O molecules/unit cell. An intercalated iron content of 23% in the room-temperature polycation-exchanged material and $d = 25$ Å yields about 7 Fe and about 31 H_2O molecules/unit cell in the gallery space (OH^- was considered as H_2O in the calculation; ferrous and ferric iron were considered as part of the exchangeable complexes). Table 1 summarizes the values of density, molecular weight, and the mass of the inter-

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calate in the gallery space for the specimens subjected to various treatments. Similar calculations for the other samples yield values of 7−8 Fe/unit cell and H_2O content that varies from 31 to 45 molecules in the gallery space. The latter is obtained for a specimen heated at 500 °C for 48 h. Heating the intercalated montmorillonite samples activates their ability to sorb water from the atmosphere as soon as they are exposed to ambient conditions. Indeed, Rightor et al.[14] observed that the pillared specimens degraded after prolonged exposure to the ambient atmosphere. Not until the collapse of the silicate complex to 9.9 Å at 750 °C does the diffraction pattern show weak and broad diffraction lines that can be assigned to hematite. When this material was further treated with polycation solution, the layers reexpand, and the material has a density of 3.27 and contains 35 wt % Fe.

The structure of the intercalated Fe−polycation is unknown, but the pillaring height of about 15 Å may be indicative of a trinuclear, octahedral, corner-sharing complex $Fe_3(OH)_m(H_2O)_n$, $m + n = 16$, where m and n adjust to impart a positive charge to the polycations to satisfy the exchange capacity. Its structure may possibly be related to that of the mineral ferrihydrite, $Fe_5O_7OH{\cdot}4H_2O$, which can be prepared by slow hydrolysis of ferric salts between $3 < pH < 9.5$.[31,32] As has been mentioned previously, Bradley and Kydd[15] reported the fleeting existence in solution of the ion $[FeO_4Fe_{12}(OH)_{24}(H_2O)_{12}]^{7+}$. Its structure appears to be related to the Al_{13} Keggin structure type. They also reported that the addition of Fe^{2+} during the preparation of the Fe_{13} ion appears to stabilize the latter and occasionally they observed a 19 Å X-ray diffraction line in those intercalates. However, they conclude that "the proposed Fe_{13} species has not been unambiguously characterized". It may be serendipitous that the use of the glycol-expanded montmorillonite produced the Fe^{2+} ions necessary to stabilize a form of the Fe−polycation that intercalated into our specimens. We interpreted the diffraction patterns of some heated specimens as being due to mixed layering of 25 and 19 Å periodicities.

The BET surface areas, S_0, were determined using nitrogen at liquid nitrogen temperature for the freshly prepared sample and for the sample heated at 500 °C for 48 h. The values were 297 and 365 m^2/g, respectively. S_0 of iron pillared clays (Fe−PILC) have been reported by Rightor et al.[14] and Yamanaka and Hattori.[33] Their reported values are somewhat lower.

The Mössbauer spectrum at room temperature of an iron-pillared montmorillonite heated at 500 °C for 22 h shows one quadrupole split doublet. The spectrum was fit with two Lorentzian functions. An isomer shift of 0.35 mm/s (relative to Fe metal) and $E = 1.60$ mm/s are consistent with high-spin Fe^{3+} in an octahedral environment.[34] The shape of the absorption lines is broad, which is characteristic of superparamagnetism and spin glasses.[35,36]

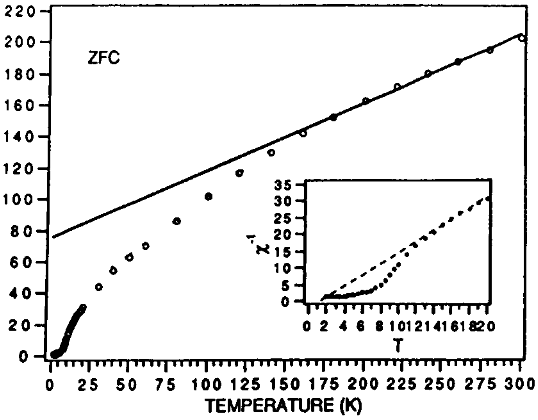

Figure 3. Variation of χ^{-1} vs T for the amorphous powder of Fe−polycation.

Magnetic Properties. The origins of the different aspects of magnetism in crystalline, periodic solids lie in the short- and long-range interactions of electronic spins that are part of the periodic nature of the crystal structure. When this periodicity is disturbed, such as in amorphous solids or in nonmagnetic solids containing low concentrations of magnetic ions, the character of the magnetic interactions changes. In spin glasses the magnetic moments are frozen in some average local orientation but are spatially aperiodic below a freezing temperature, T_f. Local order is the result of competition among thermal energy, direct, super, and indirect magnetic exchange forces, local crystalline electric fields, etc. The magnetic effects result from a compromise between ferromagnetism and antiferromagnetism, frequently leading to an inability to satisfy local requirements because of disorder and causing frustration. Magnetic moments for a spin glass result, then, from a statistical preference for a given spin alignment. They are history dependent and therefore results differ for field-cooled and zero-field-cooled measurements. The magnetic behavior has been labeled aspero-, speri-, and speromagnetism, corresponding respectively to ferro-, ferri-, and antiferromagnetism in crystalline solids.[37,38]

Fe−Polycation. Figure 3 shows the ZFC inverse susceptibility data for a dried, amorphous Fe−polycation sample measured between 2 and 300 K in a field of 1 kOe. The straight line portion between room temperature and about 160 K was fit to the Curie−Weiss law yielding $\theta = -172$ K and $\mu_{eff} = 4.3\ \mu_B$. The material is an antiferromagnet and below 160 K the spin structure gradually changes toward its final speromagnetic state (Figure 3 insert). This behavior is consistent with speromagnetic ordering in an amorphous solid where the tendency toward local antiparallel alignment is strong but absence of long-range order produces a noncollinear spin structure that approaches eventually zero net magnetization. The freezing temperature exhibits a wide range of values centered near 4 K because of the nonuniformity of the material. The large value of $|\theta|/T_f$, 43, and the reduced value of μ are

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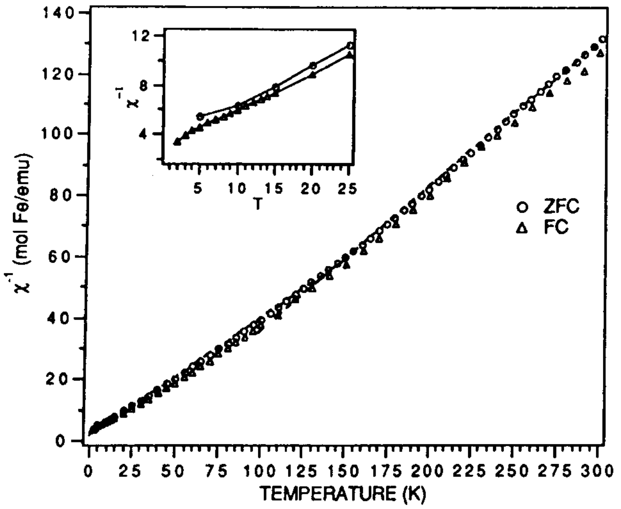

Figure 4. Variation of χ^{-1} with temperature for the sample heated at 200 °C for 22 h.

evidence of a high degree of frustration among the antiferromagnetic interactions. Similar behavior has been observed in amorphous FeF_3 and $MFeF_4$ ($M = Na, K$).[37]

Ca-montmorillonite. Measurements were made on a room-temperature preparation and on a sample heated at 200 °C. The samples are paramagnetic and the data were fit to the expression

$$\chi = \chi_0 + C/T$$

with $\chi_0 = 0.0012$ emu/mol Fe and $\mu_{eff} = 2.70\ \mu_B$, which is consistent with the presence of 0.2 Fe^{3+} in the octahedral site of the silicate layer.

Fe–Pillared Montmorillonites. (a) Samples at room temperature and 200 °C heated for 22 h. The ZFC inverse susceptibility vs *T* plot of the room-temperature preparation shows that it is paramagnetic. The data were fit with the Curie law and yielded $\mu_{eff} = 4.2\ \mu_B$. A contribution of the antiferromagnetism of the intercalated Fe–polycation is not observed. The separation of the pillars and the presence of water in the gallery space prevent intermolecular magnetic interactions. The data for the sample heated at 200 °C for 22 h (Figure 4) are nearly the same for ZFC and FC measurements and begin to show onset of antiferromagnetism at about 125 K. Below about 10 K (Figure 4 insert) the FC data begin to curve toward the origin while the ZFC data begin to curve upward, characteristic behavior of a speromagnetic spin structure.

(b) Samples heated at 200 °C/48 h, 500 °C/22 h, 500 °C/48 h. The magnetic properties of these samples are qualitatively similar and differ from the previous two specimens. In Figure 5a,b are shown data for the specimen heated at 500 °C for 22 h and they are representative for this group. The ZFC and FC data are slightly displaced from each other between 300 and about 20 K (Figure 5a) but they behave quite differently below that temperature (Figure 5b). The ZFC susceptibility decreases from 2 to 3 K and then is nearly constant between 3.2 and 4.4 K. This behavior is characteristic of an asperomagnetic spin ordering of an amorphous solid where the initial local order, induced when the field is first switched on, begins to relax. The discontinuity at 4.5 K indicates that a spin reorganization occurs as thermal energy supplied to the system lowers the barriers to reorientation of the magnetic units with a resultant increase in the magnetization at the transition temperature. As the temperature increases further toward 8 K, the asperomagnetic spin structure relaxes as before to a speromagnet and the magnetization decreases. The convex dome near 15 K represents a distribution of freezing temperatures, T_f, below which the material exhibits speromagnetic behavior. The FC data turn down toward the origin as expected for a speromagnetic spin structure (Figure 5a insert).

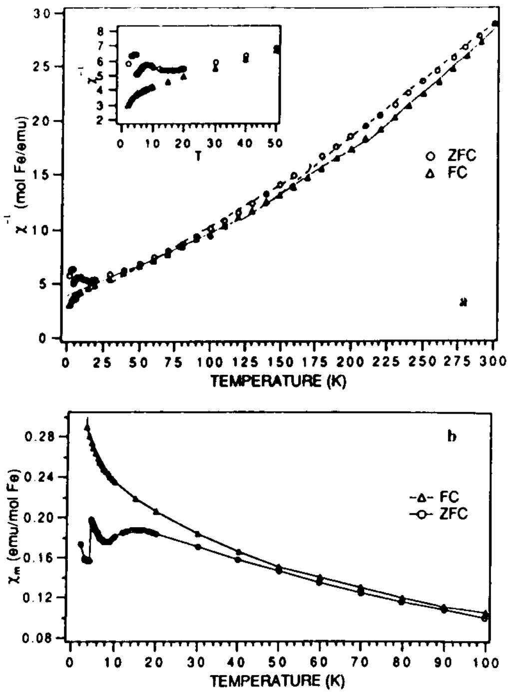

Figure 5. Magnetic behavior of a pillared specimen heated at 500 °C for 22 h. (a) Variation of inverse susceptibility between 2 and 300 K and (b) the susceptibility below 100 K. The lines serve as a guide to the eye.

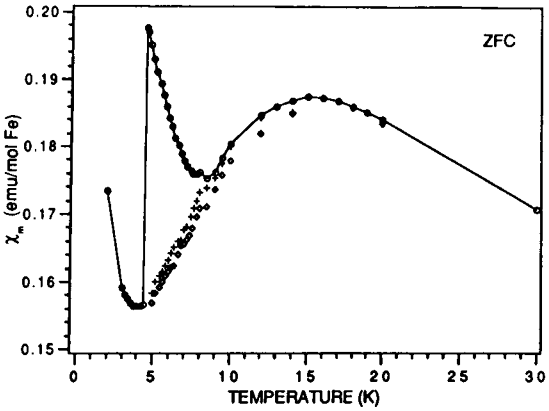

Figure 6. Magnetic susceptibility of a pillared specimen heated at 500 °C for 22 h. Circles are data for a specimen cooled to 2 K and then heated to 30 K in a field of 1 kOe. Crosses are for a specimen cooled to 5 K and then measured in a field of 1 kOe. Diamonds are for a specimen cooled to 2 K, warmed to 5 K in the absence of a field, and then measured in a field of 1 kOe.

To study the transition near 5 K, a series of experiments with different starting temperatures were carried out for ZFC samples, and the results are shown in Figure 6. The circles represent measurements as done previously starting at 2 K. The crosses represent

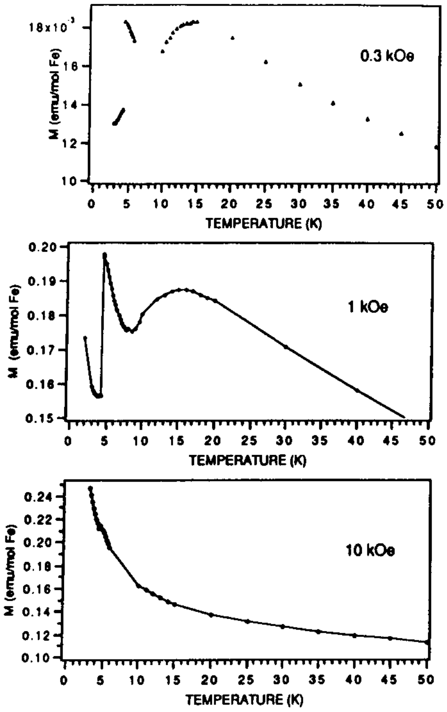

Figure 7. Effect of the field on magnetization vs temperature. The solid line is a guide to the eye.

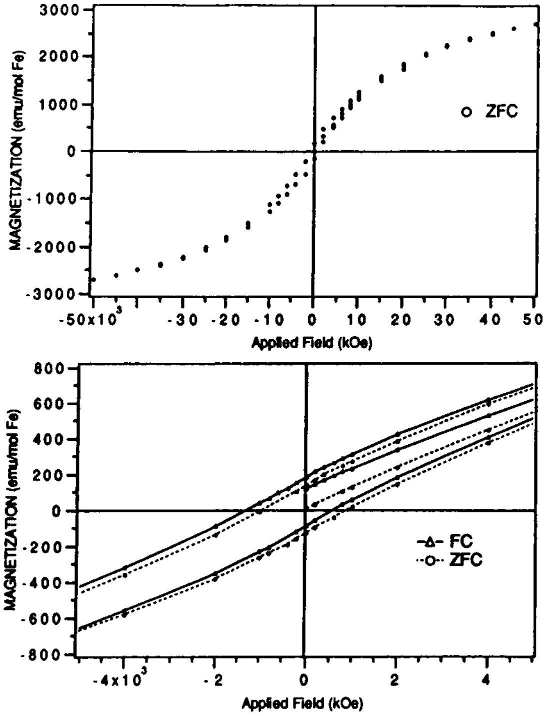

Figure 8. Curve of magnetization vs applied field at 3 K for the sample heated at 500 °C for 22 h. The solid line is a guide to the eye.

measurements for a sample cooled in ZF to 5 K, at which point a 1 kOe field was switched on and susceptibility measured to 20 K. The diamonds represent data for a sample cooled in ZF to 2 K and then heated to 5 K, at which point a 1 kOe field was turned on and measurements taken to 20 K. As mentioned previously the data between 2 and 4.4 K show asperomagnetic behavior. The discontinuity represents a reorientation of the spin structure that subsequently relaxes until 8 K when the barriers to spin alignment have decreased and a speromagnetic behavior below T_f is observed. The sample heated from an initial temperature of 5 K never experienced the magnetic spin reorientation that occurs near 4.4 K and follows the path expected for a speromagnet below T_f. The data represented by diamonds in Figure 6 for the specimen that was warmed through the transition zone in zero field behaves the same way as the 5 K sample. When a magnetic field is switched on at 2 K for a ZFC sample there is an initial spin orientation with the field, the isothermal remanence, providing a maximum moment that begins to relax as the temperature increases. At constant temperature this moment should increase with the applied field, and the data of Figure 7 show that this is the case. Indeed, at 10 kOe the transition zone has almost disappeared. At 0.3 kOe the field is small enough where the magnetization below the transition zone follows speromagnetic spin glass behavior. With increasing field strength the barriers to spin alignment are overcome and at 10 kOe the sample behaves as a superparamagnet.

The magnetic field dependence of the various magnetic configurations at different temperatures were investigated by measurements of M vs H for ZFC and FC specimens as well as the thermoremanent moment (TRM). Figure 8 shows the M vs H plot at 3 K. Hysteresis and near saturation are observed as expected for a spin glass. The ZFC loop is symmetric about $H = 0$ with a small remanent magnetization of about ±170 emu/mol Fe and a small coercive force of ±1000 Oe (Figure 8b). The field-cooled sample loop is shifted to the negative field side yielding a coercive force of −1400 and +600 Oe and a remanent magnetization of +190 and −100 emu/mol Fe (Figure 8b). The saturation magnetization is reached at about 2700 emu/mol Fe at a field of 50 kOe equivalent to a saturation moment of 0.48 μ_B/atom of Fe. A similar experiment was carried out at 8 K corresponding to the temperature where the asperomagnetic spin structure changes to the speromagnetic. As expected, hysteresis is observed for ZFC and FC samples, and the loop is symmetric for the ZFC and shifted to the negative field side for the FC sample. M_r and H_c are smaller than at 3 K. Saturation is not reached and the curve becomes a straight line between 10 and 50 kOe, suggesting an antiferromagnetic contribution. The same experiment was repeated at 50 K for the ZFC and FC samples. The curves are identical, and no hysteresis is observed. A straight line dependence is observed above 10 kOe.

Relaxation phenomena were studied by equilibrating a sample in the SQUID at 100 K in zero field; a field of 1 kOe was applied at 100 K and the temperature was lowered to the desired value. At that point the field was turned off and the thermoremanent moment, TRM, was recorded as a function of time.[39] Néel pointed out that thermal fluctuations can cause the direction of magnetization of small, single-domain particles to undergo random changes that result in a decay of the remanent magnetization according to $M_r(t) = M_r(0)\exp(-t/\tau)$, where t is the time after removal of the field and τ a relaxation time following an Arrhenius law.[40] However the particle size distribution in real systems causes a

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(39) Rossel, C. In *Relaxation in Complex Systems and Related Topics*; Campbell, I. A., Giovanella, C., Eds.; Plenum Press: New York, 1990.

(40) Néel, L. *Compt. Rend.* **1949**, *228*, 664.

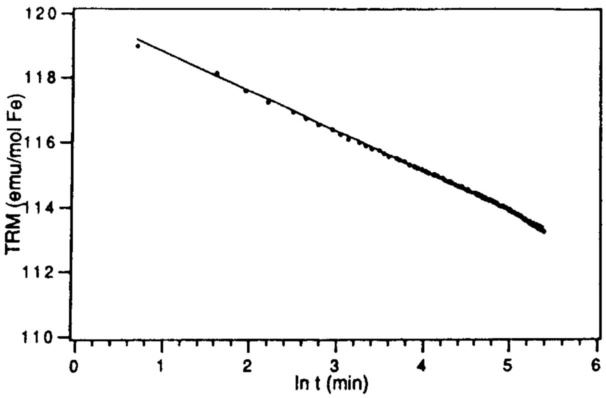

Figure 9. Variation of TRM with ln(t) [t in min] at 3 K for a specimen heated at 500 °C for 22 h.

Table 2. Magnetic Relaxation Parameters

sample	T (K)	TRM(0)[a] (emu/mol Fe)	$-S$ (emu/mol Fe)
200 °C/48 h	3	138.0	2.58
	8	40.3	3.70
	8	36.3	2.23
	20	4.2	0.18
500 °C/22 h	3	120.0	1.2
	8	107.0	2.3
	20	41.0	1.1
500 °C/48 h	8	80.5	2.1
	20	18.4	0.9

[a] Esd's are ±0.3.

distribution in τ and the time dependence is more complex. The relaxation data are commonly analyzed with a logarithmic function:

$$\mathrm{TRM}(t) = \mathrm{TRM}(0) - S\ \ln(t)$$

where TRM(0) is the initial value, and $S = \Delta[\mathrm{TRM}(t)]/\Delta[\ln(t)]$ is the coefficient of magnetic viscosity. Figure 9 is representative of the data for the three specimens except for the 200 °C, 22 h, sample at 8 K that showed two distinct slopes. Table 2 summarizes the magnetic relaxation parameters. The values of TRM(0) decrease with increasing temperature as expected because the barriers to the randomization of the spins are lowered by the thermal energy. As the freezing temperature is approached $|S|$ nears a maximum. This is consistent with the behavior of other spin glass systems.[39] Above T_f the barriers to spin randomization have nearly vanished and relaxation occurs quickly.

(c) Samples heated at 500 °C/60 h, 750 °C/72 h. The inverse magnetic susceptibility vs T of the specimen heated at 500 °C for 60 h shows no discontinuity near 4.4 K, and the ZFC and FC curves coincide. Below 6 K the curve turns toward the origin consistent with a speromagnetic spin glass. The prolonged heating has destroyed the nearest-neighbor magnetic interactions, but the X-ray diffraction diagram still shows that the sample remains pillared (Figure 1f). The X-ray diffraction pattern of the specimen heated at 750 °C for 72 h (Figure 2) shows that the pillaring has been destroyed, and a 9.9 Å spacing characteristic of a collapsed montmorillonite structure is discernible. In addition weak, broad diffraction lines due to Fe_2O_3 can be identified. The ZFC χ^{-1} vs T plot for this sample (Figure 10) shows a straight-line section from about 25 to 300 K, and when these data are fit to the Curie−Weiss law, $\theta = -92$ K and $\mu_{\mathrm{eff}} = 13.9\ \mu_B$. The high value of the effective moment is due to the presence of finely divided particles of hematite. Below 25 K (Figure 10 insert) the curve turns down to the origin, characteristic of a speromagnetic spin glass. Since the silicate framework was still present, this specimen was treated with a polycation solution at room temperature and the X-ray diffraction pattern shows that pillaring has taken place (Figure 1g). The Fe concentration in the sample has increased by about 9% and the density to 3.27 g/cm^3 (Table 1). The ZFC χ^{-1} vs T plot shows a concave curvature between 25 and 300 K as is observed for other heated pillared specimens, e.g., 500 °C/22 h. Near 25 K there is an inflection point, and the curve turns down to the origin.

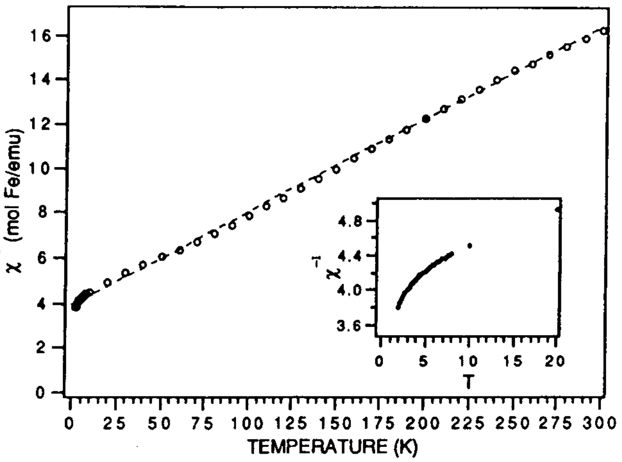

Figure 10. Variation of χ^{-1} in ZFC as a $f(T)$ for the sample heated at 750 °C for 22 h.

Summary and Conclusion

The intercalation of Fe−polyoxocation into montmorillonite expands the silicate layers approximately 15 Å and chemical analysis indicates that between 7 and 8 Fe atoms are present per unit cell. The structure of the polyoxocation is unknown, but the 15 Å height is consistent with a linear, trinuclear, octahedral complex in which the atoms occupying the apexes of the central octahedron are shared. The ligands are most likely OH^- and H_2O. Other configurations of the intercalate molecule are likely, and they coexist with the trinuclear complex in the gallery space to give rise to the observed mixed layering of montmorillonite. Thermal treatments of the intercalated montmorillonite indicate that they are stable at 500 °C when heated for 60 h although the magnetic behavior is changed. After heating for 72 h at 750 °C, the structure collapses to 9.9 Å with the formation of Fe_2O_3. This specimen can be reexpanded by treating it with Fe−polycation solution.

The magnetic susceptibility measurement of a dried specimen of the Fe−polycation shows that it behaves as a speromagnet. A room-temperature pillared montmorillonite specimen exhibits paramagnetic behavior. When heated at 200 °C for 22 h, the ZFC and FC magnetic measurements below about 25 K show speromagnetism. The specimens heated at 200 °C for 48 h, 500 °C for 22 h, and 500 °C for 48 h exhibit similar magnetic properties. A magnetic phase transition is observed at about 4.4 K for ZFC samples. When a field of 1 kOe is applied to the specimen at 2 K, the interactions among various anisotropies and thermal barriers create an asperomagnet that begins to relax to 4.4 K, at which temperature a pronounced rise in the magnetization is observed due to a reorganization of spins into a different asperomagnetic structure. The input of thermal energy has been effective in lowering the barriers that prevented the spins to align with the field at 2 K. This phase change should disappear with increasing field strength, and indeed at 10 kOe it is barely visible and the sample behaves as a superparamagnet. The phase change is observed only for specimens that experienced a magnetic field below 4.4 K. Cooling to 2 K, warming the sample to 5 K in the absence of a field, and then measuring the susceptibility produce a speromagnet. The freezing temperature is about 15 K.

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