Magnetic susceptibilities of representative smectites

WILLIAM S. CALLAWAY, 3RD, AND JAMES L. MCATEE, JR.

Chemistry Department
Baylor University, Waco, Texas 76798

Abstract

The magnetic susceptibilities (χ) of low iron phyllosilicates montmorillonite, beidellite, hectorite, and saponite were measured and compared with those found after cation exchange with Na, Ca, La, and H and dehydration at 300°C. The observed χ values of all samples were greater than that attributable to Fe substitution in the structure of the smectites and varied significantly with the type and amount of the substitutions in the octahedral, tetrahedral, and interlayer positions. Dehydration at 300°C produced only small decreases in χ for the clays.

The calculated values of χ attributed to Na-exchanged smectite structures increased in the order montmorillonite < hectorite < beidellite < saponite, the predicted order of increasing instability of the apical O^{2-} ions in these structures. The defect centers might be formed by subsequent population of electron traps and/or formation of electron holes localized on Si–O or Al–O bonds adjacent to sites of isomorphic substitution.

Introduction

Recent advances in instrumental techniques have led to increased knowledge of the structure of clay minerals. X-ray fluorescence and X-ray photoelectron spectroscopy (XPS) have been used both for chemical analysis and for determining binding energies of various species within the clay layers (Marfunin, 1979; Koppelman, 1980). Due to the common inclusion of iron in the structure of clay minerals, Mössbauer spectroscopy has been utilized to define the electrical nature of different possible substitution locations (isomer shifts) and the distribution frequency of iron ions among them (quadrupole splitting) (Goodman, 1980). The recent expansion in the study of luminescent phenomena, such as triboluminescence and natural and radiation-induced thermoluminescence, associated with the layer silicates has provided data concerning the energetics of the electronic configurations of clays (McDougall, 1968; Lemons and McAtee, 1982). The application of electron paramagnetic measurements, EPR, to phyllosilicate systems has yielded information regarding the nature of specific paramagnetic species and their environment, orientation, electronic configuration, and mobility within clay lattices (Pinnavaia, 1980; Marfunin, 1979; McBride et al.; 1975; McBride, 1976).

Directly related to EPR is the measurement of bulk magnetic susceptibilities. Whereas EPR measures transitions between sets of energy levels, magnetic measurements are generally dependent on the thermally averaged populations of these sets of magnetically induced levels (Carlin and Van Duyneveldt, 1977). Kendall and Yeo (1951) noted that the average magnetic susceptibility of micas varied linearly with the total iron content, whereas the paramagnetic ani-sotropy was proportional to the Fe^{2+} content. Hood and Custer (1967) correlated variations of χ with Fe^{2+} and Fe^{3+} concentrations and the ionic-covalent nature of the Fe–O bond in octahedral sites of several trioctahedral micas. Beginning in the sixties, several researchers applying magnetic measurements to the characterization of samples of geological interest (Jones and Beavers, 1964; Osipov and Kinoshita, 1970) generally attributed the magnetic properties to inclusions of various ferro- and/or antiferromagnetic impurities. Prasad and Ghildyal (1975) presented results of χ determinations of several members of the phyllosilicate class from which external iron had been removed and suggested that the amount of Fe^{3+} substituting for Al affected the type of bonding undergone by the iron ions in the lattice.

To date, reports of bulk χ studies have stated that the samples had relatively high concentrations of lattice iron (1–15% by weight). Therefore, the possible presence of other paramagnetic sites has been masked by the strong iron moments. Also, the χ and EPR studies have, in large part, been restricted to materials which formed large single crystals, i.e., micas, or highly oriented micro-crystalline aggregates, such as kaolinites, of sufficient size to make the measurement of anisotropic properties feasible. In the current work, samples of various 2:1 smectites were obtained to avoid these problems and constraints. To assess the differences, if any, in magnetic properties of these minerals, member species representing di- and trioctahedral lattice types and tetrahedral and octahedral lattice substitutions were chosen. Each species was exchanged with four different cations in order to study the possible χ variations generated by lattice electronic perturbations caused by exchange cations in both hydrated and dehydrated samples.

Experimental

Materials

Samples were chosen to cover a range of structures and chemical compositions (Table 1). Indian talc is a trioctahedral species with minimal substitution while the Texas montmorillonite and Black Jack, Idaho beidellite are dioctahedral species with the major substitutions in the octahedral and tetrahedral sheet, respectively. California hectorite and California Ballarat saponite are trioctahedral smectites with octahedral and predominantly tetrahedral substitution, respectively.

Approximately 2% by weight aqueous dispersions were prepared. Primary purification consisted of the sequential gravity-sedimentation procedure detailed by Jackson (1975). X-ray powder diffraction patterns showed the resulting <2-μm fractions to be free of mineralogical impurities (i.e., quartz, calcite, dolomite). Each sample was then subjected to a 10-min citrate-bicarbonite-dithionite (CBD) extraction treatment (Jackson, 1975), for the removal of iron oxide, phosphate, and calcite impurities under conditions where structural iron is minimally affected. The CBD extraction was then repeated to ensure the complete removal of noncrystalline iron oxides. Portions of each dispersion were then dried and Fe determinations were made by energy dispersive X-ray fluorescence.

Each sample was exchanged with Na^+, Ca^{2+}, La^{3+}, and H^+. Na-, Ca-, and La-exchange were achieved by adding 1 N solutions of the chloride salts to the Na clays resulting from the CBD treatment. The suspensions were then repeatedly centrifuged and rinsed with water until a negative $AgNO_3$-chloride test was achieved with the supernatant (Jackson, 1975). H-exchange was carried out by stirring the clay suspensions with H-exchanged Dowex 50 exchange resin at 30°C for 5 min and then filtering it through a 40-mesh sieve. The final volume of each of the exchanged clay dispersions was then adjusted to obtain clay concentrations of 1% by weight.

Methods

X-ray powder diffraction (XRD). Oriented samples of each dispersion were prepared by pipetting aliquots onto glass slides, drying at room temperature, and equilibrating at 52% relative humidity (RH) by storing them in closed containers over saturated $Ca(NO_3)_2$ solution. The remaining suspensions were dried at 90°C, then ground to pass through a 270 mesh sieve (53 μm), and equilibrated at 52% RH.

XRD patterns were obtained on a Philips High-angle diffractometer with a theta-compensator using CuKα radiation with a graphite curved-crystal monochromator.

Chemical analysis. Chemical formulae were calculated on the basis of elemental analysis obtained by energy-dispersive X-ray fluorescence (XRF) analysis. Uncoated pellets of each exchanged species mounted on carbon planchets were examined at 25 kV in a JSM-35 scanning electron microscope equipped with a Si(Li) X-ray detector and a Tracor NS-880 pulse-height analysis system. The Tracor Northern Super ML (multiple least squares) program was used to deconvolute the spectra and to calculate elemental ratios based on Si peak/continium values. By calculating Si based elemental ratios rather than direct elemental percentages possible matrix effects were minimized. Silicon peak/background (P/B) ratios were converted to Si weight percents using a calibration curve constructed from Si P/B ratios obtained from independently analyzed Si-containing minerals with similar matrices supplied by the National Bureau of Standards and the Bureau of Analyzed Samples, Ltd. of Great Britain. The remaining elemental ratios were then converted to weight percents. Analyses for iron in each sample, after dissolving in HF, were also made by atomic absorption spectroscopy by the method of Jackson (1975). The EPR data for each of the Na-exchanged samples indicated an amount of iron proportional to that found by the XRF and chemical analysis. The formulae were calculated following the cation-allocation procedure of Jackson (1975).

Electron Paramagnetic Resonance (EPR) analysis. EPR data were obtained using a Varian E-104 X-band spectrometer. The samples were run as dry powders at room temperature. (McBride, 1984).

Magnetic susceptibility measurements. A Model DTL Faraday Magnetic Susceptibility System produced by Cahn Instruments was used for the measurement of the magnetic susceptibility. In this method, specimens are maintained in a region of constant

Table 1. Calculated unit cell formulae and sources of phyllosilicate samples

Sample	Unit cell formula[1]	Exchange[2] cations	Source
Talc	$(Si_{7.92}Al_{0.08})Mg_{5.92}Al_{0.04}Fe_{0.03}O_{20}(OH)_4$	0.00	India; Magcobar Houston, Texas
Hectorite	$(Si_{8.00})(Mg_{4.70}Li_{1.15}Fe_{0.06})O_{20}(OH)_4$	1.04	Hector, California; Baroid Division, NL Industries, Houston,TX
Saponite	$(Si_{6.85}Al_{1.15})(Mg_{5.79}Al_{0.12}Fe_{0.07})O_{20}(OH)_4$	0.98	Ballarat, California J.L.Post, CA. State University, Sacramento, California
Montmorillonite	$(Si_{8.00})(Al_{3.20}Mg_{0.72}Fe_{0.06})O_{20}(OH)_4$	0.73	Texas, Gonzales County The Clay Minerals Society
Beidellite	$(Si_{6.95}Al_{1.05})(Al_{3.91}Mg_{0.02}Fe_{0.06})O_{20}(OH)_4$	1.10	Black Jack Mine, Idaho J.S. White--Smithsonian Institution (#24679)

1. Calculated from X-ray fluorescence analysis with Fe values determined by atomic adsorption spectroscopy.

2. Exchange cations calculated as +1 species.

field gradient ($H(dH/dx)$) and the force acting on them are measured. The constant field gradient constraint requires that the displacement of a specimen upon application of the external magnetic field be kept very small or eliminated; for this reason the specimen size is kept as small as possible (Figgis and Lewis, 1960).

In order to increase the sensitivity and precision of the Cahn instrument several modifications were made: (1) Measurement of weight changes (ΔW) in the 0–2 mg range to ± 0.01 mg was facilitated by feeding the Cahn balance recorder output into a Keithley 190 Digital Multimeter. (2) The track mechanism was rebuilt, strengthened and a spring-loaded bearing on the carriage was added which snapped into a track indentation to insure consistent horizontal positioning of the sample between the pole pieces when making in-field measurements. (3) Specially designed pole caps gave a well defined, constant $H(dH/dx)$ region of 0.64 cm. (4) Construction of a very stable balance platform, adjustment of the length of the hangdown wire, and careful design of the sample stirrup were designed to maintain the total sample volume within this constant $H(dH/dx)$ region. (5) A new stirrup made from brass wire, using silver solder, was ground with fine corundum paper to limit weight to 52 mg, consistent with good structural rigidity.

In order to further increase the sensitivity of the χ measurements, new sample holders of increased size (to hold more sample) but decreased weight were fabricated. They were made by crimping 1.6×3.8 cm sheets of thinned aluminum foil into capsules of 8 mm diameter and 9 mm depth. The average capsule weight was approximately 27 mg. As with the brass stirrup, every effort was made to achieve the minimum weight possible so as to increase the sensitivity of the apparatus. The sample holders were checked for magnetic susceptibility and only those showing $\Delta W = 0.00 \pm 0.01$ mg were retained and placed in scrupulously clean, numbered, aluminum block holders.

Preliminary weighings indicated that a maximum of 50 mg of sample could be placed in the 8 mm diameter holders, without packing, before the depth exceeded the 0.64 cm limit. Packing was avoided to minimize effects of magnetic anisotropy.

Triplicate samples of each of the exchanged, ground, 52% RH equilibrated powders were prepared by placing approximately 40 mg of powder in the Al capsules. Following the χ measurements of 22°C and after dehydration at 300°C, the dry weights of the mineral samples were determined by triplicate weighings.

The samples dehydrated at 300°C were transferred from the oven directly to the hangdown wire and the glass weigh chamber raised around it. The weigh chamber was then flushed with dry N_2 for 30 seconds to allow sample cooling and to minimize rehydration. At no time was the N_2 flow of sufficient strength to jar the mechanical taring of the balance. Immediately following the N_2 purge, ΔW_{sample} was obtained as the average of fire consecutive determinations. Consistent ΔW readings varying by no greater than ± 0.01 mg were obtained.

The χ values were calculated from the equation

$$\chi = (\Delta W/W)(K)$$

with $K = \chi_{standard}(W/\Delta W)_{standard}$

$Hg[Co(SCN)_4]$ was used as the calibration standard because of its definite composition, high stability, and accurately known susceptibility of 16.44×10^{-6} cgs/g ($\pm 0.5\%$ at 20°C) (Figgis and Lewis, 1960).

χ values were calculated for the 52% RH and 300°C measurements of each sample. The total error calculated by compounding the percent errors of each of the terms in the χ calculation was $\pm 0.1 \times 10^{-6} - 0.2 \times 10^{-6}$ cgs/g depending on the magnitude of χ.

Results

Inspection of the chemical formulae of the samples used in this study (Table 1) show that the only atomic species that would be expected, a priori, to be paramagnetic is iron. The unavailability of iron-free structures precludes an experimental determination of the diamagnetism of the clay lattices. An approximation of χ-diamagnetic can be made based on the additivity of specific ionic susceptibility by assuming the lattice ions to possess the same susceptibility values of isoelectronic noble gases as do free ions. That is, $Li^+ = He = -1.9 \times 10^{-6}$ cgs/mole; O^{2-}, Na^+, Mg^{2+}, Al^{3+}, $Si^{4+} = Ne = -6.74 \times 10^{-6}$ cgs/mole; and Ca^{2+}, $Fe = Ar = -19.6 \times 10^{-6}$ cgs/mole; $La^{3+} = Xe = 43.9 \times 10^{-6}$ cgs/mole (Weast, 1975). The resulting calculated values agree well with measured values obtained on various clay minerals (Kendall and Yeo, 1951 and Prasad and Ghidyal, 1975). The measured susceptibility values and the iron content of the samples are given in Table 2. χ_{wet} and χ_{dry} are the values determined for the 52% RH and 300°C treated samples respectively. It is immediately obvious from Table 2 that the relationship between χ and iron content for these phyllosilicates is not a direct one. Additionally, the nature of the balancing exchangeable cation is seen to have a very significant effect on the measured paramagnetism.

Possible explanations of bulk χ values

Three explanations can be proposed for the variations in the susceptibilities of the phyllosilicates studied: (1) the presence of additional paramagnetic atoms in the lattice or

Table 2. Bulk magnetic susceptibilities and Fe contents of samples. χ values are given in cgs units/g $\times 10^6$

Sample		mg Fe/g	χ_{wet}	χ_{dry}
			52% RH 22°C	300°C
Talc	-Na	2.4	1.2 (1)	1.2 (1)
	-Ca	2.4	0.8 (1)	0.8 (1)
	-La	2.4	0.8 (1)	0.8 (1)
	-H	2.4	1.0 (1)	1.0 (1)
Hectorite	-Na	4.6	2.0 (1)	1.9 (1)
	-Ca	4.6	1.1 (1)	1.2 (1)
	-La	4.4	1.2 (1)	1.3 (1)
	-H	4.7	1.2 (1)	1.0 (2)
Saponite	-Na	5.3	4.1 (2)	4.0 (2)
	-Ca	5.3	6.0 (2)	5.8 (2)
	-La	5.2	8.2 (2)	7.9 (2)
	-H	5.4	6.8 (2)	6.6 (2)
Montmorillonite	-Na	4.6	1.5 (1)	1.5 (1)
	-Ca	4.6	2.2 (1)	2.3 (1)
	-La	4.5	2.2 (1)	1.8 (1)
	-H	4.7	3.5 (1)	3.3 (1)
Beidellite	-Na	4.3	3.2 (1)	3.3 (1)
	-Ca	4.3	3.8 (1)	3.8 (2)
	-La	4.2	3.3 (1)	3.4 (1)
	-H	4.4	4.2 (2)	4.3 (2)

in separate phases, (2) the presence of iron in differing oxidation and/or spin states, and (3) the existence of paramagnetic centers intrinsic to the lattice.

Additional paramagnetic atoms. Following initial chemical screening, physical purification, and the CBD treatment, no evidence of non-ferrous lattice substituents or extra-lattice impurities was found in X-ray diffraction patterns or in elemental microprobe analysis data. The quantitative detection limits for those paramagnetic ions which are commonly found as trace lattice substituents, particularly Ti^{3+} and Mn^{2+}, are approximately 0.1 wt.%. EPR signals of solid-state Mn^{2+} were observed in the saponite, talc and beidellite samples, although the high sensitivity of EPR in detecting paramagnetic impurities suggests that Mn content of the samples was small (McBride, 1984). Calculations indicated that 0.1% or more of these trace elements should have produced observable changes in the χ obtained experimentally.

Presence of iron in different oxidation and/or spin states. The number of unpaired electrons and, therefore, the magnetic moment possessed by silicate lattice iron varies with its charge and spin state. In a strong octahedral field, low spin Fe^{2+} has zero and low-spin Fe^{3+} has one unpaired electron. In a weak octahedral field, high spin Fe^{2+} has four and high-spin Fe^{3+} has five unpaired electrons. The state of the iron in the silicates studied might therefore be expected to account for the observed χ variations (Hood and Custer, 1967). Mössbauer spectroscopy studies (Rozenson and Heller-Kallai, 1977; Taylor et al., 1968; Goodman, 1980) have indicated that iron present in the aluminosilicate lattice occurs in the high spin state. Further, Taylor et al. (1968) confirmed Grim's (1968) prediction that Fe^{2+} is restricted by size and charge considerations to the octahedral layer. It was also observed (Taylor et al., 1968; Rozenson and Heller–Kallai, 1977) that, while iron-rich, trioctahedral layer silicates such as biotite may contain Fe^{3+} in tetrahedral coordination, the presence of Fe^{3+} in the tetrahedral layer of the low-iron minerals used here is relatively rare and is limited to a maximum of approximately 5% of the iron present. The effects of iron on χ should thus be determined by the properties and relative amounts of high spin ferrous and ferric octahedral iron.

Paramagnetic centers intrinsic to the lattice. To assess the probability of the existence of other, lattice-related, magnetic centers in the minerals, values of χ due to lattice iron, obtained by assuming the maximum high-spin Fe^{3+} value of 2.66×10^{-4} cgs/g Fe and no dipole interactions, were subtracted from the χ bulk values. The results are shown in Table 3 as $\chi_{lattice}$.

Discussion

Nature of $\chi_{lattice}$

With the exception of substituting transition metal cations such as iron, the atomic constituents of the lattice should have electronic configurations possessing only paired electrons and, therefore, should exhibit only weak diamagnetism. The formation of paramagnetic centers

Table 3. Estimation of non-iron paramagnetism, $\chi_{lattice}$, of samples from: $\chi_{lattice} = \chi_{bulk} - (2.66 \times 10^{-4}$ cgs/g)(g Fe/g sample). All χ values are in cgs units/g $\times 10^6$.

Sample		χ_{Fe}	$\chi_{lattice}$	
			Wet (52% RH, 22°C)	Dry (300°C)
Talc	-Na	0.6	0.6	0.6
	-Ca	0.6	0.2	0.2
	-La	0.6	0.2	0.2
	-H	0.6	0.4	0.4
Hectorite	-Na	1.2	0.8	0.7
	-Ca	1.2	-0.1	0.0
	-La	1.2	0.0	0.1
	-H	1.3	-0.6	-0.3
Saponite	-Na	1.4	2.6	2.5
	-Ca	1.4	4.6	4.4
	-La	1.4	6.8	6.5
	-H	1.5	5.4	5.2
Montmorillonite	-Na	1.2	0.3	0.3
	-Ca	1.2	1.0	1.1
	-La	1.2	0.6	0.6
	-H	1.3	2.2	2.0
Beidellite	-Na	1.2	2.0	2.1
	-Ca	1.2	2.6	2.6
	-La	1.1	2.2	2.3
	-H	1.2	3.0	3.1

must, therefore, require the alteration of the lattice electronic configurations to produce the necessary unpaired electrons.

Recent quantum mechanical modeling of the smectite lattice by Aronowitz et al. (1982) indicated that the highest energy, filled molecular orbitals in the structure were virtually localized on the oxygens of the shared apical plane. Marfunin (1979) pointed out that the last electron added to oxygen is the one least strongly bound and it would occupy the highest energy molecular orbital and be the most easily removed. He further proposed that substitution of lower charged cations (Al for Si for example) would further destabilize the apical oxygens and lead to the production of stable hole-trapping centers. Jones et al. (1974) from EPR measurements on kaolin designated these framework paramagnetic centers as A-centers. Meads and Malden (1975) observed evidence of hyperfine splitting due to interaction with Al^{27} in some samples and suggested that the same defect could also be stabilized by tetrahedral Al for Si substitution. Both groups of researchers noted the high chemical and thermal stability of these A-centers.

McBride (1976) reported that the EPR defect spectra of compression-oriented samples of talc and pyrophyllite were very similar to those observed in the kaolinites and suggested the presence of similar stabilized holes in these 2:1 layer silicates. The first evidence of the occurrence of A-centers in the more highly substituted smectites was provided by Friedlander et al. (1963) from EPR studies of

Wyoming montmorillonite and an Illinois illite. Wauchope and Haque (1971) indicated the presence of highly stable, intralayer radicals in smectites and showed that the differences in the EPR spectra of different clays were due to varying lattice environments.

This proposal by Wauchope and Haque (1971) also suggests that the $\chi_{lattice}$ variations observed in this study (Table 3) might be attributable to the presence of stable hole traps in the silicate layers with the number and precise nature of the paramagnetic centers being determined by the lattice in which they occur. These holes would be formed at the expense of the electrons on the oxygens of the internal oxy-hydroxy sheets and stabilized on tetrahedral Si-O or Al-O bonds adjacent to sites of isomorphic substitution.

The formation of the $\chi_{lattice}$ centers can be caused by ionizing radiation, grinding or the magnetic field used in the measurement of χ. The samples used in this study were not irradiated in the period (several months) between the preparation of the exchanged forms of the samples and the measurement of the magnetic susceptibilities; therefore, this is probably not a significant factor.

In the hand grinding of the samples used, large pressures can be brought to bear on small sample areas thus imparting significant energies to the system. Zeller et al. (1955) suggested that such pressures could create high electrostatic voltages in local areas sufficient to release electrons and/or create new holes in the crystal lattice of a solid. Johnson and Daniels (1961) confirmed this by observing that triboluminescent intensity was directly proportional to the electric potential created during grinding. Keller (1955) observed similar effects in montmorillonite.

Recent studies (Lahav et al., 1982) of the effects of grinding on the luminescent properties of clays have been inconclusive. It seems reasonable, however, that if stable framework paramagnetic centers are formed in the grinding process their numbers would be related to the nature of the lattices.

The remaining physical perturbation applied to the samples which might cause the observed χ variations is the magnetic field itself. Systems with one unpaired electron which would be expected to show small paramagnetism, and systems with no unpaired electrons which would be expected to be diamagnetic, are sometimes observed to exhibit weak paramagnetism which is independent of temperature. This temperature-independent paramagnetism (TIP) arises from a mixing into the ground state of higher energy states which are not thermally populated. The magnitude of TIP is inversely proportional to the energy separation to a higher orbital state and is generally small in magnitude. (Figgis and Lewis, 1960; Carlin and Duyneveldt, 1977; Cotton and Wilkinson, 1972).

From the foregoing considerations, it is clear that the oxygens of the shared tetrahedral-octahedral sheet are central to any proposed magnetic centers in the layer silicates not involving a paramagnetic metal species. They are involved in the possible formation of hole traps (A-centers) in the lattice, and are the probable source of electrons which

might be trapped elsewhere in the system (Lemons, 1982). In both cases, factors which decrease the stability of the apical O^{2-} species in the lattice would lead to greater values of χ by either increasing the concentration of the framework paramagnetic centers, or by increasing TIP effects.

Intralayer effects. Pauling's electrostatic valence rule (Pauling, 1960) indicates that formation of an electrostatically stable lattice requires that the sum of the strengths of the electrostatic bonds to a lattice anion must equal the absolute value of the anion charge. Such calculations based upon the lattice environment about the apical oxygens (O_1) shown in Figure 1 indicate that all the clay configurations of this study are predicted to be unstable with the tetrahedrally substituted species (saponite and beidellite = -1 9/12, montmorillonite and hectorite = -1 10/12) showing the larger departure from the stable values of -2. The χ values measured for the Na-exchanged minerals (Table 3) suggest that this greater instability is manifested in the larger values of $\chi_{lattice}$ exhibited by the tetrahedrally substituted saponite and beidellite.

The quantum calculations of Aronowitz (1982) predicted that the energies of the topmost, filled MO's were inversely proportional to the electron density transferred from the oxygens (O_1 in Fig. 1) to the octahedral cations. The complete sequencing of the clays studied must, however, also include the remaining Al-O_1 or Si-O_1 tetrahedral bonds. Krauskopf (1979) has indicated that the Si-O bond is 52% covalent, while the Al-O bond is 40% covalent. The Al-O oxygen should, therefore, have significantly higher electron density and lower binding energy than the Si-O oxygen. The predicted ordering of the minerals in terms of increasing energy of the O_1 localized orbitals (increasing instability) would be montmorillonite < hectorite < beidellite < saponite which agrees with the ordering of the observed magnitudes of the $\chi_{lattice}$ values for the Na-exchanged species (Tables 2 and 3). The intralayer effects on $\chi_{lattice}$ thus seem to be dominated by the varying cationic arrangements generated by isomorphic substitution.

Interlayer effects. The variations of the measured χ values for samples of the minerals with differing exchange cations were significant (Tables 2 and 3) and are further illustrated in Figure 2. Differences between $\chi_{measurements}$ at 52% RH and 300°C generally were insignificant (Table 2). The positions and interactions of exchanged cations with the clay layers are generally sensitive to the hydration state of the interlayer space. Lemons and McAtee (1982), for instance, suggested the amount of stabilization imparted to a surface electron trap was inversely proportional to the rate of dehydration of the interlayer cation. Similarly, EPR studies (McBride et al., 1975) have indicated a sensitivity to the position of the cation in the structure unit which is in turn very much affected by hydration of the cations and the clay surface.

The variations in χ with cation exchange in saponite were the largest observed (Fig. 2). The magnitude of $\chi_{lattice}$ was seen to vary directly with the cation valence ionization
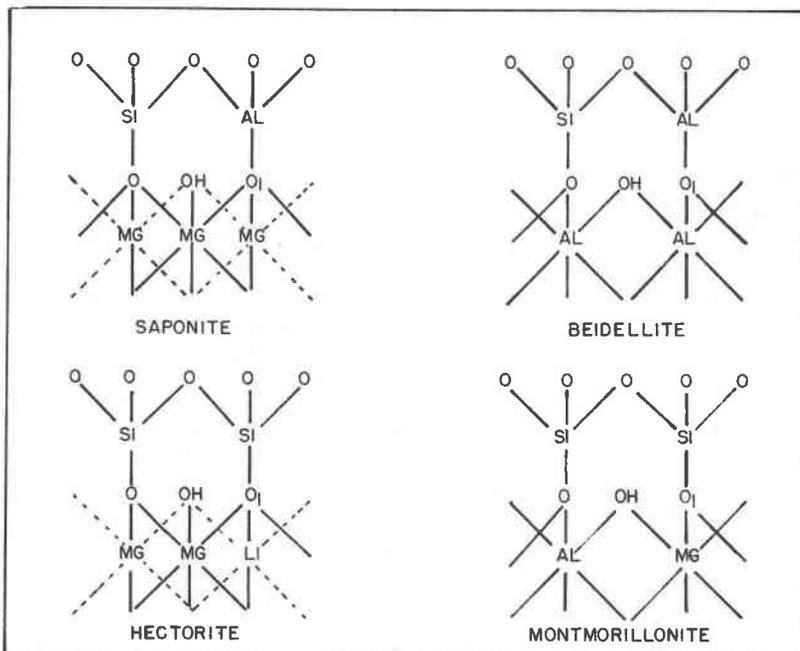
Fig. 1. Representations of smectite samples at sites of isomorphous substitution.

energy (proportional to polarizing power) of the cations if they are considered to be present with their full catonic charge, i.e., Ca^{2+}, La^{3+} (Fig. 3). EPR curves for the saponites show broad absorption peaks between $g = 4$ and $g = 2$, especially in the case of the La^{3+} saponite (Fig. 4) which may be due to structural defects. Kaolinite with structural defects show up as much narrower detailed spectra (McBride, 1976). The broad EPR absorption occuring for the saponites (and many of the other clays of this study) may arise from structural defects or adsorbed oxygen radi-

cals at the surface. The more acid exchangeable cations (La^{3+} and H^+) generate the most surface acidity (Rozenson and Heller–Kallai, 1978) and in general produce the most EPR absorption between $g = 4$ and $g = 2$.

The trend shown in Figure 3 fits well with the predictions made concerning the relationship between $\chi_{lattice}$ and the electronic instability of the apical oxygens, O_1 (Fig. 1). Bringing positively charged species near the basal oxygens coordinated to the Al might be expected to increase their electronegativity and, indirectly, the electronegativity of the
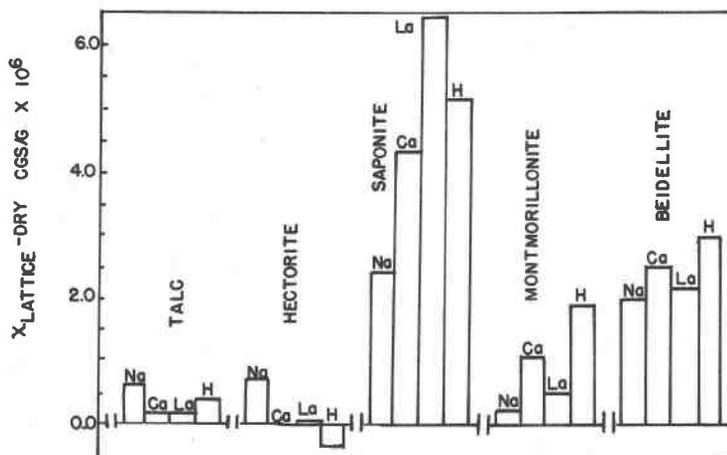
Fig. 2. Variation of $\chi_{lattice}$ with exchange cation.
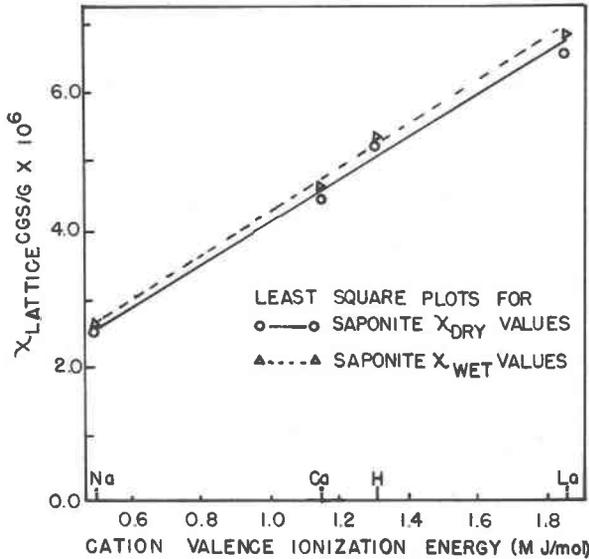
Fig. 3. Variation of $\chi_{lattice}$ with exchange cation polarizing power for saponite.

Al to which they are bound. Similar effects on Al binding energies have been observed in X-ray photoelectron spectroscopy studies of aluminum oxides (Lindsay et al., 1973).

The effects of exchange cations on χ and EPR spectra is somewhat different for the other clays in that they do not follow an orderly relationship with electronegativity as do the saponites. The effects of cation exchange on the measured χ values (Fig. 2) and EPR spectra are significant. Aronowitz et al. (1982) and Leonard and Weed (1970) have suggested that the presence of exchange ions may have a significant role in determining the electron density patterns in the silicate layers. The χ and EPR variations can be explained in terms of the ability of the exchange cations to change the instability of these oxygens adjacent to lattice substitution sites.
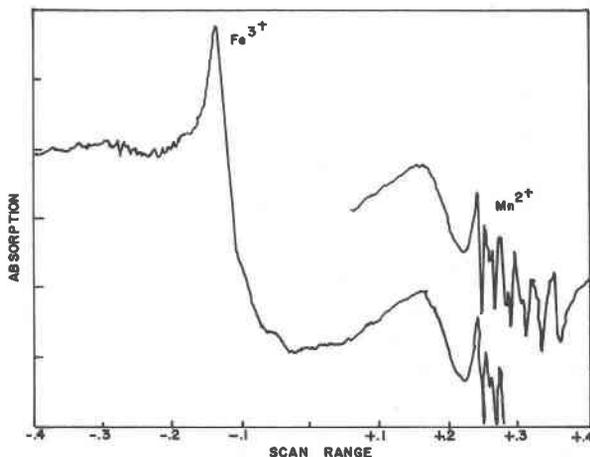
Fig. 4. EPR curve for La^{3+} saponite.

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