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Electron Spin Relaxation and the Mobility of Manganese(II) Exchange Ions in Smectites

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Abstract

The electron spin resonance spectra of Mn^{2+} exchange forms of vermiculite, nontronite, montmorillonite, and hectorite have been investigated at room temperature. Dipolar interactions between neighboring exchange ions and between the exchange ions and structural Fe^{3+} are the most important factors affecting the Mn^{2+} line widths. These relaxation mechanisms operate whether the interlayers are hydrated or dehydrated. Oriented film samples tend to exhibit different line widths when the magnetic field direction is oriented $\|$ and $\perp$ to the silicate sheets, indicating that the interactions between paramagnetic centers are anisotropic.

In hectorite, which contains little structural Fe^{3+}, dipolar effects have been eliminated by doping 5 percent Mn^{2+} into a Mg^{2+} exchange form, and the doped mineral has been used to examine the solution-like nature of the interlayers. Under fully hydrated conditions where the $Mn(H_2O)_6^{2+}$ is present in *ca* 12.5 Å interlayers containing several molecular layers of water, the lifetime of the complex ion between collisions with solvent molecules is estimated to be only 30 percent longer than for $Mn(H_2O)_6^{2+}$ in bulk solution. Under air-dried conditions, where the $Mn(H_2O)_6^{2+}$ ion is sandwiched between silicate sheets containing two molecular layers of water, a solution-like spectrum is retained, but the interlayer is considerably less mobile. When the mineral is thermally dehydrated at 200°C, the Mn^{2+} ions move into hexagonal positions in the silicate structure, and the solution-like spectrum is replaced by one characteristic of Mn^{2+} in certain crystalline matrices and frozen glasses.

Introduction

The significant chemical and physical properties of smectites often depend on the nature of the interlayer exchange ions. To better elucidate the structure and mobility of the exchange ions, several workers have recently applied electron resonance spectroscopy to certain Cu^{2+}- and Mn^{2+}-saturated forms. Fully hydrated Cu^{2+}-montmorillonites, for example, have been shown to possess tetragonal $Cu(H_2O)_6^{2+}$ ions which tumble rapidly in expanded interlayers containing several molecular layers of water (Clementz, Pinnavaia, and Mortland, 1973). Upon drying the mineral in air, the exchange ions lose two axial water ligands, which are held weakly because of Jahn-Teller distortion of the d^9 electronic configuration of the metal ion. The resulting planar $Cu(H_2O)_4^{2+}$ ions are confined to 2.8 Å-thick interlayer regions with the symmetry axis of the complex ion oriented at 90° to the silicate lamellae.

Furuhata and Kuwata (1969) have reported that the widths of the hyperfine (hf) lines of hydrated Mn^{2+} are broader on the exchange sites of montmorillonite than in bulk solution. The increase in line width was attributed to relaxation effects of the more restricted surface-adsorbed ions. Also, Mn^{2+}-montmorillonite has been reported to exhibit broader hf lines when larger molecules (*i.e.*, pyridine) replace water on ligand positions, a result again interpreted in terms of reduced mobility of the Mn^{2+}-solvent complex because of the size or bonding nature of the ligand molecules (Pafomov *et al*, 1971; Taracevich and Ovcharenko, 1972). However, in addition to mobility effects, other factors such as the site symmetry of the paramagnetic ion and dipolar interactions can also contribute to the observed ESR line widths. The present study investigates the ESR spectra of Mn^{2+} smectites of differing charge density and structural Fe^{3+} content under hydrated and anhydrous conditions. The relaxation mechanism controlling the hf widths of the mineral-bound ion has been defined, and a quantitative estimate of interlayer mobility has been obtained for fully hydrated hectorite.

Materials and Methods

The smectites used in this study are given in Table 1 along with their cation exchange capacities and reported unit cell formulas. The Mn^{2+}-saturated exchange forms were prepared by washing the native mineral ($<2\ \mu$ fraction) with aqueous 1.0 *M* $MnCl_2$. Excess salt was removed by dialysis with distilled water, and the mineral was recovered from the slurry by freeze-drying methods. Average $Mn^{2+} - Mn^{2+}$ distances within an interlayer were estimated from the CEC values and the theoretical surface area of 800 m^2/g (Grim, 1968).

X-ray basal spacings were determined with a Norelco diffractometer and Ni-filtered Cu/radiation. The magnetic susceptibilities of Mn^{2+}-hectorite, -montmorillonite, and -nontronite were measured by the Gouy method. The susceptibilities were corrected for paramagnetic contributions due to structural Fe^{3+} by subtracting the susceptibilities obtained for the Na^+ or Ca^{2+} exchange forms of the minerals. Only Na^+-hectorite, which has a low Fe^{3+} content, showed no paramagnetism. X-band ESR spectra were obtained with a Varian E-4 spectrometer. Oriented, self supporting film samples, in which the crystallographic *a* and *b* axes of each clay platelet lie in the plane of the film, were prepared by previously described methods (Clementz *et al,* 1973). The average widths of the $m_I = \pm 5/2$ transitions (outer two resonance components) of the mineral-bound Mn^{2+} signals were estimated by measuring the peak-to-peak separation between the lines and subtracting the field separation of analogous lines for the ion in dilute solution. This method assumes that the hyperfine splitting *A* is the same in the mineral and in dilute solution. The validity of the assumption was verified by observing an *A* value of 90 ± 1 *G* for the 5 percent Mn^{2+}-doped Mg^{2+}-hectorite, which is in agreement with the value of 95 ± 1 *G* reported for $MnCl_2$ in dilute solution (Levanon and Luz, 1968).

Results and Discussion

X-Ray Spacings

Because $Mn(H_2O)_6^{2+}$ is stable in aqueous solution, the ion is expected to be the major species present on the exchange sites of hydrated smectites. When two molecular layers of water are present in the interlayer, alignment of the octahedral faces of the ion with the silicate surfaces should give 001 basal spacings in the range 14-15 Å as is observed for $Mg(H_2O)_6^{2+}$ and $Cu(H_2O)_6^{2+}$ in vermiculite (Hougardy *et al,* 1970; Clementz *et al,* 1973) and for $Ca(H_2O)_6^{2+}$ (Brown, 1961) on montmorillonite. The observed spacings (Table 2) for the minerals under air dried conditions confirm the presence of the $Mn(H_2O)_6^{2+}$ ion.

With the exception of vermiculite, all of the Mn(II) clays expand at 100 percent relative humidity to give basal spacings of 19.2-22.0 Å. In general the degree of interlayer expansion increases with decreasing silicate charge density. Thermal dehydration at 200° for 24 hours leads to migration of the Mn(II) ions to hexagonal cavities formed by the surface oxygen atoms or, in the case of the dioctahedral minerals, to vacant octahedral positions in the silicate structure (McBride and Mortland, 1974). Thus the dehydrated minerals exhibit basal spacings (*ca* 9.5 Å) typical of totally collapsed layers.

TABLE 1. Mn^{2+}-Saturated Smectites

	C.E.C., meq/100g	Unit Cell Formula	Reference
Vermiculite Llano, Texas	200	$Mn_{1.00}[Al_{0.30}Fe_{0.02}Mg_{5.66}](Al_{2.28}Si_{5.72})O_{20}(OH)_4$	Foster, 1961
Montmorillonite Chambers, Arizona	116	$Mn_{0.48}[Al_{2.84}Fe_{0.35}Mg_{0.85}](Al_{0.22}Si_{7.78})O_{20}(OH)_4$	Schultz, 1969
Nontronite Garfield, Washington	104	$Mn_{0.42}[Al_{0.26}Fe_{3.70}Mg_{0.04}](Al_{1.00}Si_{7.00})O_{20}(OH)_4$	API, H-33A
Montmorillonite Upton, Wyoming	92	$Mn_{0.32}[Al_{3.06}Fe_{0.32}Mg_{0.66}](Al_{0.10}Si_{7.90})O_{20}(OH)_4$	Ross and Mortland, 1966
Hectorite Hector, California	73	$Mn_{0.32}[Mg_{5.42}Li_{0.68}Al_{0.02}](Si_{8.00})O_{20}(F,OH)_4$	API, Project 49

TABLE 2. Basal Spacings (Å) of Mn^{2+}-Smectites

	Air Dry Mineral	Fully Hydrated Mineral
Hectorite	15.0	22.0
Montmorillonite (Upton)	14.9	19.6
Nontronite	14.9	19.4
Montmorillonite (Chambers)	13.9*	19.2*
Vermiculite (Llano)	14.35†	14.35†

*Broad diffraction line, indicating interstratification.
†Very sharp diffraction peak.

Magnetic Susceptibilities

The high spin ($S = 5/2$) configuration of octahedral Mn^{2+} is preferred to the low-spin state with almost all ligands, including water, so that a magnetic moment near 5.9 B.M. is expected. Based on the reported unit cell compositions of hectorite, montmorillonite, and nontronite, susceptibilities corresponding to effective moments in the range 6.5-7.1 B.M. were obtained for the mineral-bound $Mn(H_2O)_6^{2+}$ ions under air-dried conditions. Deviations of the observed moments from the expected moment are attributed to uncertainties in the Gouy method and unit cell compositions. Within experimental error, however, no change in the susceptibility was observed upon dehydrating the minerals at 200°. Thus no spin pairing or change in oxidation state of Mn^{2+} occurs upon thermal dehydration.

Esr Spectra

The ESR spectrum of Mn^{2+} in solution normally consists of six hf lines due to coupling of the $S = 5/2$ electron spin with the $I = 5/2$ nuclear spin. Each hf component consists of three superimposed Lorentzian lines due to the five $\Delta m_s = 1$ transitions $|\pm 5/2\rangle \leftrightarrow |\pm 3.2\rangle$, $|\pm 3/2\rangle \leftrightarrow |\pm 1/2\rangle$, and $|-1/2\rangle \leftrightarrow |+1/2\rangle$ which are not resolved at X band frequencies. The non-degeneracy of the $\Delta m_s = 1$ transitions leads to inhomogeneous line broadening. The line widths are the sum of two contributions, $\Delta H = \Delta H_I + \Delta H_D$ where ΔH_I is the width arising from ion-solvent collisional relaxation processes (Rubinstein, Baram, and Luz, 1971; Luckhurst and Pedulli, 1971) and ΔH_D is the width due to dipolar interactions between neighboring Mn^{2+} ions (Hinckley and Morgan, 1966). The ΔH_D term is concentration dependent, because the dipolar interactions are proportional to r^{-3}, where r is the average $Mn^{2+} - Mn^{2+}$ distance. In dilute solution (<0.01 M, $r > 55$ Å) the lines are narrow and determined exclusively by ΔH_I. Increasing the concentration causes the six hf components to broaden markedly until at concentrations of 2.3 M or greater ($r < 9.0$ Å) the hf structure is lost and the spectrum appears as a single broad line (Hinckley and Morgan, 1966).

A typical spectrum for $MnCl_2$ in dilute solution is shown in Figure 1a. Fully hydrated Mn(II)-hectorite exhibits a similar "solution-like" spectrum, except that the hf lines are broader (Figure 1b). Reducing the amount of interlayer water from several to two molecular layers by allowing the mineral to dry in air at ~50 percent relative hu-

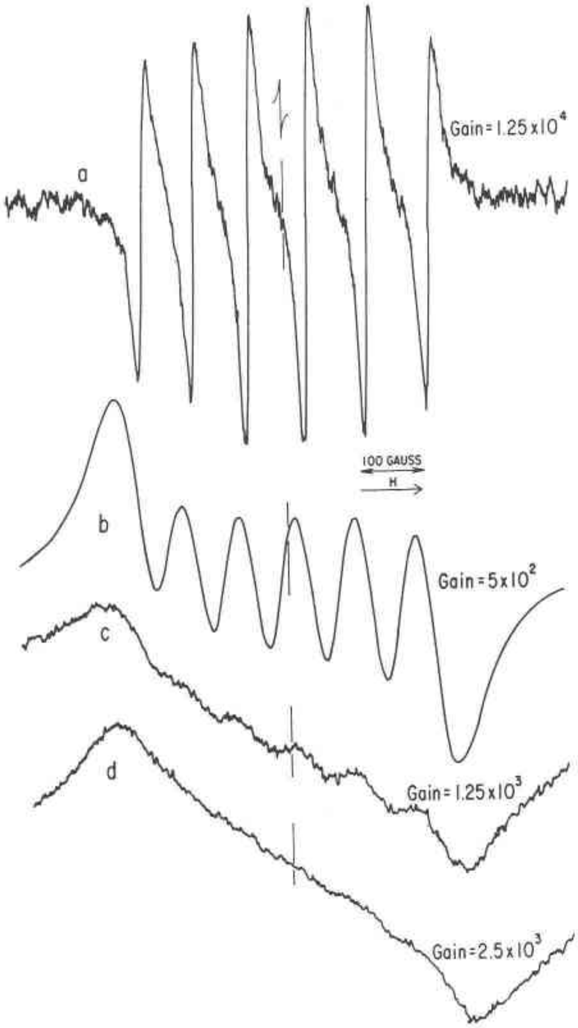

FIG. 1. Room temperature ESR spectra for (a) $MnCl_2$ in methanol ($5.0 \times 10^{-5} M$), and powder samples of hectorite (b) fully hydrated, (c) air-dried, and (d) dehydrated at 200°C for 24 hours. The vertical lines represent the resonance position of a standard pitch sample ($g = 2.0028$).

midity causes the lines to broaden markedly (Figure 1c). Thermal dehydration at 200° for 24 hours leads to still further line broadening and almost complete loss of hf structure (Figure 1d). Similar increases in line width with decreasing hydration are observed for the Mn^{2+}-saturated montmorillonites and nontronite.

Since the average interlayer exchange ion distance for each mineral is in the range 10–14 Å, the widths of the Mn^{2+} signals should be determined mainly by the ΔH_D term. This is verified by the comparison in Figure 2 of the average width of the $m_I = \pm 5/2$ lines for $MnCl_2$ in methanol solutions and the fully hydrated minerals. Further evidence for the importance of dipolar broadening is provided by the spectrum of Mn^{2+}-vermiculite. The interlayer exchange ion distance in this latter mineral (6.9 Å) is substantially smaller than 9.0 Å, and, as expected, only a single, broad line with a width of 710 *G* is observed. The broadening is similar to that observed for the solid $MnCl_2$ salt (830 *G*) and consistent with dipole-dipole coupling between magnetic ions 3 to 8 Å apart (Abragam and Bleaney, 1970).

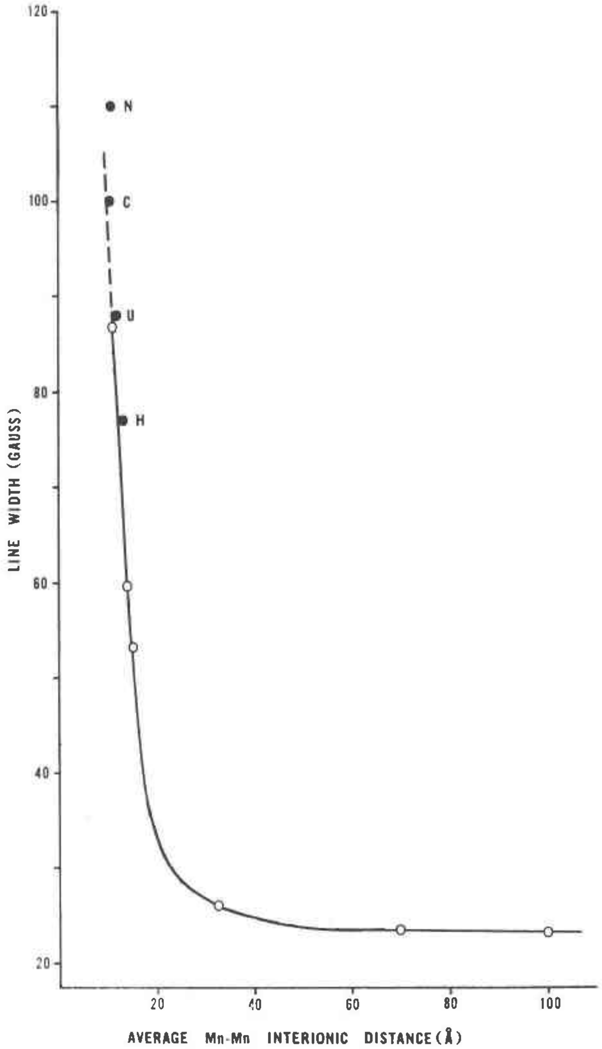

FIG. 2. Dependence of the average $m_I = \pm 5/2$ line widths of Mn^{2+} on interionic distance. Open points are for $MnCl_2$ in methanol solution, solid points are for nontronite (**N**), Upton (**U**) and Chambers (**C**) montmorillonites, and hectorite (**H**) under fully hydrated conditions.

In addition to dipolar coupling between Mn^{2+} ions within an interlayer, analogous interactions between ions in adjacent interlayers may occur. Also, the Mn^{2+} ions may be relaxed by coupling to Fe^{3+} in the silicate structure. These dipolar interactions along the crystallographic *c* direction should differ from those in the *ab* plane and should be manifested as differences in line widths and *g* values when the magnetic field direction is oriented $\|$ and $\perp$ to the silicate sheets. Figure 3 illustrates the spectra obtained for an oriented film sample of air-dried Upton montmorillonite. The average width of the $m_I = \pm 5/2$ lines is 15 *G* larger for the $\|$ than for the $\perp$ orientation. The *g* values also differ slightly for the two orientations, 2.005 *vs* 2.000 for the $\|$ and $\perp$ orientation, respectively.

Table 3 summarizes the widths for oriented samples of each mineral under air-dried and fully hydrated conditions. With the exception of hectorite, the widths for the air-dried samples differ by *ca* 15 *G* for the two orientations, whereas the widths are more nearly equal for the fully hydrated samples.

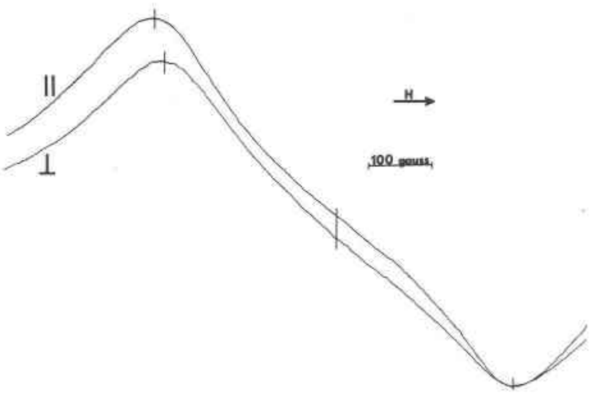

FIG. 3. ESR spectra for an oriented film sample of Upton montmorillonite with the magnetic field direction $\|$ and $\perp$ to the plane of the silicate sheets.

TABLE 3. ESR Line Widths of Oriented Mn^{2+}Smectites

	Interlayer Mn^{2+} - Mn^{2+} Distance, Å†	Air-Dried Mineral		Fully Hydrated Mineral	
		$\parallel$	$\perp$	$\parallel$	$\perp$
Montmorillonite (Chambers)	10.7	125	110	105	97
Nontronite	11.3	165	148	113	106
Montmorillonite (Upton)	12.0	125	110	89	86
Hectorite	13.6	93	90	75	79

*The widths are the average values in gauss for the $m_I = \pm 5/2$ resonance components with the magnetic field direction oriented $\parallel$ and $\perp$ to the crystallographic a b plane.

†This is the average distance between Mn^{2+} ions within an interlayer.

The dependence of the magnetic anisotropy on hydration state is not unexpected. In the air-dried minerals, the motion of the $Mn(H_2O)_6^{2+}$ ions is confined to the *ab* plane, but in the fully hydrated state the ions may tumble more nearly randomly. Near random tumbling would tend to average the magnetic anisotropy.

Both dipolar interactions between Mn^{2+} and structural Fe^{3+} and differences in the average Mn^{2+} — Mn^{2+} distances in the *ab* plane and the *c* direction appear to contribute to the observed anisotropy. Among the four minerals, hectorite has the lowest Fe^{3+} content (<0.14 percent). Also, in the air-dried state it exhibits the minimum disparity between Mn^{2+} distances within an interlayer and across interlayers. Consequently it shows little or no anisotropy in the air-dried as well as the fully hydrated state. Air-dried nontronite and the montmorillonites on the other hand contain greater amounts of Fe^{3+} (*cf* Table 1) and exhibit a greater disparity in exchange ion distances. Thus these minerals exhibit anisotropic line broadening in the air-dried state. Even in the fully hydrated state, however, the tumbling of $Mn(H_2O)_6^{2+}$ in nontronite and Chambers montmorillonite does not appear sufficiently random to completely average the anisotropy.

The importance of Mn^{2+} — Fe^{3+} dipolar interactions in the case of Mn^{2+}-nontronite is indicated by line widths which are larger than those for Chambers montmorillonite, despite longer exchange ion distances in the latter mineral. Their importance is further underscored in the dehydrated mineral where the ion occupies a hexagonal position or a vacant octahedral site very near Fe^{3+} in the silicate structure. Under these conditions the lines are so broadened that they are not detectable. There is little doubt that much of the line broadening observed on passing from fully hydrated to air-dried and thermally dehydrated nontronite is due to increasing dipolar interactions with Fe^{3+} as the Mn^{2+} ions move nearer the silicate structure. Similar effects are probably less important but still operative for the montmorillonites. In hectorite, where little Fe^{3+} is present, the increase in line widths with decreasing hydration state can only be interpreted in terms of reduced mobility of the interlayer. However, even in this latter case, it is difficult to assess quantitatively the interlayer mobility, because the line widths are still determined by an interionic dipolar relaxation mechanism involving neighboring Mn^{2+} exchange ions.

In absence of dipolar interactions, spin relaxation of $Mn(H_2O)_6^{2+}$ in solution results from molecular collisions between the solvated ion and solvent molecules which cause random distortions of the complex and induce a zero field splitting (Rubinstein *et al*, 1971; Luckhurst and Pedulli, 1971). Under appropriate conditions it is possible to obtain a quantitative comparison of the correlation time τ for the ion on the exchange surfaces and in bulk solution from the relative ESR line widths in the two environments. When $\omega_o\tau \ll 1$, which is generally the case for $Mn(H_2O)_6^{2+}$ at room temperature and at *X*-band frequency ($\omega_o = 0.58 \times 10^{11}$ radians/sec), the width of the $|-1/2\rangle \leftrightarrow |+1/2\rangle$ transition is directly proportional to τ and the inner product (D:D) of the zero field splitting tensor (Burlamacchi, 1971; Burlamacchi, Martini, and Tiezzi, 1970). Therefore, if the reasonable assumption is made that (D:D) is the same in bulk solution and on the exchange surfaces of the mineral, then the relative correlation times should be directly proportional to the ratio of line widths.

Dipolar interactions between $Mn(H_2O)_6^{2+}$ ions in hectorite were eliminated by doping a Mg^{2+} exchange form of the mineral with 5 percent Mn^{2+}. As illustrated in Figure 4a, the doped sample exhibits six, almost fully resolved HF lines under fully hydrated conditions. The width of the fourth highest field component at room temperature, which is a reliable estimate of the width of the $|+1/2\rangle \leftrightarrow |-1/2\rangle$ transition (Garrett and Morgan, 1966), is 28.7 *G*. In comparison, the width of $Mn(H_2O)_6^{2+}$ in dilute aqueous solution at room temperature is 22 *G*. Therefore the value of τ, which can be taken physically to be the precollision lifetime of the ion (Rubinstein

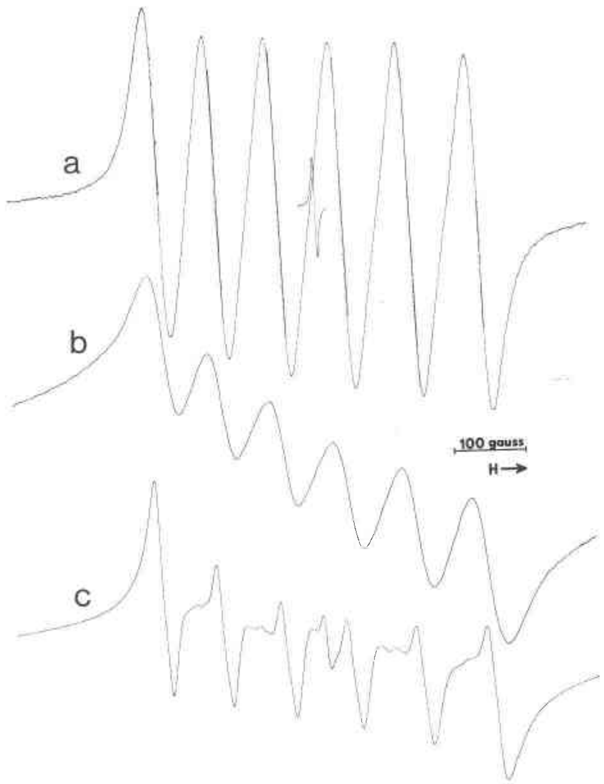

FIG. 4. Room temperature ERS spectra of powder samples of 5 percent Mn^{2+}-doped Mg^{2+}-hectorite (**a**) fully hydrated, (**b**) air-dried, and (**c**) thermally dehydrated at 200°C.

et al, 1971), is only *ca* 30% longer in the interlayer than in bulk solution where it has been estimated to be 3.2×10^{-12} sec. (Rubinstein *et al*, 1971). Thus the interlayer of the fully hydrated mineral is indeed very much solution-like. In contrast, τ for $Mn(H_2O)_6{}^{2+}$ has been estimated to be *ca* 2.2 times larger in three-dimensional synthetic zeolites than in bulk solutions (Tikhomirova *et al*, 1973).

Intuitively, drying the mineral down to two molecular layers of water should cause the mobility of the interlayer to decrease. This is confirmed by an increase in the line widths for the doped mineral, as illustrated in Figure 4b. However, the lines are too broad and overlapping (average width 48 *G*) to obtain a simple quantitative estimate of the $|-1/2\rangle \leftrightarrow |+1/2\rangle$ transition (Burlamacchi, Martini, and Romanelli, 1973).

Figure 4c shows the spectrum of the doped mineral under thermally dehydrated conditions where the interlayers are collapsed and the Mn^{2+} ions are coordinated to silicate oxygens in hexagonal positions. The spectrum consists of six main lines which represent the allowed $\Delta m_I = 0$ transitions and 5 pairs of weaker doublets which are due to forbidden transitions with $\Delta m_I = \pm 1$. This type of spectrum is characteristic of Mn^{2+} in certain crystalline matrices and in frozen glasses in absence of dipolar coupling (Allen and Nebert, 1964). Thus, as expected under anhydrous conditions, there is no solution character to the interlayer Mn^{2+} ions.

Conclusions

Because of the short exchange ion distances and the presence of structural Fe^{3+} in most smectite minerals, the ESR line widths of interlayer Mn^{2+} ions under hydrated and anhydrous conditions are controlled by anisotropic dipolar coupling between paramagnetic centers. In the case of hectorite, which has a low Fe^{3+} content, $Mn^{2+} - Mn^{2+}$ interactions can be eliminated by doping Mn^{2+} into a diamagnetic Mg^{2+} exchange form of the mineral. When the mineral is fully hydrated with the $Mn(H_2O)_6{}^{2+}$ ions in *ca* 12.5 Å interlayers containing several molecular layers of water, the interlayers are solution-like with the mean lifetime between ion-solvent collisions only slightly longer than found for bulk solutions. Under air-dried conditions, where the $Mn(H_2O)_6{}^{2+}$ ions are sandwiched between silicate sheets in interlayers two molecules of water thick, the interlayers are still solution-like but considerably less mobile than bulk solutions. Thermal dehydration transforms the solution-like ESR spectrum into one characteristic of the solid state as the Mn^{2+} ions move into hexagonal arrays of oxygen atoms in the silicate structure.

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