

# EPR Study of Montmorillonites from Several Deposits

<sup>a</sup>R. LÜCK, <sup>b</sup>R. STÖSSER, <sup>c</sup>D. GYEPESOVÁ, <sup>dt</sup>H. SLOSIARIKOVÁ, and <sup>e</sup>L. KOLDITZ

<sup>a</sup>*Institute of Physical Chemistry, University of Hamburg, W-2000 Hamburg, 13, Germany*

<sup>b</sup>*Institute of Analytical Chemistry, Humboldt University, O-1080 Berlin, Germany*

<sup>c</sup>*Institute of Inorganic Chemistry, Slovak Academy of Sciences, CS-842 36 Bratislava*

<sup>d</sup>*Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, CS-842 15 Bratislava*

<sup>e</sup>*Centre of Inorganic Polymers, O-1199 Berlin, Germany*

Received 7 November 1990

Accepted for publication 12 October 1992

EPR spectroscopic and magnetochemical investigations of natural montmorillonites originating from different deposits reveal the nature and localization of paramagnetic centres contained in the samples. The EPR spectra show that all montmorillonites investigated especially contain  $\text{Fe}^{3+}$  ions. These ions occupy lattice sites of the montmorillonite structure of maximal and, to a larger extent, slight to moderate rhombic deformation in the region  $g' \approx 4$  ( $g'$  = effective  $g$ -factor). Effective magnetic interactions (dipole—dipole and exchange interactions) occur between the  $\text{Fe}^{3+}$  ions located in  $\text{Al}^{3+}$  sites of the montmorillonite structure and those located in the interlayer space or on the surface of the crystallites. Analysis of the EPR spectra and of the dependence of magnetic susceptibility  $\chi$  values on the strength of the external magnetic field indicates that magnetically ordered phases are only rarely formed.

Additionally, the EPR spectra of montmorillonites from Jelšový Potok, Askangel, Borša, and Pyzhevskii display hyperfine structures of isolated  $\text{Mn}^{2+}$  ions in the  $g' \approx 2$  range. In the case of the montmorillonite from Jelšový Potok these  $\text{Mn}^{2+}$  ions are localized in moderately deformed octahedral sites of the montmorillonite structure.  $\text{Mn}^{2+}$  ions in samples of montmorillonites from Askangel, Borša, and Pyzhevskii are preferentially located in  $\text{Ca}^{2+}$  sites of calcite impurities. A resonance at  $g' \approx 2.009$  indicates the existence of paramagnetic oxygen defect centres in the samples. Measurements of the static magnetic susceptibility disclose strong paramagnetism for the samples from Borša, Braňany, and Taganskii. In contrast, those from Askangel, Jelšový Potok, and Pyzhevskii are only weakly paramagnetic.

The macroscopic properties of natural clay minerals determine the possibilities of their purification and applications. There is a strong connection between the macroscopic properties, structure, genesis and deposit of the mineral. Depending on the geological situation of the deposit, clay minerals contain various substitutional ions in different amounts. These substitutional ions can serve as probes for the study of the structure and dynamics of the clay minerals.

Clay minerals usually contain paramagnetic centres such as paramagnetic transition metal ions (e.g.  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$  ...  $x^+$ ,  $\text{V}^{4+}$ ,  $\text{VO}^{2+}$ ,  $\text{Cu}^{2+}$ ), paramagnetic defect centres ( $\text{O}^-$ ,  $\text{O}_2^-$ ,  $\text{Al}-\text{O}^-$ ,  $\text{Si}-\text{O}^-$ ,  $\text{Al}-\text{O}^--\text{Al}$ ), as well as radicals of organic com-

pounds ( $-\overset{\cdot}{\text{C}}^*$ ,  $\text{RCO}^*$ ) as constituents of natural

samples or incorporated by intercalation [1]. There are various possibilities for the localization of paramagnetic centres in clay minerals: They can be incorporated directly into the lattice occupying  $\text{Al}^{3+}$  sites (to a lesser extent  $\text{Si}^{4+}$  sites, too). They can also be found in the interlayer space as well as on the sur-

face of the crystallites. In addition, the paramagnetic ions can be constituents of autonomous impurity phases (e.g. iron oxides and their precursors) or of other minerals.

Due to very low amounts these ions are not detectable by diffraction methods in almost all cases. For investigating the magnetic properties of paramagnetic centres especially in low amounts (e.g.  $10^{16}$  spins  $\text{mT}^{-1} \text{g}^{-1}$ ), specific methods such as EPR spectroscopy are useful. Information from EPR spectroscopic investigations can be enhanced by static magnetic susceptibility measurements.

EPR studies dealing with montmorillonites from various deposits are found in the literature. They are mainly concerned with the incorporation of  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  ions into the montmorillonite structure [2–7], with the intercalation of paramagnetic ions such as  $\text{Cu}^{2+}$  and organic molecules such as pyridine, glycine, alanine, benzene, biphenyl, anthracene, and others [8–11] into the interlayer, and, in some cases, with ion exchange processes [5, 12]. However, the interpretation of the complex EPR spectra of natural montmorillonites evoked by

various paramagnetic species published has not been consistent [13]. This work was aimed at studying the nature, localization and function of paramagnetic centres in natural montmorillonites from different deposits, thereby contributing to the understanding of their complex EPR spectra.

## EXPERIMENTAL

The montmorillonite samples were collected at various deposits in Slovakia, Bohemia, Georgia, and Ukraine. To increase the sensitivity of the spectroscopy the montmorillonites were enriched by the sedimentation of particles  $\leq 2 \mu\text{m}$  from an aqueous suspension of bentonites [14], yielding samples with a montmorillonite content  $> 95 \%$ .

The EPR measurements were carried out using the continuous wave spectrometer ERS 300 and E4 (Varian) at X band frequency and temperature  $77 \text{ K} \leq T_M \leq 300 \text{ K}$  ( $T_M$  – the temperature of measurement). The values of static magnetic susceptibility were obtained using a Gouy balance.

## RESULTS AND DISCUSSION

The X band EPR spectra of natural montmorillonite samples of various deposits are illustrated in Fig. 1. Table 1 lists the deposits of montmorillonites investigated and their crystal chemical composition. The evaluation of the data in Table 1 shows that the total charge  $Q_t$  (esu/cell unit) of the montmorillonite from Blšany (1.33) is unexpectedly high. Values above 1 indicate the presence of mica-like minerals in the sample. The montmorillonite from Braňany also displays a high content of  $\text{Fe}^{3+}$  ions in  $\text{Al}^{3+}$  structural sites, which does not correspond with the intensity of the EPR signal observed in the  $g' \approx 4$  region (Fig. 1). These findings are, however, in agreement with findings by *Wiegmann et al.* [20] reporting an incorporation of  $\text{Fe}_{0.46}$ . Generally, number of iron atoms above 1 in  $\text{Al}^{3+}$  sites of montmorillonites are not found.

The EPR spectra illustrated in Fig. 1 may be viewed as follows. The general feature of all montmorillonite spectra is the appearance of resonances at  $g' > 3$  (especially at  $g' \approx 8.6$  and  $g' \approx 4.3$ ), a broad signal at  $g' \approx 2.2$  and a signal at  $g' \approx 2.009$ . Moreover, another broad signal ( $\Delta B \gg 0.1 \text{ T}$ ) having a small amplitude overlaps all the spectra of montmorillonites; it exhibits antiferromagnetic behaviour and represents antiferromagnetic iron oxides and their precursors (notably evident in the strongly deflected base line of the montmorillonite from Borša recorded at room temperature). Spectral differences observed for the montmorillonites investigated allowed us to classify them into two groups:

i) Montmorillonites with high iron content showing EPR spectra with less intense and poorly resolved resonances at  $g' \approx 8.6$  and  $g' \approx 4.3$  but very intense signals at  $g' \approx 2.2$  having pronounced low field tails. This type of spectra was observed for montmorillonites from Blšany, Braňany, and Taganskii (Fig. 1).

ii) Montmorillonites with low iron content showing EPR spectra with distinct resonances at  $g' \approx 8.6$ ,  $g' \approx 4.3$  and even at  $g' \approx 3.7$ ; the intensity of the signal at  $g' \approx 2.2$  is comparatively low. Additionally, in most of the samples investigated the hyperfine structure (hfs) of  $^{55}\text{Mn}^{2+}$  can be observed. This type of spectra was found for montmorillonites from Askangel, Borša, Pyzhevskii, and Jelšový Potok (Figs. 1 and 2).

The EPR spectra allow a classification of most of the natural montmorillonites, e.g. the spectra of montmorillonites reported by *Goodman* [21] and *McBride* [22] as Wards montmorillonite (Ca-form) and as Wyoming bentonites (Na-form) belong to the types i and ii, respectively.

Signals in the  $g' > 3$  range and parts of the high-field spectrum are due to  $\text{Fe}^{3+}$  ions in lattice sites of different rhombic distortion. The  $\text{Fe}^{3+}$  ions in sites of strong rhombic distortion describable by the spin Hamiltonian cause in the range  $g' \approx 4$  one resonance at  $g' = 4.3$  [23–25]. Additional resonances in the range  $g' \approx 4$  are assigned to  $\text{Fe}^{3+}$  ions in  $\text{Al}^{3+}$

**Table 1.** Deposits and Crystal Chemical Composition of Natural Montmorillonites Investigated

Sample	Deposit	$Q_t$	$Q^{\text{VI}}$	$Q^{\text{IV}}$	Crystal chemical composition	Ref.
1	Askangel, Georgia	1.06	0.98	0.08	$(\text{Si}_{7.92}\text{Al}_{0.08})(\text{Al}_{2.78}\text{Fe}_{0.36}\text{Mg}_{0.80})\text{O}_{20}(\text{OH})_4\text{Ca}_{0.52}$	[15]
2	Blšany, Bohemia	1.33	0.44	0.91	$(\text{Si}_{7.09}\text{Al}_{0.91})(\text{Al}_{3.10}\text{Fe}_{0.46}\text{Mg}_{0.44})\text{O}_{20}(\text{OH})_4\text{Ca}_{0.67}$	[16]
3	Borša, Slovakia	0.74	0.56	0.18	$(\text{Si}_{7.82}\text{Al}_{0.18})(\text{Al}_{2.93}\text{Fe}_{0.59}\text{Mg}_{0.44})\text{O}_{20}(\text{OH})_4\text{Ca}_{0.37}$	[17]
4	Braňany, Bohemia	0.96	0.19	0.77	$(\text{Si}_{7.23}\text{Al}_{0.77})(\text{Al}_{2.24}\text{Fe}_{1.57}\text{Mg}_{0.19})\text{O}_{20}(\text{OH})_4\text{Ca}_{0.48}$	[15]
5	J. Potok, Slovakia	0.95	0.54	0.41	$(\text{Si}_{7.59}\text{Al}_{0.41})(\text{Al}_{3.06}\text{Fe}_{0.34}\text{Mg}_{0.63})\text{O}_{20}(\text{OH})_4\text{Ca}_{0.48}$	[18]
6	Pyzhevskii, Ukraine	0.97	0.82	0.15	$(\text{Si}_{7.85}\text{Al}_{0.15})(\text{Al}_{3.05}\text{Fe}_{0.19}\text{Mg}_{0.73})\text{O}_{20}(\text{OH})_4\text{Ca}_{0.48}$	[19]
7	Taganskii, Georgia	0.89	0.63	0.26	$(\text{Si}_{7.74}\text{Al}_{0.26})(\text{Al}_{2.87}\text{Fe}_{0.54}\text{Mg}_{0.57})\text{O}_{20}(\text{OH})_4\text{Ca}_{0.45}$	[16]

$Q_t$  – total charge calculated for  $\text{O}_{20}(\text{OH})_4$  (esu/cell unit),  $Q^{\text{VI}}$  – charge of the octahedron (esu/cell unit),  $Q^{\text{IV}}$  – charge of the tetrahedron (esu/cell unit).

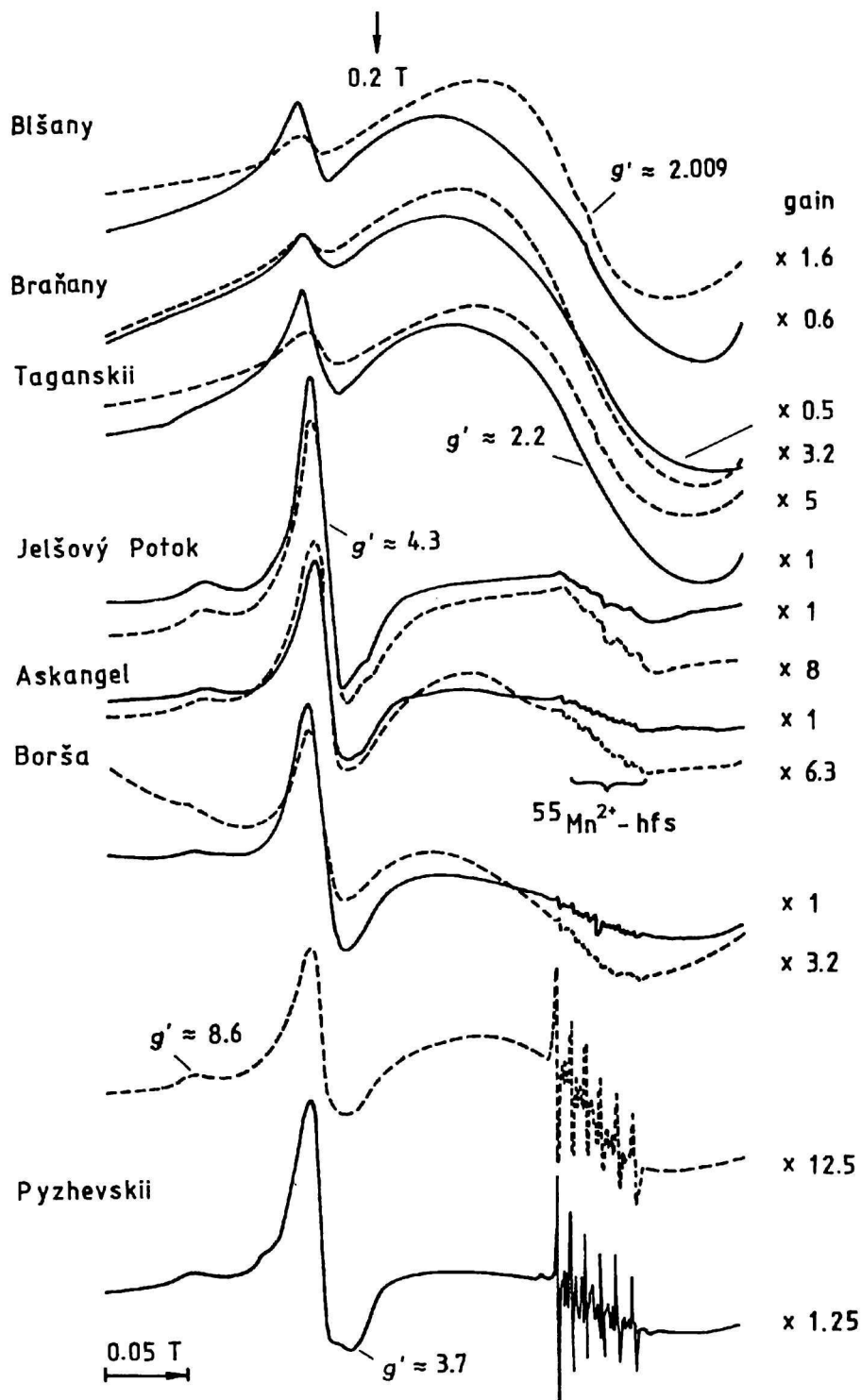
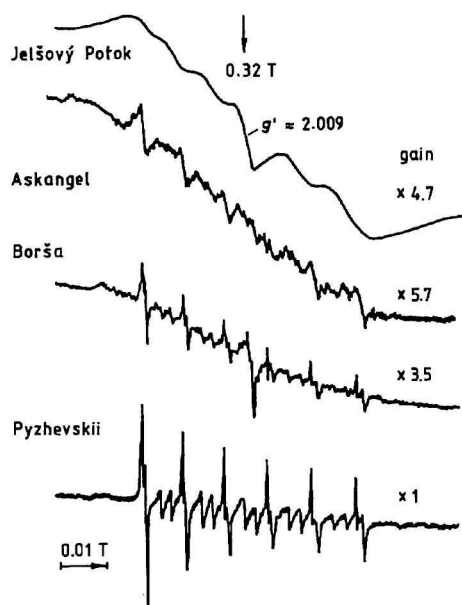


Fig. 1. EPR spectra of natural montmorillonites of various deposits measured at — 77 K and - - - 300 K.

sites of smaller rhombic distortion. The EPR signal at  $g' \approx 4.3$  is assigned to  $\text{Fe}^{3+}$  ions in  $\text{Al}^{3+}$  sites of strong rhombic distortion in interaction with other  $\text{Al}^{3+}$  ions of the lattice (*i.e.* the so-called  $\text{Fe}^{3+}-\text{Al}^{3+}$  pairs). Reports in literature favour  $\text{Fe}^{3+}-\text{Mg}^{2+}$  pairs to cause the resonance at  $g' \approx 3.7$ . Such pairs are formed by  $\text{Fe}^{3+}$  ions in  $\text{Al}^{3+}$  lattice sites in the neighbour-

hood of  $\text{Mg}^{2+}$  ions. The existence of  $\text{Fe}^{3+}$  ions in the low-spin state is not to be expected in the samples investigated.

The analysis of the integral intensities (calculated from the product of the signal amplitude and the square of the peak-to-peak line width) of the signals at  $g' \approx 4.3$  measured at 300 K and 77 K re-



**Fig. 2.** EPR hyperfine structure of  $\text{Mn}^{2+}$  ions in montmorillonite samples from Jelšovský Potok, Askangel, Borša, and Pyzhevskii (temperature of measurement 77 K).

veals a considerable deviation from the theoretical paramagnetic behaviour. The quotient of the signal areas at these two temperatures  $f_C = I(77 \text{ K})/I(300 \text{ K})$  (called Curie coefficient; see Table 2) lies significantly above the value expected from the Curie law for pure paramagnetism ( $f_C \approx 3.8$ ). The observed increase of the line width with decreasing temperature is remarkable. The dependence of the signal area and line width on the temperature is reflected by effective magnetic interactions between the unpaired electron spins (dipole–dipole and exchange interactions) and/or fine structure contributions due to lattice deformations.

The position and form of the signals as well as their dependence on the temperature and microwave power provide the following information concerning the nature and localization of the paramagnetic centres responsible for the signal at  $g' \approx 4.3$ : The signal is evoked by  $\text{Fe}^{3+}$  ions occupying  $\text{Al}^{3+}$  sites of strong rhombic distortion in the montmorillonite

structure. Strongly distorted  $\text{FeO}_6$  polyhedra in oxidic impurity phases can also contribute to these signals. The magnetic interactions observed can result for different reasons:

1. In the neighbourhood of  $\text{Fe}^{3+}$  ions (located in  $\text{Al}^{3+}$  sites of the montmorillonite structure) other  $\text{Al}^{3+}$  or  $\text{Mg}^{2+}$  ions can be substituted by  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$  ions, forming  $\text{Fe}^{3+}\text{—O—Fe}^{x+}$  pairs or clusters.

2.  $\text{Fe}^{3+}$  ions can be adsorbed on the surface of the crystallites, located in the water layer of the montmorillonite, e.g. forming aquacomplexes, or intercalated into the interlayer space (e.g. as  $\text{FeOOH}$  particles).

The formation of  $\text{Fe}^{3+}\text{—O—Fe}^{x+}$  pairs or aggregates in the montmorillonite matrix and their contribution to the signal intensity at  $g' \approx 4.3$ , especially at 77 K, appears to be probable due to the content of iron in the sample. The presence of  $\text{FeOOH}$  particles (e.g. goethite, lepidocrocite) in montmorillonites is well known from diffraction methods.

The EPR spectra of the most samples show a signal in the  $g' \approx 2.2$  region, having a line width above 0.1 T and paramagnetic behaviour. The intensity of this signal is lowered after extraction of the samples with 6 M-HCl [26]. On the other hand, its intensity and line width increases after additional intercalation of  $\text{FeCl}_3$  into the interlayer. These findings indicate that this signal is associated with Fe species, located in the interlayer. Such species may be  $\text{FeOOH}$  and could lead to the spectral pattern observed if the particle size of this mineral phase is extremely small (maximum volume  $\ll 10^4 \text{ \AA}^3$  [21]) and, consequently, result in volume-dependent magnetization.

In addition to the temperature dependence of the intensity of the resonance at  $g' \approx 2.2$  and results from diffraction methods, Mössbauer spectroscopic investigations reported by Goodman [21] indicate that the  $\text{Fe}^{3+}$  species responsible for this signal are located in a  $\text{FeOOH}$  phase, having small particles in the interlayer. This is supported by the temperature dependence of the line width and measurements of the dependence of the static magnetic susceptibility  $\chi$  on the strength of the external magnetic field applied. These suggest that the resonance at

**Table 2.** Peak-to-Peak Line Width  $\Delta B_{pp}/\text{mT}$ , Relative Intensities  $I_{rel}$  and Ratio of the Intensities (Curie Coefficient)  $f_C = I(77 \text{ K})/I(300 \text{ K})$  of the EPR Signals of  $\text{Fe}^{3+}$  Ions in Various Natural Montmorillonites Investigated

Deposit	$g' \approx 4.3$					$g' \approx 2.2$				
	$T_M = 300 \text{ K}$		$T_M = 77 \text{ K}$		$f_C$	$T_M = 300 \text{ K}$		$T_M = 77 \text{ K}$		$f_C$
	$\Delta B_{pp}$	$I_{rel}$	$\Delta B_{pp}$	$I_{rel}$		$\Delta B_{pp}$	$I_{rel}$	$\Delta B_{pp}$	$I_{rel}$	
Blišany, Bohemia	13.0	0.11	17.0	1.71	15.55	109.0	83.72	155.0	462.56	5.53
Braňany, Bohemia	15.0	0.07	17.5	1.42	20.29	146.5	129.89	163.0	1034.34	7.96
Taganskii, Georgia	20.0	0.17	21.0	2.81	16.53	128.5	46.08	146.0	366.37	7.95
Askangel, Georgia	21.0	0.90	20.0	7.19	7.99	105.0	13.95	105.0	38.35	2.75
Borša, Slovakia	21.5	1.60	22.5	8.38	5.24	124.0	39.25	145.5	91.95	2.34
Pyzhevskii, Ukraine	23.0	0.40	24.0	6.41	16.03	112.0	7.90	146.5	61.32	7.76
Jelšovský Potok, Slovakia	16.5	0.61	17.0	5.63	9.23	77.0	3.63	77.0	16.82	4.63

$g' \approx 2.2$  does not result from a totally ordered oxidic iron phase.

All experiments show a general field independence of  $\chi$  values at 300 K, thus excluding the existence of pure positive exchange interaction; but not contrasting to effects observed in the EPR spectrum. Exchange interactions were clearly evident in EPR spectra even at temperatures far from the Curie or Neel points [27].

Analysis of the EPR spectra of montmorillonites from different deposits allowed us to propose the following hypothesis in respect to the process responsible for embodying iron in the samples: At the beginning of the montmorillonite crystallite growth only a slight amount of impurity ions are incorporated. Relatively pure montmorillonite crystallites are formed, in which the few of  $\text{Fe}^{3+}$  ions present are fixed in  $\text{Al}^{3+}$  sites. The amount of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions incorporated depends considerably on the concentration and valence of iron in the environment (e.g. nature of the primary rock and its weathering), and on the growth conditions (temperature, pressure, growth rate, pH value, etc.). Small, slow-growing crystallites usually embody only small amounts of impurity ions. Further crystal growth can cause an enrichment of  $\text{Fe}^{3+}$  ions in the direct environment; this favours their incorporation with increasing crystal size.

At the same time the lattice tolerates, similarly to oxides and silicates, only a certain amount of impurity ions. In extreme cases up to 25 % of the  $\text{Al}^{3+}$  sites of the montmorillonite lattice can be occupied by  $\text{Fe}^{3+}$  ions. The signal intensity in the  $g' \approx 4$  region is characteristic of them.

The low iron content in the environment decreases even further upon prolonged crystallization; as a result, montmorillonites of low iron content with slight amounts of individual Fe—O phases corresponding to the spectrum type ii are formed (cf. the EPR spectrum of the montmorillonite from Jelšový Potok in Fig. 1).

If the supply of iron from the environment is higher,  $\text{Fe}^{3+}$  ions are incorporated into the lattice only up to a limiting  $\text{Fe}^{3+}$  content. Simultaneously, resulting from structural rearrangement, diffusion and hydrolysis processes, the formation of iron oxide hydrates occurs; these can be intercalated into the interlayer space of the montmorillonites and are responsible for the intensive signal at  $g' \approx 2.2$ . Magnetically ordered iron phases can also be formed separately. Montmorillonites, rich in iron content are generated; they are characterized by EPR spectra of the type i (cf. the EPR spectrum of montmorillonite from Braňany shown in Fig. 1).

The EPR spectra of montmorillonite from Jelšový Potok, Askangel, and Pyzhevskii exhibit additional hyperfine structures in the  $g' \approx 2$  region due to  $^{55}\text{Mn}^{2+}$

ions located in sites of various symmetry (Fig. 2). Montmorillonites from Jelšový Potok display in this region an incompletely resolved hfs with six lines and a hfs splitting constant  $\bar{A} \approx 9.7$  mT. Comparison with numerous Mn-containing compounds makes it possible to ascribe these hfs to a six fold coordinated  $\text{Mn}^{2+}$  ion with medium hfs contributions. The line width of the signal was found to be comparably large, which can be caused by interaction with adjacent  $\text{Fe}^{2+}$  ions, fine structure components, etc. It is not clear where  $\text{Mn}^{2+}$  ions in montmorillonite from Jelšový Potok are localized. They can be either incorporated into the montmorillonite structure, filling  $\text{Al}^{3+}$  or  $\text{Mg}^{2+}$  sites, or occupy sites on the surface, in the interlayer space, or in the aqueous layer (as deformed aquacomplexes). The incorporation of  $\text{Mn}^{2+}$  ions into the structure of montmorillonite from Jelšový Potok is supported by the following arguments:

a) Whereas in the case of the montmorillonite from Pyzhevskii the intensities of the signals of  $\text{Mn}^{2+}$  ions localized in the calcite impurity phase strongly decreased after treating the sample with HCl, the corresponding treatment of the montmorillonite sample from Jelšový Potok did not cause the same result without degrading the montmorillonite structure. Analogous findings were found upon HCl treatments of kaolins from Keokuk or Caminau.

b) Analogous spectral patterns in the  $g' \approx 2$  region were obtained upon incorporation of  $^{55}\text{Mn}^{2+}$  ions into heteropolyanionic compounds of Anderson or Keggin types. It has been shown that in this case Mn is incorporated into sites with six fold oxygen coordination with medium rhombic deformation [28]. A weak Anderson type Mn—Mn interaction is to be expected.

c) Spectra analogous to the Mn hfs of the montmorillonite from Jelšový Potok were first obtained after cooling  $5 \times 10^{-3}$  M aqueous solution of  $\text{MnSO}_4$ ; this can be rationalized by the decrease in the mobility of the solvent molecules and, consequently, the deformation of the  $\text{Mn}^{2+}$  sites is averaged out to a lesser degree [29]. If  $\text{Mn}^{2+}$  ions in the montmorillonite from Jelšový Potok are localized in a mobile aqueous phase, then a spectrum with comparably narrow lines has to be obtained at room temperature; this, however, is not the case.

The  $^{55}\text{Mn}$  hfs of EPR spectra of montmorillonites from Askangel, Borša, and Pyzhevskii are different from those of the samples from Jelšový Potok. Its EPR pattern exhibited signals of small line width ( $\Delta B < 0.5$  mT). The allowed transitions are resolved into two lines, the forbidden ones ( $\Delta m_l \neq 0$ ) are clearly evident. The spectral parameters were determined with  $g' \approx 2$ , hfs splitting constants  $\bar{A} \approx 9.7$  mT and  $|D| = 8.8$  mT for the montmorillonite from Pyzhevskii from the ratio of allowed ( $I_a$ ) and forbid-

den ( $I_i$ ) transitions according to [30].

The comparison of EPR spectra of various  $\text{CaCO}_3$  samples shows that the experimental parameters  $g'$ ,  $\bar{A}$ , and  $|D|$ , as well as the spectral patterns are characteristic of  $\text{Mn}^{2+}$  ions substituting  $\text{Ca}^{2+}$  ions. Therefore, calcite admixtures or calcite intergrowths can be anticipated. The signal intensities indicate that these are present in the greatest amounts in the samples from Pyzhevskii. Similarly, the sample from Askangel should contain only very little amounts of calcite. Based on these EPR results a calcite phase in the montmorillonite from Pyzhevskii ( $\approx 5\%$ ) could then be detected with X-ray diffraction.

In addition to hyperfine multiplets from  $\text{Mn}^{2+}$  ions another signal at  $g' \approx 2.009$  was observed; it is strongly overlapped by signals from  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  species. Signal positions and comparison with other systems [31] suggest that this signal can be ascribed to  $g$ -factor of the trapped holes ( $X-O^-$ ) or to oxygen containing species as  $O^-$ ,  $\text{RO}_2^*$ , and others.

Comparable findings concerning the total content of magnetic impurities allow the determination of static magnetic susceptibility. All montmorillonites investigated disclose a paramagnetic behaviour. The samples from Borša ( $\chi = 63.5 \times 10^{-6}$ ), Blšany ( $\chi = 38.3 \times 10^{-6}$ ), Braňany ( $\chi = 12.7 \times 10^{-6}$ ), and Taganskii ( $\chi = 12.9 \times 10^{-6}$ ) are strongly paramagnetic resulting from their relatively high content of iron impurities. In contrast, samples from Askangel ( $\chi = 6.80 \times 10^{-6}$ ), Jelšovský Potok ( $\chi = 3.30 \times 10^{-6}$ ), and Pyzhevskii ( $\chi = 1.93 \times 10^{-6}$ ) are weakly paramagnetic.

## REFERENCES

- Poole, C. P., Farach, H. A., and Bishop, T. P., *Magn. Reson. Rev.* 4, 225 (1978).
- Furuhata, A. and Kuwata, K., *J. Clay Sci. Soc. Jpn.* 9, 19 (1969).
- McBride, M. B., Pinnavaia, T. J., and Mortland, M. M., *Am. Mineral.* 60, 66 (1975).
- McBride, M. B., Pinnavaia, T. J., and Mortland, M. M., *J. Phys. Chem.* 79, 2430 (1975).
- Olivier, D., Vedrine, C., and Pezerat, H., *Bull. Groupe Fr. Argilles* 27, 153 (1975).
- Pafamov, N. N., Silchenko, V. A., Tarasevich, Yu. I., Telichkun, V. P., and Bratashevskii, Yu. A., *Ukr. Khim. Zh.*

- 37, 672 (1971).
- Silchenko, V. A. and Matyash, N. V., *Ukr. Khim. Zh.* 36, 342 (1970).
- Clementz, D. M., Pinnavaia, T. J., and Mortland, M. M., *J. Phys. Chem.* 77, 196 (1973).
- Clementz, D. M., Mortland, M. M., and Pinnavaia, T. J., *Clays Clay Miner.* 22, 49 (1974).
- Nagai, S., Ohnishi, S., Nitta, I., and Koizumi, M., *Chem. Phys. Lett.* 26, 517 (1974).
- Ruppert, J. P., *J. Phys. Chem.* 77, 784 (1973).
- Olivier, D., Vedrine, C., and Pezerat, H., *Proceedings of the International Clay Conference, Mexico City, 1975*, p. 231. (Bailey, S. W., Editor.) Applied Publishing, Wilmette, Illinois, 1976.
- Lück, R., *Thesis B. Academy of Sciences of GDR, Berlin, 1989*.
- Slosiariková, H., Čičel, B., and Hronský, J., *Chem. Papers* 40, 585 (1986).
- Novák, I. and Čičel, B., *Clays Clay Miner.* 26, 341 (1978).
- Čičel, B., private communication.
- Čičel, B. and Machajdík, D., *Clays Clay Miner.* 29, 40 (1981).
- Machajdík, D. and Čičel, B., *Proceedings of the 7th Conference on Clay Mineralogy and Petrology, Karlovy Vary, 1976*, p. 61. (Konta, J., Editor.) Charles University, Prague, 1978.
- Horváth, I. and Novák, I., *Proceedings of the International Clay Conference, Mexico City, 1975*, p. 185. (Bailey, S. W., Editor.) Applied Publishing, Wilmette, Illinois, 1976.
- Wiegmann, J., Horte, C.-H., and Kranz, G., *Ber. Dtsch. Ges. Geol. Wiss. B, Mineral. Lagerstätten* 11, 317 (1966).
- Goodman, B. A., *Clay Miner.* 13, 351 (1978).
- McBride, M. B., Pinnavaia, T. J., and Mortland, M. M., *Clays Clay Miner.* 23, 162 (1975).
- Aasa, R., *J. Chem. Phys.* 52, 3919 (1970).
- Meads, R. E. and Malden, P. J., *Clay Miner.* 10, 313 (1975).
- Blumberg, W. E., *Magnetic Resonance in Biological Systems*, p. 118. (Ehrenberg, A., Halström, B. E., and Baumgärt, T., Editors.) Pergamon Press, London, 1967.
- Lück, R., Stösser, R., Gyepesová, D., and Čičel, B., *Proceedings of the 7th EUROCLAY Conference, Dresden, 1991*, Vol. 2, p. 715. (Störr, M., Henning, K.-H., and Adolphi, P., Editors.) Ernst-Moritz-Arndt-Universität, Greifswald, 1991.
- Stösser, R., Kaläne, R., Möckel, K., and Backhaus, E., *J. Mol. Struct.* 195, 311 (1989).
- Lück, R., Stösser, R., and Lunk, H.-J., *Proc. Magn. Reson. Conf., Reinhardsbrunn, 1987*.
- Kaläne, R., *Thesis A. Academy of Sciences of GDR, Berlin, 1985*.
- Sheperd, R. A. and Graham, W. R. M., *J. Chem. Phys.* 81, 6080 (1984).
- Nofz, M., Stösser, R., and Wishmann, F. G., *J. Non-Cryst. Solids* 129, 249 (1991).

Translated by Z. Votický