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ELECTRIC FIELD GRADIENT AT Fe²⁺ SITES IN TRIOCTAHEDRAL LAYER SILICATES

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Résumé.- Nous avons étudié une série de silicates en feuillets aussi bien en cristaux et sous champ magnétique (biotite, chlorite, vermiculite) qu'en poudre dans l'état antiferromagnétique (greenalite et berthierine). On trouve que dans les minéraux 1:1 l'axe Z du gradient de champ électrique est proche de l'axe c des silicates, que V_{ZZ} est négatif et que η < 0,2, résultats cohérents avec un état |0> de Fe²⁺. Ceci implique un plan c de facile aimantation. Dans les minéraux 2:1, au contraire, η = 0,9(1), le signe de V_{ZZ} est indéterminé, mais l'axe Z est encore proche de l'axe c.

Abstract.- We have examined a series of sheet silicates, both in single crystal form in an applied magnetic field (biotite, chlorite, vermiculite) and as powders in the magnetically ordered state (greenalite, berthierine). It is found that V_{ZZ} is negative in the 1:1 minerals, that η < 0.2 and that the Z-axis is close to the c-axis of the silicate. These results indicate a |0> ground state for the Fe²⁺ ion and a c-plane of easy magnetization. In the 2:1 minerals however, η = 0.9(1). The sign of V_{ZZ} was not determined, but the Z axis is again close to the c-axis.

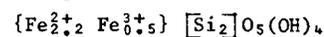
The layer silicates can be classified in two main structural families /1/. In the 1:1 layer minerals, a Si₂O₅ sheet of tetrahedrally-coordinated silicon is associated with a sheet of octahedrally-coordinated cations so that two of their ligands are oxygens, also coordinated to Si and the remaining four are hydroxyl ions. The mineral is made up of a stack of these double sheets (layers) bonded by van der Waals forces. In the 2:1 minerals, the octahedral sheet is sandwiched between two tetrahedral ones, and the octahedral cations are surrounded by four oxygens and two hydroxyls in trans- or in cis- configuration. In trioctahedral minerals, the cation sites in the octahedral sheet are fully occupied.

In this paper, we use the electric field gradient at ferrous ion sites to derive some information about the local environments. Three angles are necessary to define its orientation relative to the crystal axes. The most important of these will be α, the angle between the Z-axis of the gradient and the c-axis of the crystal (the direction perpendicular to the layers). The most complete information is obtained using oriented crystals and an applied magnetic field. However, powders can also be used if they order magnetically at low temperatures, in which case the EFG can be located relative to the moment direction by the angles θ and φ.

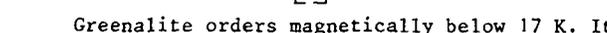
The principal contribution to the EFG at Fe²⁺ nuclei is the ionic term produced by the 3d shell. A smaller contribution, usually of opposite sign is the lattice term due to the charges on all the

nearby atoms. Since many layer silicates contain Fe²⁺ and Fe³⁺ in almost equivalent sites, the latter term, being the only contribution to the ferric field gradient, can be evaluated directly /2,3/.

1:1. Minerals.- No single crystals from this family were available, so we have examined two clay-grade samples of iron-rich minerals belonging to the Serpentine group. These samples which order magnetically at low temperatures were berthierine (chamosite) :



and greenalite :



where, in these ideal formulas, { } denotes the octahedral cations and [] the tetrahedral ones.

Greenalite orders magnetically below 17 K. It is a metamagnet, with ferromagnetic coupling within the sheets /4/. Chamosite does not present such a well-defined ordering transition. The spectrum at 4.2 K (Fig. 1) shows a broad magnetically-ordered spectrum coexisting with a paramagnetic doublet. Analysis of these spectra, together with these in the paramagnetic region, allows us to determine the most probable values of V_{ZZ}, η, θ and φ, which are given in the table I. φ is almost indeterminate because of the small value of η.

Table I : Ferrous EFG parameters of 1:1 minerals at 4.2 K

	2 e ² q Q (mm/s)	η	δ relative to iron) (mm/s)	θ
Greenalite	-2.96(2)	0.05(5)	1.30(2)	90(10)
Berthierine	-2.74(6)	0.2 (2)	1.23(5)	90(20)

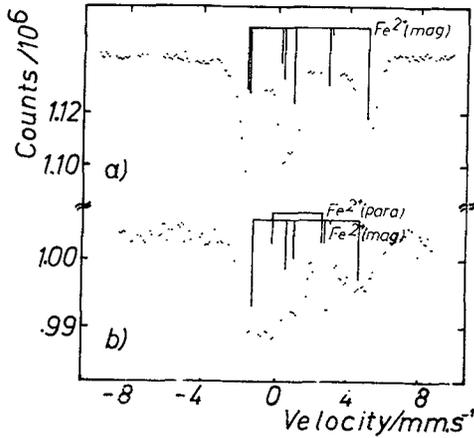
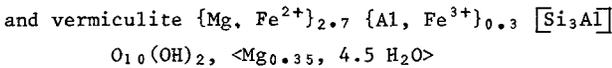
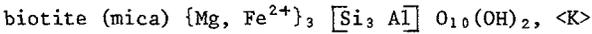
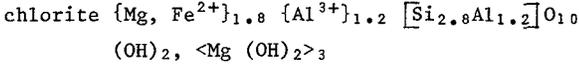


Fig. 1 : Mössbauer spectra at 4.2 K, on powder samples, showing magnetic order. a) greenalite b) berthierine. A paramagnetic doublet coexists with the magnetically-split spectrum.

2:1 Minerals.- The three examples we have examined from this family are :



In these ideal formulas $< >$ denotes the intercalates. Only small crystals of chlorite, some mm² in area, were available, so an oriented mosaic was used as the absorber. Much larger crystals of the other two minerals were used directly as single-crystal absorbers. In each case, the c-axis was perpendicular to their plane.

Room temperature spectra were taken of all three minerals with the c-axis making angles of $\psi = 0^\circ, 30^\circ$ and 55° with the γ -direction. Some of these are shown in figures 2 and 3. The asymmetry of the spectrum of oriented biotite crystals was also reported in reference /5/.

All the spectra at $\psi = 0^\circ$ are asymmetric with the high-energy Fe^{2+} line about half as intense as the low-energy line. At the magic angle of $\cos^{-1} \frac{1}{\sqrt{3}} \approx 55^\circ$, the doublets appear with equal intensity in each transition.

Interpretation of these spectra is complicated by the possibility that the field gradients at cis and trans sites may be quite different. In chlorite, at least, this does not seem to be a problem as the spectra are adequately fitted with a single ferrous component with $\Delta = 2.62$ mm/s and δ (relative to iron) = 1.13 mm/s. The observed ratios of 2.15:1 and 1.55:1 for the intensities of the ferrous lines in the spectra at $\psi = 0^\circ$ and $\psi = 30^\circ$ respectively would

imply that V_{ZZ} is negative, assuming $\eta \sim 0$. In any case V_{ZZ} makes on average an angle α with the c-axis such that $30^\circ > \alpha > 10^\circ$.

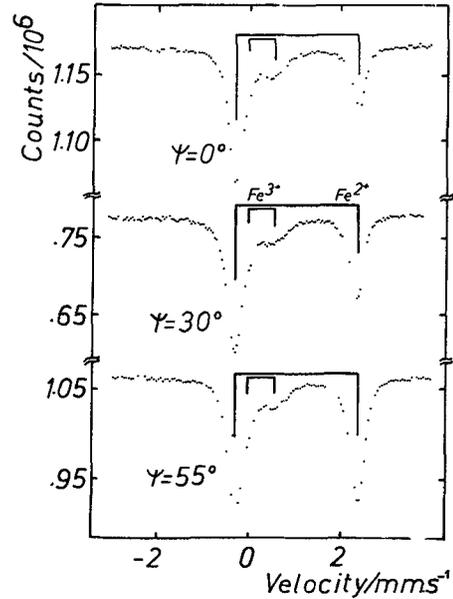


Fig. 2 : Mössbauer spectra at 296 K of an oriented chlorite mosaic with angles of $\psi = 0^\circ, 30^\circ$ and 55° between the c-axis and the γ -direction.

Unlike chlorite, the shape of the lines comprising the ferrous doublet in biotite is obviously non-lorentzian, and this is usually taken as showing that the quadrupole splitting of iron populating cis and trans sites are rather different /6/. The asymmetry of the lineshape does not change greatly between $\psi = 0^\circ$ and 55° , so we conclude that the orientation of the field gradient relative to the c-axis is much the same at each site. This assumption is born out by the spectrum in the applied field of 100 kOe (Fig.3b). After allowing for the weak Fe^{3+} absorption the remaining spectrum can be interpreted as due to an average site Fe^{2+} with parameters $V_{ZZ} = \pm 2.2(1)$ mm/s, $\eta = 0.9(1)$ and $\alpha = 15(15)$ as shown table II.

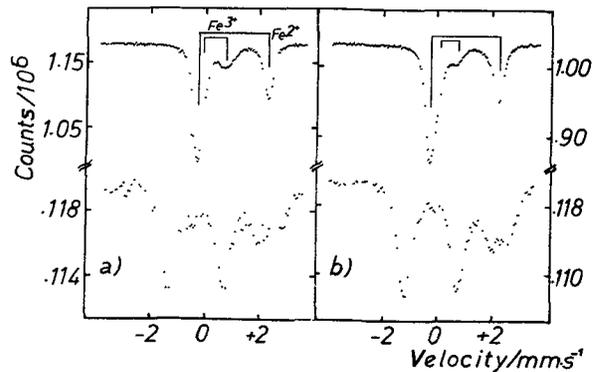


Fig. 3 : Mössbauer spectra at 296 K of crystals oriented with $\psi = 0^\circ$. a) vermiculite - b) biotite. Above, H=0, and below, H=100 kOe along the γ -direction.

Table II : Average ferrous EFG parameters of 2:1 minerals at 296 K.

	$ 1/2 e^2 q' Q $ (mm/s)	η	δ (relative to iron) (mm/s)	α
Chlorite	2.62(2)	n.d.	1.13(1)	20(10)
Biotite	2.49(3)	0.9(1)	1.12(1)	15(15)
Vermiculite	2.57(2)	0.9(1)	1.13(2)	15(15)

$$q' = q \sqrt{1 + \frac{\eta^2}{3}}$$

The vermiculite spectra are quite similar, though less well-defined on account of the lower iron-content. Like the biotite spectra, they were fitted with a single ferrous pattern.

The principal result is that the electric field gradient is quite different in two families of sheet silicates. In the 1:1 layer minerals, V_{ZZ} at the ferrous sites is negative and η is small. V_{ZZ} increases by less than 10% between 296 K and the liquid helium range. The purely ionic contribution to the ferrous field gradient is obtained as -3.3(2) mm/s after correcting for the lattice contribution, as measured at the ferric sites. These values indicate that the ground state is essentially the $|0\rangle$ singlet /7/. The weak temperature dependence of the quadrupole splitting suggests that the first excited state is at least 800 cm^{-1} higher in energy /8/. The singlet is the ground state for the ferrous iron in trigonal point symmetry, as, for example, in the layer compound $\text{Fe}(\text{OH})_2$ whose structure resembles that of an octahedral sheet in the phyllosilicates. There is a close resemblance between the spectra of this compound in its magnetically ordered state /9/ and those of greenalite and berthierine. Therefore, despite the low absolute symmetry of the crystal field at the octahedral ferrous sites, the effective symmetry is trigonal. Furthermore the direction of V_{ZZ} is in all cases close to the c-axis, which proves that the disposition of oxygen and hydroxyl ligands is not the determining factor for the orientation of the EFG.

In the 2:1 larger minerals, however, the spectra in the applied field suggest that $\eta \sim 1$ and the sign of V_{ZZ} is consequently indeterminate.

A final point concerns the magnetic anisotropy of sheet silicates, which should be governed by the electronic ground state of the Fe^{2+} ions they contain. The $|0\rangle$ singlet favours an easy plane perpendicular to the direction of Z^{ion} . In greenalite, Z^{ion} coincides with the c-axis, so the moments tend to lie in the c-plane. The c-direction will there-

fore be the hard direction.

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