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GREENALITE - A CLAY SHOWING TWO-DIMENSIONAL MAGNETIC ORDER

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Résumé. - Un échantillon purifié de Greenalite contenant 31 % en poids de fer s'ordonne magnétiquement à 17 K. Les feuillets de ce phyllosilicate sont ferromagnétiques, les moments étant dans le plan des feuillets. L'interaction entre plans est faiblement antiferromagnétique, un champ de 7 kOe appliqué à une poudre suffisant à retourner les moments.

Abstract. - A purified sample of clay-grade Greenalite containing 31 weight % of iron orders magnetically at 17 K. The moments lie in the plane of the octahedral sheets. They are ferromagnetically coupled within the sheets, and an applied field of 7 kOe suffices to overcome the weak antiferromagnetic interlayer coupling.

Clays are mainly composed of tiny particles of sheet silicates (<20). There is strong ionic bonding within the sheets, but since the hydrogen or Van der Waals bonding between them is weaker, the crystals structure has a clear two-dimensional character. In kaolinite, for example, the sheets are composed of a layer of Si<sup>4+</sup> tetrahedrally coordinated by 4 OH<sup>-</sup>, 2/3 of the octahedral sites being filled (dioctahedral structure)/1/. The ideal formula is then [Si]<sub>2</sub>(Al)<sub>2</sub>O<sub>6</sub>(OH)<sub>4</sub>. The distances between octahedral cations within the plane is 3.0 Å, but between planes it is 7.3 Å.

Greenalite is related to kaolinite with the substitution of 3 Fe<sup>3+</sup> for 2 Al<sup>3+</sup> in the octahedral layer (trioctahedral structure). The ideal formula is then [Si]<sub>2</sub>[Fe<sup>3+</sup>]<sub>3</sub>O<sub>6</sub>(OH)<sub>4</sub>. The sample we have studied contained 40 weight % iron as FeO compared with 58 % for the ideal formula. Therefore the substitution is incomplete. If such a mineral shows any magnetic order at low temperature, this order may be expected to have a two-dimensional character.

The susceptibility of a randomly oriented powder in effect shows a peak characteristic of antiferromagnetism in magnetic fields less than 5 kOe (figure 1 a). The peak becomes sharper in lower fields, and the temperature of the maximum tends to a limit of 19 K as the field tends to zero. The magnetization curve at 4.2 K (figure 1 b) shows that a large fraction of the magnetization can be saturated in 7 kOe, but much larger fields are needed to completely align the moments.

Mössbauer spectra above 17 K show a predominant ferrous doublet: at room temperature (figure 2 a), the isomer shift δ is 1.15 mm/s relative to iron, the quadrupole splitting Δ is 2.75 mm/s. These values are typical of Fe<sup>3+</sup> in octahedral sites.
of sheet silicates/2/. A weak doublet with \(\delta = 0.29\) and \(\Delta = 0.65\) mm/s, accounting for 14\% of the absorption, is due to Fe\(^{3+}\).

Below 17 K, the spectra display both magnetic and electric hyperfine interactions. The 4.2 K spectrum can be well fitted with the following parameters:

- \(H_{\text{hf}} = 158\) kOe
- \(\delta = 130\) mm/s
- \(1/2 J e^2qQ = -2.96\) mm/s
- \(\eta = 0.05\)
- \(\phi = 90^\circ\)

as shown in figure 2 b.

Since the direction of the principal axis \(Z\) of the electric field gradient tensor in sheet silicates is close to the c-axis/3/, the moments are therefore in the plane. The Mössbauer spectrum at 4.2 K is very similar to that of Fe(OH)\(_2\)/4/ which has the CdI\(_2\) layer structure. The structure of the octahedral sheet in Greenalite resembles closely a sheet of Fe(OH)\(_2\). There the electronic ground state of Fe\(^{2+}\) in the trigonal crystal field is the \(^5A_g\), orbital singlet for which the magnetic anisotropy favours an easy plane. We conclude that the Fe\(^{2+}\) ions in Greenalite are also in an approximately trigonal field.

The ease with which a fraction \(\frac{\sigma}{\mu}\) of the saturation magnetization is obtained (all the moments of the particles along the projections of the field upon the plane of their sheets) shows the planes are ferromagnetic, with only anisotropy within the planes and weak exchange coupling between them. Analysis of the magnetization curve at 4.2 K (figure 1 b) assuming fully trigonal symmetry for the ferrous ions, leads to the following parameters:

- \(zJ/\mu = 5.5\) K
- \(z'J'/\mu = -0.06\) K
- \(H_A \approx 50\) kOe

\(J\) is the intra-plane exchange constant between a spin and its \(z\) neighbours in the plane, given by the paramagnetic Curie temperature 22 K; \(z'J'\) is the inter-plane exchange constant between a spin and its \(z'\) neighbours of the two adjacent planes. It has been obtained from the field \(H_A\) at which the metamagnetic transition occurs within the easy plane. \(H_A\) is the anisotropy field corresponding to the difficult magnetization axis, perpendicular to the plane. The exchange interactions are therefore 100 times more important within the planes than between planes, a value typical of inorganic two-dimensional magnets/5/.

Although clays are among the most abundant materials on the face of the earth, they have attracted little interest on the part of physicists. In this paper we have established the two-dimensional character of the magnetism occurring at low temperatures in Greenalite. In fact clays present a number of advantages for future study of two-dimensional magnetism, notably the possibility of expanding the interlayer spacing by intercalation with organic substances, and oxidization or reduction of iron in situ without necessarily destroying the structure. The present work represents a first step in studying the magnetism of this "new" class of materials.

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References

/1/ Grim, R.E., Clay Mineralogy, McGraw Hill (1973)