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Experimental and modeled electron paramagnetic resonance spectra of Cr^{3+} in kaolinite

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Abstract. Two hydrothermal Cr kaolinites were investigated by EPR at both the X-band and the Q-band frequencies. At the X-band frequency, for unoriented powder spectra, Cr^{3+} presents two main sets of resonances: one at about 170 mT and the other near 600 mT. For oriented films, the spectra present a strong anisotropy, which proves that the signal arises from Cr^{3+} inside the structure of the phyllosilicates. A transition line at about 110 mT appears and reaches its maximal intensity, like the high-field lines, when the field is perpendicular to the oriented film. At the Q-band frequency the presence of Cr^{3+} is characterized by the presence of a strong line with a derivative shape near 240 mT. The Cr^{3+} spectra can be described exactly by a complete spin Hamiltonian, and a computed simulated spectrum for the X-band frequency can be built. The results permit us to conclude that all the observed signals belong to only one EPR spectrum that comes from Cr^{3+} substituted for Al^{3+} in the octahedral sites of the kaolinites.

1. Introduction

Evidence of the presence of Cr in the lattice of kaolinite has been obtained using several techniques. Maksimovic *et al* (1981) showed by optical absorption that the spectra of chromium-containing samples are fully consistent with octahedral Cr^{3+} electronic transitions which are responsible for the blue–green colour of the samples. Maksimovic and White (1973) and Maksimovic *et al* (1981), using IR spectroscopy, attributed some unknown bands to AlCrOH vibrations by analogy with Fe^{3+} – Al^{3+} substitution effects. Transmission electron microscopy (TEM) observations coupled with energy-dispersive x-ray spectrometry (EDXS) analysis and IR and EPR spectroscopies (Mosser *et al* 1992) give certainties for Cr^{3+} in the structure and good probabilities for its octahedral position. However, there is no precise information about the location of Cr^{3+} in the lattice.

For Fe^{3+} there are two kinds of spectrum generally labelled E and I (Meads and Malden 1975, Herbillon *et al* 1976, Angel and Vincent 1978, Mestdagh *et al* 1980, Bonnin *et al* 1982, Brindley *et al* 1986). Spectra E are in fact the superposition of two spectra arising from Fe^{3+} substituted for Al^{3+} at the two octahedral positions, but there is no sure interpretation for the origin of the I spectra (Gaité *et al* 1993).

The aim of the present paper is to see whether for Cr^{3+} the EPR signal arises from one or several EPR spectra, and to determine their characteristics.

2. Material and experiments

Two different natural hydrothermal kaolinites, MILO and GEY, from Sonoma County,

CA, were investigated. MILO is a miloschite; it comes from The Geysers and is a sky-blue material, identified by x-ray diffraction (XRD) and chemical analyses as a Cr kaolinite (Brookins 1973). GEY comes from Geyserville and is a greenish Cr kaolinite. The Hinckley (1963) 'crystallinity index' is 0.96 for MILO and 0.75 for GEY. The Cr contents of the MILO and GEY samples (less than $2 \mu\text{m}$ fractions) are 0.8 wt.% Cr and 2.3 wt.% Cr, respectively. Both samples also contain some iron: 0.14 wt.% Fe for MILO and 0.84 wt.% Fe for GEY. Most of that iron is localized in small oxides detected by TEM EDXS analysis (Mosser *et al* 1992) and give a large EPR signal near 350 mT (figure 1). Superimposed modulations on that large signal are due to the VO^{2+} present in the less than $2 \mu\text{m}$ fraction.

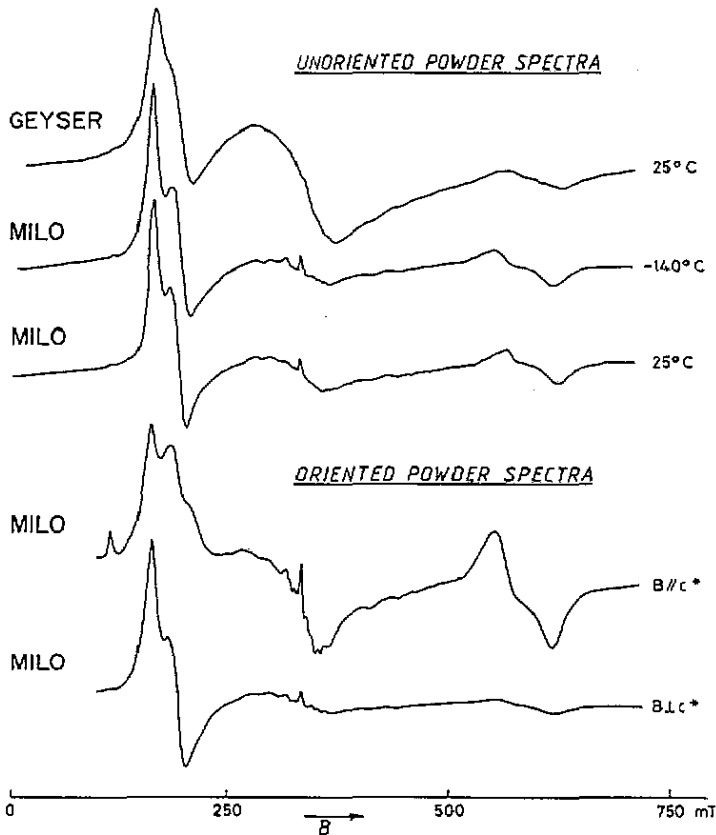


Figure 1. X-band frequency spectra.

The EPR spectra of the MILO sample (unoriented powder spectra) are more resolved than those of GEY (figure 1). So the measurements of the transition fields were more precise for MILO and we shall mainly report the results concerning this sample.

Experiments were performed at the X-band frequency on both unoriented and oriented powder films, at both room temperature and low temperatures down to -140°C .

We used a V 4500 Varian spectrometer with 100 kHz modulation. The microwave frequency was measured directly with a Hewlet-Packard frequency meter. The magnetic field which can reach 950 mT was calibrated with a NMR gaussmeter. The original spectrometer was modified in order to obtain numerical memorized records of spectra.

The oriented films studied were obtained by mechanical pressure. As kaolinite is quite a soft mineral, we controlled the pressure in order to obtain no modification of the sample as a result of that effect. Oriented autosupported films of about $0.5 \text{ mm} \times 3 \text{ mm} \times 10 \text{ mm}$ were put in a silica tube and oriented in the magnetic field.

The measurements were completed by a Q-band experiment on a MILO powder using a Bruker spectrometer.

3. Results

3.1. Description of the EPR spectra

3.1.1. X-band frequency: unoriented powder spectra. Between low temperatures (-140°C) and room temperature (figure 1), there is no significant change in the EPR spectra; only the signal-to-noise ratio was better at low temperatures for the transitions were slightly sharper.

3.1.2. X-band frequency: oriented powder spectra. For the oriented film (figure 1), we observe a very strong anisotropy of the spectrum. This is proof that it arises from Cr^{3+} inside the kaolinite structure. One main feature of the angular dependence of the spectra is that the transition line at about 110 mT, which is very small in the powder spectra, reaches its maximal intensity when the field is perpendicular to the oriented film ($B \parallel c^*$), together with the high-field lines.

From all experiments done at the X-band frequency, it was observed that the low-field line near 110 mT is more or less observable on powder spectra. In our opinion, we think that it is certainly due to partial orientation of the particles inside the sample. Such an orientation may change the relative intensities of some transitions but does not affect their positions and their linewidths.

Another point which should be mentioned is that, in all experiments with MILO samples, we did not observe EPR lines near $g = 9$ arising from Fe^{3+} at the octahedral position. As a consequence it is concluded that such iron is not present in our sample. This is in good agreement with previous observations (Mosser *et al* 1992).

3.1.3. Q-band frequency. As complementary information we recorded one spectrum at the Q-band frequency ($\nu = 34.3 \text{ GHz}$). This spectrum (figure 2) is well resolved, and several sharp transition lines due to Cr^{3+} are present.

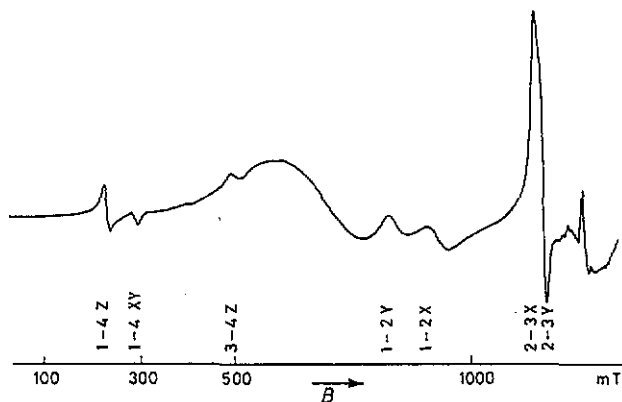


Figure 2. Q-band frequency spectrum.

The main problem is to identify the transitions and to see whether they arise from one or from several EPR spectra.

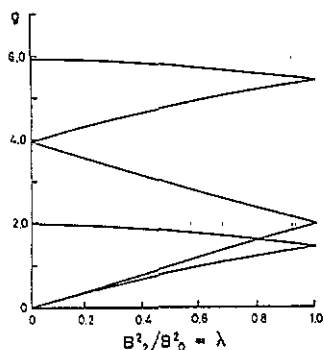


Figure 3. g position according to the rhombic character when in a high crystal field.

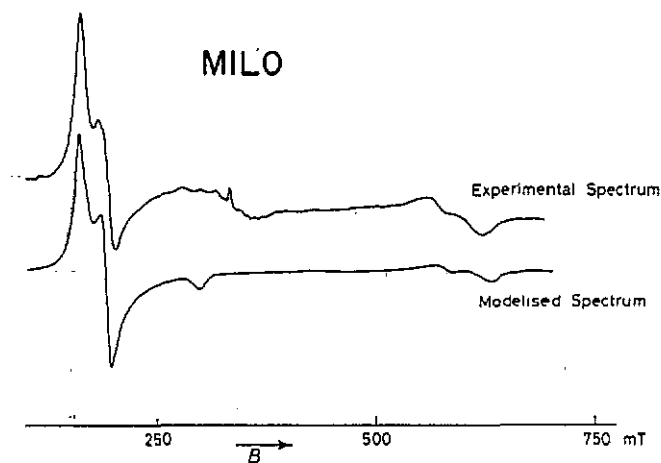


Figure 4. Comparison between experimental and modeled spectrum.

3.2. Analysis of the EPR spectra

The Cr^{3+} spectra can be described exactly by the complete spin Hamiltonian

$$H = \sum_{ij} g_{ij} \beta B_i S_j + \sum_m B_2^m O_2^m$$

where g_{ij} are the components of the \mathbf{g} -matrix, O_2^m are the Stevens equivalent operators, B_2^m are the fine-structure constants, B_i are the components of the magnetic field and S_j are the spin operators. In fact, in most cases the \mathbf{g} -matrix is nearly isotropic with a mean g value given by

$$g = g_{ii} = 1.98.$$

Since we are concerned only with polycrystalline samples, we have no precise information about the orientation of the fine structure tensor, and it can be represented by its diagonal form. Then, to describe the spectra, we can use the simplified spin Hamiltonian

$$H = \sum_i g \beta B_i S_i + B_2^0 O_2^0 + B_2^2 O_2^2.$$

If the g value is fixed at 1.98, any EPR spectrum can be described by the two constants B_2^0 and B_2^2 .

As a first attempt to interpret our spectra, we computed a diagram of the apparent g_a values of the transitions arising inside the Kramers doublets as a function of the parameter $\lambda = B_2^2/B_2^0$. The quantum $h\nu$ of the transition is smaller than B_2^0 . This diagram presented in figure 3 is similar to that often used for Fe^{3+} , first established by Wickman *et al* (1965). From this diagram, using the g values observed at the X band, two distinct EPR spectra, characterized by the values of $\lambda = 0.1$ and $\lambda = 0.6$, can be expected. However, for $\lambda = 0.6$, not only high-field transitions should be observed.

We focused first on the three low-field transitions at the X band, interpreted by $\lambda = 0.1$ in our diagram.

To calculate the constants for this spectrum, we used a general program built for single-crystal studies (Michoulier and Gaité 1972). Since approximate values were obtained, we identified some of the Q-band transitions which were included in our computation.

After some attempts, all Q-band transition lines (table 1) and low-field lines at X band were interpreted as belonging to only one spectrum characterized by the constants $B_2^0 = 0.116 \text{ cm}^{-1}$ and $B_2^2 = 0.018 \text{ cm}^{-1}$. The X-band transition lines are only slightly sensitive to the value of B_2^0 ; they mainly depend on the ratio $\lambda = B_2^2/B_2^0$, and therefore the precise determination of both B_2^0 and B_2^2 was possible only because we used two different frequencies, the X band and Q band.

Table 1. Transitions of Cr^{3+} in kaolinite. X, Y and Z are the EPR axes and the numbers indicate the levels joined by the transitions. The energy levels are numbered in increasing energy to avoid any confusion about the labelling of the transitions due to low-field or high-field descriptions.

Transition	Magnetic field (mT)	
	$\nu = 9228 \text{ MHz}$	$\nu = 34300 \text{ MHz}$
	X band	Q band
1-2 X	190.4	934.0
1-2 Y	158.2	826.0
3-4 Z	112.3	493.0
2-3 X		1132.6
2-3 Y		1143.1
1-4 Z		237.3
1-4 X-Y plane		300.0
2-3 Z-X plane	570.0	
2-3 Z-Y plane	617.5	

As the high-field lines of the X-band spectrum were not explained, we computed a simulated spectrum using the EPR parameters previously obtained. There are several ways to compute EPR spectra, and for Cr^{3+} a general presentation was reported by Bonomo and Di Bilio (1991). For the present study we built a program similar to that reported for Fe^{3+} in kaolinites (Gaité *et al* 1993). This program calculates the resonant fields and the intensities of the transitions for several orientations of the magnetic field using an iterative process. One of the main characteristics of our computation is that the absorption spectrum, without a lineshape, is first calculated. The simulated spectrum is obtained by convolution of the absorption curve by the derivative of a given lineshape. In this way, the lineshapes and linewidths can be varied easily without great expense in computation time.

The result of the simulation using Lorentzian lineshapes characterized by a 7 mT width at low fields and 11 mT at high fields is presented in figure 4 together with one experimental spectrum.

From the comparison between the simulated and the experimental spectra, it is clear that the high-field transitions also belong to the same spectrum.

In our previous calculations they were not explained as they do not occur along the EPR axes, but they are due to steady states of the $\frac{1}{2}-\frac{1}{2}$ transitions in the Z-X and Z-Y planes at 20-30° of the Z axis. This last fact can explain also why these transitions are more intense when the magnetic field is parallel to c^* .

It can be concluded from all these results that all the observed signals belong to only one EPR spectrum.

4. Discussion

The only reasonable assumption for Cr^{3+} in kaolinite, strengthened by IR AlCrOH vibrations, is a possible substitution of Al^{3+} by Cr^{3+} . Since there are two octahedral sites which are not related by symmetry, and since Cr^{3+} spectra are very sensitive to small changes in the crystal field, one should expect the presence of two spectra. This is not the case here. A preference of Cr^{3+} for one of the two octahedral sites could explain this, but no crystallochemical evidence can be given for this. If Cr^{3+} enters the two octahedral sites, then the crystal fields at the two Cr^{3+} positions are very close.

Looking, by analogy, at the result obtained for Fe^{3+} at the Al position, two distinct spectra were observed, but they were so similar that they could be distinguished in only one very well crystallized kaolinite and at low temperatures (Gaite *et al* 1993). The situation for Cr^{3+} may be the same, the difference being so small that the transitions overlap even at low temperatures.

By chance, the two samples that we studied did not contain enough Fe^{3+} to obstruct our EPR study. However, one can try to see what could happen if these two ions were present in the same sample.

At the X band, the two intense lines near 170 mT ($g_a = 4$) are at nearly the same position as those of the I Fe^{3+} spectrum and cannot be used for certain identification of Cr^{3+} , and the line near $g_a = 6$ is much too weak to be used. Cr^{3+} can be identified only by the high-field transitions which are broad and very sensitive to the 'quality' of the kaolinite (the term 'quality' includes the presence of defects, stacking faults, crystallinity, etc), while Fe^{3+} can be characterized by the presence of a transition line at $g_a = 9$, belonging to the E spectra.

At the Q band, a simple way to characterize the presence of Cr^{3+} is the presence of a strong line with derivative shape near 240 mT.

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