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DEHYDROXYLATION OF KAOLINITE-GROUP MINERALS: AN ESR STUDY

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A number of natural kaolinite-group minerals, nacrite, dickite, kaolinite and halloysite, were heated up to 1400° and investigated by means of ESR at the X band. The results show systematic differences, some of which are related to the crystallinity of the kaolinites and to the mutual orientation of adjacent layers in polytype modifications. The most intense features of the spectra, centred at g values of 4.3 and 3.0, are attributed to Fe^{3+} ions occupying different sites in the structure. Studies of the changes caused in the ESR spectra by thermal treatment led to some general conclusions about structure modification.

The technique of electron spin resonance (ESR) spectroscopy has found application in the investigation of paramagnetic species such as transition metal ions (mainly Fe^{3+}), and of lattice imperfections associated with natural kaolinites [1–4]. The present work aims to relate the changes caused by dehydroxilation in the ESR spectra of kaolinites to their structures. Of course, differences in the orientation of layers among kaolinite polytypes, as well as differences in the degree of structural order, influence both the positions of OH groups coordinating iron in the structure and the direction of hydrogen-bonds. These differences in turn influence the symmetry of the crystal field formed by the ligands surrounding Fe^{3+} in kaolinite. Dehydroxylation by loss of OH groups causes destruction of octahedral layers, which consequently changes the crystal field symmetry. Since the crystal field symmetry affects the ESR signal features, it is obvious that ESR may be helpful in investigations of the dehydroxylation process.

Materials and methods

In the previous work [1] the ESR spectra of kaolinites were investigated without thermal treatment. Methods of ESR measurements were described there, and all details relating to sample descriptions and compositions, ESR spectrometer, X-ray analysis and structural positions occupied by Fe^{3+} ions were given. The sample descriptions and positional assignments of iron ions in the present work are consistent with the earlier ones [1]. The investigated samples of nacrite (1), dickite (2), kaolinites (4, 5, 8), halloysite (10) were heated in air at various temperatures up to 1400°, and ESR spectra were then obtained at room temperature using a magnetic field range of 0–0.5 T. The present measurements do not pretend to be quantitative in terms of intensity. In the course of the work, only qualitative changes in density are involved.

Results and discussion

Selected ESR full-range spectra of the samples are presented in Figs 1–4. All of the samples studied, except nacrite, showed two main resonance regions, denoted as I and II, with g values of $g_I = 4.3$ and $g_{II} = 2.0$.

Nacrite

The lack of resonance in region I (Fig. 1) when a sample was heated up to 450° indicates that there were no positions of type *A* or *B* in its structure. Accordingly, Fe^{3+} ions must have occupied positions with only slight axial distortion. This was denoted as *C*. The line in region II is due to Fe^{3+} ions and defect centres. When the sample was heated in the range 450–550°, a weak single line began to appear in region II, and simultaneously an asymmetric double line in region II began to disappear. As the new line was a single one with $g = 4.28$, it was obvious that it was due to Fe^{3+} ions occupying positions of *A* type only. It can be assumed that the very beginning of the dehydroxilation process turned the high-symmetry positions *C* directly into positions of lowest symmetry *A*. This single line was observed up to the highest temperatures without any change in shape. On the other hand, the line in region II showed marked changes due to the formation of spinel phases in which clusters of iron ions were formed. The broad resonance lines with a g value of nearly 2.0 are commonly attributed to Fe^{3+} ion clusters existing inside the kaolinite structure or as a separate phase [2, 3, 7].

Dickite

The shape of the region I resonance (Fig. 2) for the natural sample indicates that a few centres of *B* type exist, besides the *A* type. The shape of the resonance in region II is more complicated and many other paramagnetic species may participate in it. When the sample was heated up to 600°, the intensity of resonance I systematically decreased, but its shape did not change. Then, after annealing at 650°, the four-line resonance suddenly collapsed into a single line with a g value of 4.28 (Fig. 2). Thus, we are in a position to conclude that at 650° a lowering of the symmetry of positions

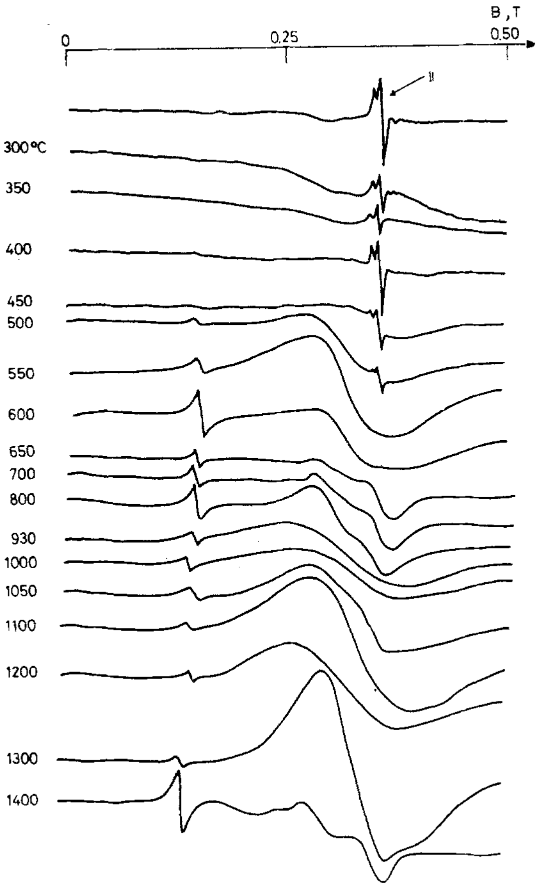

Fig. 1 Full-range ESR spectra of nacrite (1). Temperatures of annealing are denoted at left side. Region II resonance position is indicated in the Figure

occupied by Fe^{3+} ions took place: from *B* type into *A* type. The region II line underwent a significant change and became a broad one at 500°.

Kaolinite

In kaolinite, Fe^{3+} ions occupy both *A* and *B* positions, the relative populations depending on the temperature of annealing. Using the ESR line shape parameter introduced by Jones et al. [4], we found that the higher the temperature of annealing, the lower the parameter (see Table 1). In the end, a triple line collapsed into a single one at $g = 4.28$. Thus, the dehydroxylation causes an increase in the *A* site population, for the lower the value of this parameter, the higher the *A* site population relative to the *B* sites. In this way it is possible to investigate how dehydroxylation destroys an octahedral sheet. As shown in Fig. 3, the shape of the line in region II underwent a

Table 1 Temperature-dependence of "ESR line shape parameter" for investigated kaolinites (x = single line only)

Sample	Value of parameter						
	Room temperature	Temperature of annealing, °C					
		300	350	400	450	500	550
4	2.06	1.44	1.08	1.18	1.02	x	x
5	1.40	1.35	1.18	1.20	0.84	0.52	x
8	4.21	4.01	3.70	3.60	2.55	1.08	x

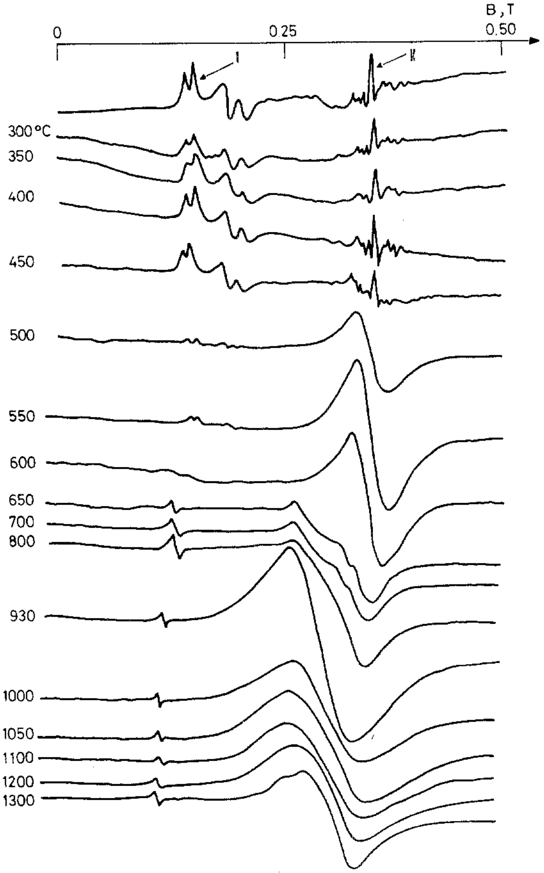

Fig. 2 Full-range ESR spectra of dickite (2). Temperatures of annealing are denoted at left side. Region I and II resonance positions are indicated in the Figure

considerable change. A triple line collapsed into a single one. The spectra in region II show an asymmetric line which disappeared during dehydroxylation. The higher the degree of crystallinity of a sample, the higher the temperature at which it vanished.

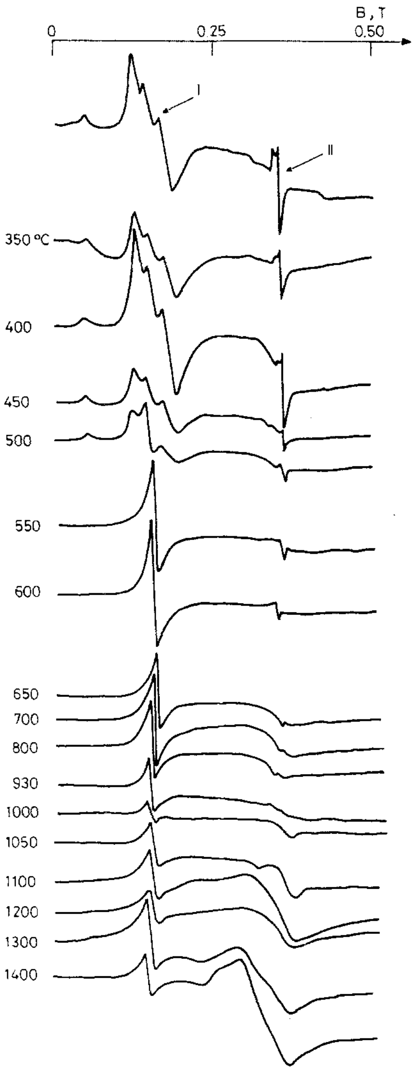

Fig. 3 Full-range ESR spectra of kaolinite (8). Temperatures of annealing are denoted at left side. Region I and II resonance positions are indicated in the Figure

In the case of a poorly-crystalline kaolinite (4) this took place at 450°, but for a highly-crystalline one (5) a temperature as high as 650° was necessary to destroy it.

Halloysite

There are only *A* positions in the structure, for the line in region I is always a single one at $g = 4.28$ (Fig. 4). The intensity of the line changes, but its shape remains the same. After annealing in the temperature range 350–550°, a narrow single line was observed in region II. This is probably due to lattice imperfections.

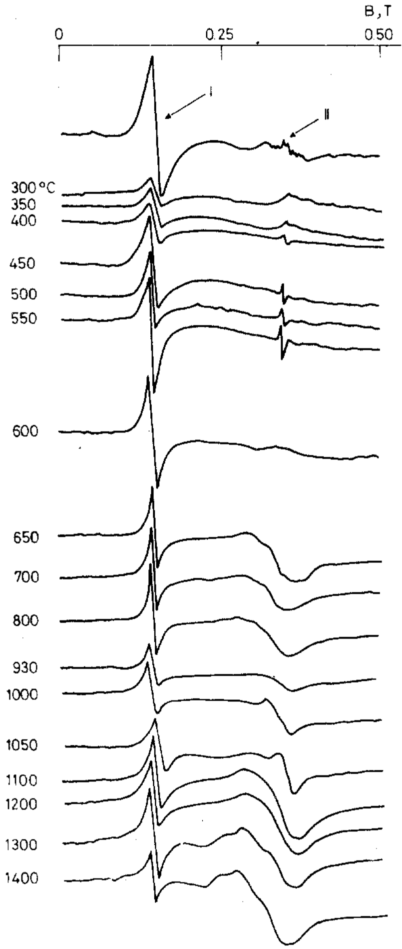

Fig. 4 Full-range ESR spectra of halloysite (10). Temperatures of annealing are denoted at left side. Region I and II resonance positions are indicated in the Figure

Discussion

Dehydroxylation causes the rise of a single line at $g = 4.28$ in region I and a very broad one at $g = 2.0$ for all the investigated minerals. This indicates that dehydroxylation produces strong anisotropy of the crystal field in the positions occupied by Fe^{3+} ions, regardless of the obvious differences in the original structures. Thus, the whole octahedral sheet undergoes a similar change. The differences in stacking order for polytypes and in crystallinity (for kaolinites) influence only the temperature at which the final ESR feature begins to appear.

Although an octahedral sheet in which a substitution $Al^{3+} \rightleftharpoons Fe^{3+}$ takes place must undergo distortion, according to Ghose and Tsang such a distortion is negligibly small [5]. By this means we can draw conclusions relating to the whole octahedral sheet on the basis of ESR analysis. In this case the Fe^{3+} ions act as a "probe".

The intensity of the region I resonance decreases when a sample is heated up to nearly 1000°, probably because of spinel phase formation. In highly-ordered minerals (nacrite, dickite) it remains weak, but in others (kaolinite, halloysite) its intensity increases as the temperature rises.

Dehydroxylation causes the rise of a broad line at $g = 2.0$, sometimes as the superposition of a few lines. Simultaneously, the characteristic lines in region II begin to disappear. The broad lines arise from clusters of iron ions. They are formed as a result of Fe^{3+} ion migration; dehydroxylation supports the process of migration [6]. As a consequence, domains arise with a higher concentration of Fe^{3+} ions inside the structure of the anhydrous phase, or as a quite separate oxygen phase. It is worth mentioning that dehydroxylation causes a pink colouring of kaolinite. This indicates that iron becomes "free" and forms disperse grains, probably of hematite.

After annealing at 1000°, the intensity of the broad lines decreases as a result of structural changes and the incorporation of iron ions into the structure of the newly-formed spinel phase. Nevertheless, above this temperature the intensity increases once again, especially in the case of poorly-crystalline kaolinite and halloysite.

On the basis of the above data, it can be stated that dehydroxylation causes lowering of the symmetry of the octahedral sheet: positions of higher symmetry (*B* and *D*) become *A*-type ones. Further, this deformation was observed at the very beginning of the process. This in turn shows that structural changes in which the OH groups participate took place. On the other hand, NMR studies have indicated that in this stage of the process the proton structure of kaolinite does not change.

In the course of dehydroxylation, characteristic lines in region II underwent changes; this confirms that some of them are due to Fe^{3+} substitutions or defect centres in the octahedral sheet, coordinated by OH groups. The temperature of their vanishing depends on the crystallinity of kaolinite, e.g. 650° for kaolinite (3) and 550° for kaolinite (8). Contributions to these lines are made by lattice imperfections of higher thermal stability. Their disappearance could be connected with the total destruction of the octahedral sheet.

ESR analysis confirmed the fact that Fe^{3+} ions underwent rearrangement during dehydroxylation. The changes in shape and intensity of the resonance lines proved useful in the explanation of the process. The course of dehydroxylation and the reconstruction of the anhydrous phases (the final product of dehydroxylation) depend on the stacking order and crystallinity of the kaolinites.

In this way, ESR should be successfully used as a supplementary tool to investigate the dehydroxylation of layer silicates.

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Zusammenfassung — Bis auf 1400 °C erhitzte natürliche Minerale der Kaolinit-Gruppe (Nacrit, Dickit, Kaolinit und Halloysit) wurden mittels ESR im X-Band untersucht. Es wurden systematische Unterschiede beobachtet, von denen einige auf die Kristallinität und auf die gegenseitige Orientierung benachbarter Schichten in Polytyp-Modifikation zurückzuführen sind. Die am deutlichsten hervortretenden Eigenheiten der Spektren liegen bei g-Werten um 4.3 und 2.0 und sind verschiedene kristallographische Positionen einnehmenden Fe^{3+}-Ionen zuzuschreiben. Die durch thermische Behandlung bewirkten Veränderungen in den ESR-Spektren sind in Übereinstimmung mit einigen die Strukturmodifikationen betreffenden allgemeinen Feststellungen.

Резюме — Группа природных минералов накрит, дикит, каолин и галоизит, нагретых до 1400°, была исследована методом ЭПР в X-полосе. Результаты показали систематические различия, некоторые из них связаны с кристалличностью каолинов и взаимной ориентацией смежных слоев в политипных модификациях. Наиболее интенсивные линии спектра при $g = 4.3$ и 2.0 отнесены к ионам Fe^{3+}, занимающим различные стороны в структуре политипов. На основе изменений в ЭПР спектрах образцов, подвергнутых термической обработке, были сделаны некоторые общие замечания о структурной модификации.

Polish Seminar material is finished.