

Temperature-Induced Changes in the EPR Spectrum of the Magnetic Center in Kaolin

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Studies of kaolin have revealed an effect characterized by an unusual temperature-induced change of the EPR spectrum of the Fe^{3+} ion, which is the magnetic probe in kaolin–clay. At low temperature ($T = 4.2$ K) a resonance line with an effective g -value $g_1 = 4.13 \pm 0.16$ is observed. At high temperature ($T = 288$ K) one observes a resonance line with the effective g -value $g_2 = 2.15 \pm 0.1$. The transition from the low- to high-temperature spectrum is gradual and it is accompanied by a redistribution of the absorption intensity. The observed properties of the temperature dependence of the EPR spectrum are characteristic of systems with a multiminimum potential. © 2002 Elsevier Science

Key Words: EPR spectrum; kaolin–clay; low temperature; polymeric composites.

INTRODUCTION

Kaolin is widely used in the formation of filled polymeric composites (1–4). The addition of kaolin to a polymer reduces the relative fraction of the latter in the final product, thus reducing its cost and enabling one to obtain materials with a new complex of properties. One method of polymer loading with a filler is polymerization filling, where the polymeric compositions are formed directly during polymer synthesis. For its realization there should be active centers on the filler surface. Kaolin, which is widely distributed in nature, possesses such centers, iron in particular.

A peculiarity of the Fe^{3+} magnetic centers is the presence of a nontraditional temperature dependence of the EPR spectrum. Recently (5), such a temperature dependence has been observed in organic materials essentially differing in composition and structure. Their EPR spectrum is a superposition of low- and high-temperature spectra. When the temperature is changed, the absorption intensity is redistributed between the low-temperature and high-temperature spectra. This is evidence of the unusual dynamics of the molecules surrounding the Fe^{3+} ion whose presence can substantially influence different properties of the substance.

Research on these dynamic transitions is of additional interest, since the systems exhibiting such properties are, as

a rule, systems with multiminimum potentials. The motion of molecules occurs in the potential well with several minima. Such systems have not been adequately investigated experimentally. The best studied is the Jahn–Teller system of a divalent copper ion in an octahedral environment (6, 7). In that case, the three potential wells of equivalent energy are determined by the Jahn–Teller interaction of the doubly degenerate orbital state with the tetragonal deformations of the octahedral environment. Crystalline methane is an example of a physically different kind of system with a multiminimum potential (8).

The peculiarities of the EPR spectrum described in Ref. (5) have been investigated in materials with the described molecular structure. One may believe that the above peculiarities are only typical of organic compounds. Therefore, in this paper, the Fe^{3+} EPR spectrum has been investigated in kaolin, a typical inorganic substance. The investigated kaolin, with a particle size of 5 to 15 μm , is the filler in ultrahigh-molecular polyethylene. The conditions for obtaining this composite, as well as its physical and mechanical properties, are described in Ref. (4).

Kaolin is based on kaolinite $\text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4$ with the crystalline structure consisting of two-layer packets containing one tetrahedral silicon–oxygen layer of composition $[\text{Si}_{2n}\text{O}_{5n}]^{2n-}$ and one octahedral alumin–oxygen–hydroxylic layer of composition $[\text{Al}_{2n}(\text{OH})_{4n}]^{2n+}$ (9). Both layers form a packet by means of common oxygen atoms from the silicon–oxygen layer. The kaolinite space group is $C_1^1 (P\bar{1})$ with the unit cell parameters $a_0 = 5.14$; $b_0 = 8.93$; $c_0 = 7.37$ Å; $\alpha = 91.8^\circ$; $\beta = 104.5^\circ$. The iron content of kaolin is 0.3 to 1.1%, depending on the origin of the deposit (10).

Figure 1 shows the nearby environment of Al^{3+} ions. It is in the form of octahedrons of two types consisting of two oxygen atoms and four OH groups. The nonequivalence in positions of the Al^{3+} ion shown in Fig. 1 is associated with the difference in location of $(\text{OH})^-$ ion in the upper triangles of octahedrons from the nearest environment. The magnetic Fe^{3+} ion substitutes the Al^{3+} ion isovalently. It is seen from Fig. 1 that the magnetic Fe^{3+} ion can be in two nonequivalent positions.

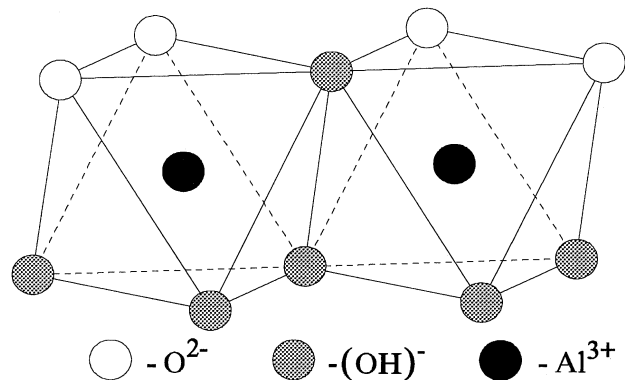


FIG. 1. The nearby environment of Al³⁺ ions in the structure of kaolinite Al₂[Si₂O₅](OH)₄. The magnetic Fe³⁺ ion substitutes the Al³⁺ ion isovalently. It is seen that the magnetic Fe³⁺ ion can be in two nonequivalent positions.

RESULTS

The spectrum of powder samples was studied on an EPR spectrometer with the microwave field frequency $\nu = 9.247 \pm 0.001$ GHz in the temperature interval $T = 4.2$ –288 K.

The EPR spectrum for $T = 4.2$ and 288 K is shown in Fig. 2. It consists of a set of narrow and broad lines. The narrow line ($\Delta H = 17$ Oe) with the effective g -value $g = 3.5$ pertains to the Cr³⁺ ion which was used to calibrate the magnetic field. The narrow line with $g \approx 2$ corresponds, according to (11), to the O₂³⁻ ion existing on the cleavage plane of the mineral. Two broad lines with $g_1 \approx 4.1$ and $g_2 \approx 2.1$ pertain to the Fe³⁺ ion, which is usually present in mineral kaolin as an impurity. The g -value

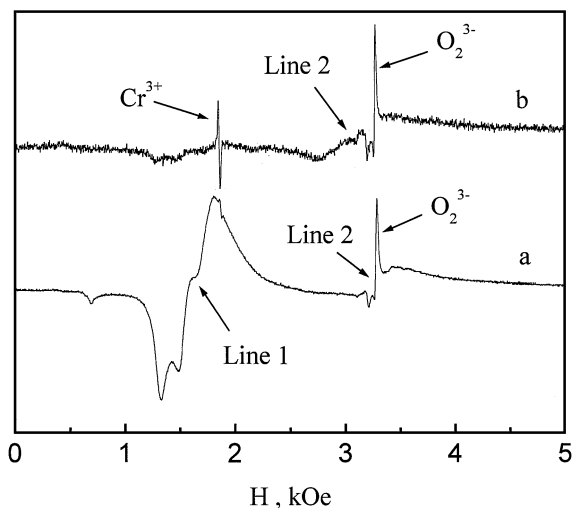


FIG. 2. Fe³⁺ EPR spectrum in kaolinite: (a) $T = 4.2$ K, (b) $T = 288$ K. The narrow line ($\Delta H = 17$ Oe) with the effective g -value $g = 3.5$ pertains to the Cr³⁺ ion which was used to calibrate the magnetic field. The narrow line with $g \approx 2$ corresponds to the O₂³⁻ ion existing on the cleavage plane of the mineral. Two broad lines 1 and 2 pertain to the Fe³⁺ ion, which is usually present in mineral kaolin as an impurity.

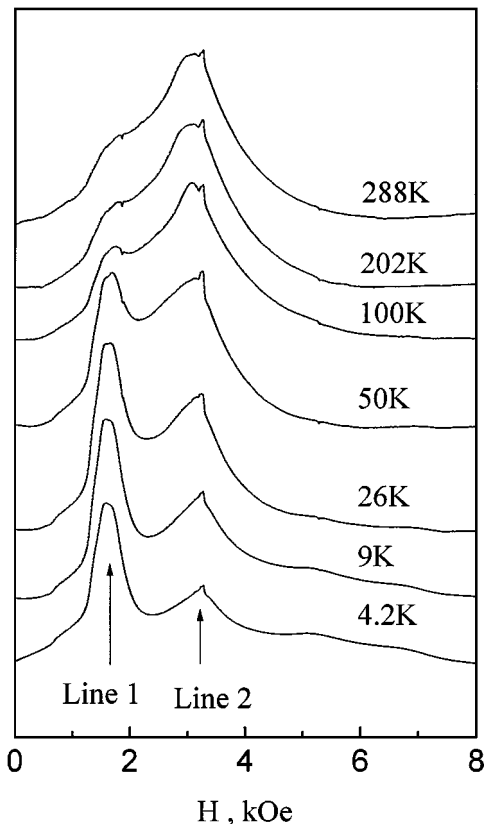


FIG. 3. Temperature-induced change of the form of the EPR spectrum in kaolinite in the form of the absorption curve for the temperatures $T = 4.2, 9, 26, 50, 100, 202,$ and 288 K. It is seen that when the temperature is increased, the intensity of resonance line 1 decreases, whereas line 2 becomes more intense. The g -values for the resonance lines do not depend strongly on temperature.

of line 1 at $T = 4.2$ K is $g_1 = 4.13 \pm 0.16$. That of line 2 at $T = 288$ K is $g_2 = 2.15 \pm 0.1$.

Lines in the EPR spectrum of Fe³⁺ are of appreciable width, changing with temperature in an unusual manner, so it is more convenient to represent the EPR spectrum in the form of the absorption curve, rather than its derivative. The latter is usually recorded using phase detection. Figure 3 shows such an EPR spectrum for seven values of the temperature, $T = 4.2, 9, 26, 50, 100, 202,$ and 288 K. The curves of Fig. 3 were obtained by integration of the experimental curves shown in Fig. 2. In the case of the Fe³⁺ ion, for $H = 10$ kOe the value of absorption is zero for the powder sample. This circumstance was taken into account upon choosing the baseline for the integration. In Fig. 3 it is seen that when the temperature is increased, the intensity of resonance line 1 decreases, whereas line 2 becomes more intense. The g -values for the resonance lines do not depend strongly on temperature. When the temperature is changed from 288 to 4.2 K, g_2 decreases from 2.15 to 2.0.

The temperature change in the EPR spectrum is defined by two mechanisms. The first mechanism leads to a usual decrease of the integral intensity of both resonance lines when the

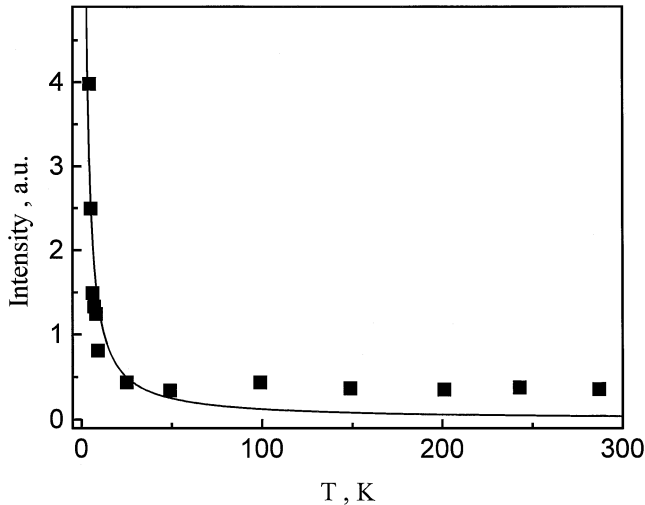


FIG. 4. Temperature dependence of the total integral intensity of resonance lines 1 and 2 in the EPR spectrum of Fe^{3+} in kaolinite. This dependence describes the first mechanism of temperature change in the EPR spectrum. The first mechanism is determined by the temperature dependence of the difference of the population in the resonance states. The solid line describes the dependence $I(T) = I_0 \tanh(hv/2kT)$.

temperature is growing. It is determined by the temperature dependence of the difference in the population in the resonance states. The temperature dependence of the total integral intensity of both resonance lines in the Fe^{3+} EPR spectrum is shown in Fig. 4. The solid line describes the dependence $I(T) = I_0 \tanh(hv/2kT)$.

The second mechanism of the temperature change in the spectrum characterizes a redistribution of the intensity between lines 1 and 2. To describe the process of intensity redistribution between line 1 and line 2, a computer resolution of the resulting absorption line has been made for each value of the temperature. In Fig. 5, the resolution for $T = 4.2$ and 288 K is shown. The form of line 2 is discussed in the Discussion.

The process of intensity redistribution is more clearly shown in Fig. 6. The figure demonstrates the temperature dependence of the relative integral intensities,

$$I_{1R} = I_1/(I_1 + I_2), \quad I_{2R} = I_2/(I_1 + I_2).$$

These dependences can be described as

$$\begin{aligned} I_{1R} &= 0.33 - 0.26 \times \exp(-E_0/kT) \\ I_{2R} &= 0.26 \times \exp(-E_0/kT), \end{aligned} \quad [1]$$

where k is the Boltzmann constant and $E_0 = 15 \text{ cm}^{-1}$ is the effective activation energy.

It should be noted that the intensity of line 2 at $T = 4.2 \text{ K}$ is greater than zero, unlike the results of (5). The mechanisms of initiation of the temperature-independent and temperature-dependent contributions are, possibly, of a different physical nature.

In (5), line 1 is referred to as the “low-temperature” EPR spectrum of the Fe^{3+} ion and line 2 as the “high-temperature” spectrum. In the case of kaolin, these terms can only be used for the temperature-dependent contribution of each line. The temperature change results in a redistribution of the absorption intensity between the low- and high-temperature spectra.

The unusual change of the spectral line intensities is not the only peculiarity. Figure 3 and more clearly Fig. 5 show that the width of resonance line 2 decreases with temperature rise. Figure 7 shows the temperature dependence of the linewidths at half-height. According to Fig. 7, the width of line 1, ΔH_1 , does not depend, within the measurement error, on temperature and equals $0.55 \pm 0.1 \text{ kOe}$. At $T = 288 \text{ K}$, the width of line 2, ΔH_2 , equals 1.58 kOe . When the temperature is decreased, the width of line 2 grows exponentially to a value of 2.26 kOe at $T = 4.2 \text{ K}$: $\Delta H_2 = 1.6 + 0.5 \exp(-T/8.1)$. The broadening of line 2 is accompanied by the lowering of the integral (and peak) intensities. It should be stressed that the ordinary mechanism

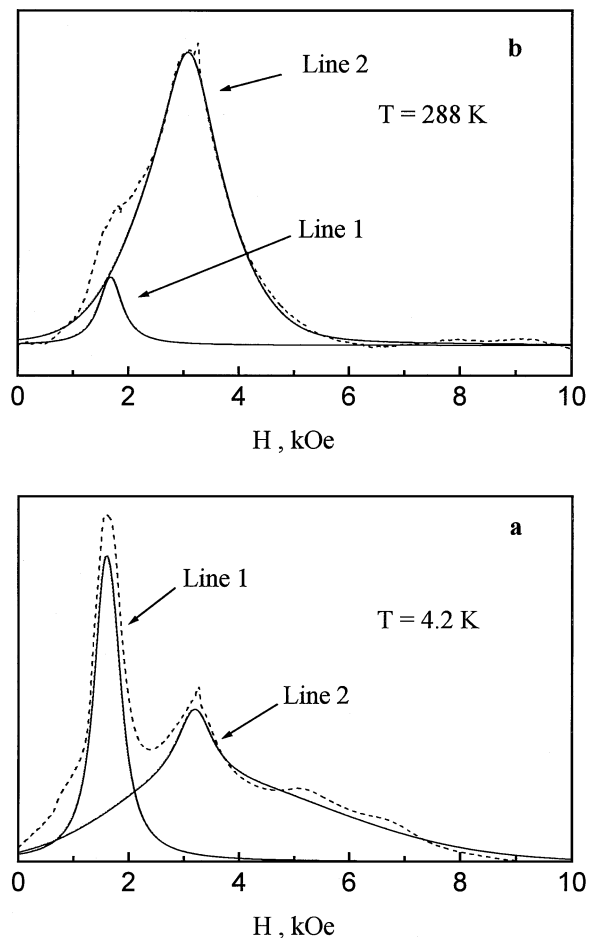


FIG. 5. A computer resolution of the resulting absorption line for $T = 4.2$ and 288 K. The intensity and form of lines 1 and 2 were chosen on the condition that there is a minimal deviation between the model line, being a superposition of lines 1 and 2, and the experimental form of the absorption line.

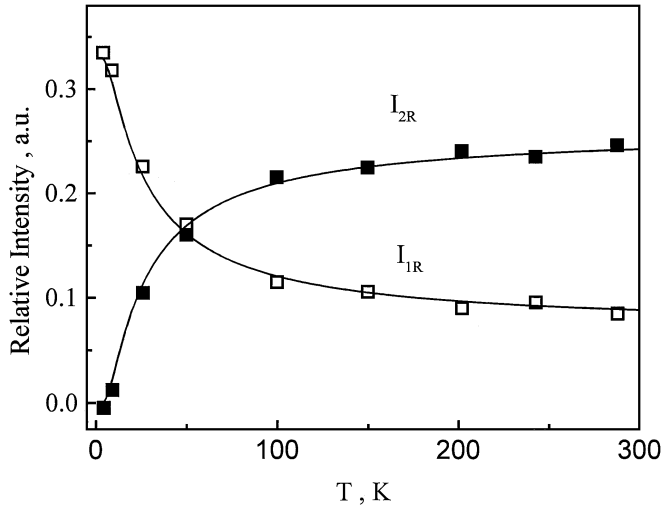


FIG. 6. Temperature dependence of the relative integral intensities of lines 1 and 2. This dependence describes the second mechanism of temperature change in the EPR spectrum which describes the process of the integral intensity redistribution between lines 1 and 2.

of the EPR spectrum resonance line broadening, due to the relaxation spin–lattice processes, results in increased linewidth when the temperature is increased. The inverse temperature dependence of this parameter, observed experimentally, testifies to an additional and more efficient mechanism determining the width of the EPR resonance line. The behavior of the intensities of lines 1 and 2 and the above arguments are sufficient grounds to conclude that lines 1 and 2 are interrelated.

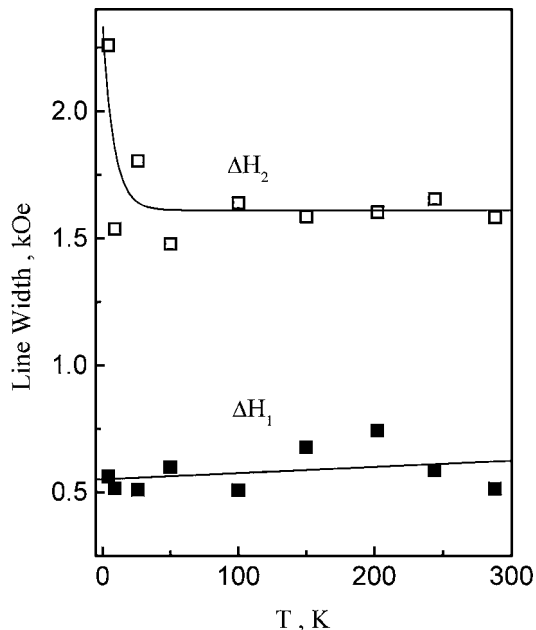


FIG. 7. Temperature dependence of the width of resonance lines. The width of line 1, ΔH_1 , does not depend on temperature. When the temperature is decreased, the width of line 2 grows exponentially.

DISCUSSION

The described EPR spectrum of Fe^{3+} in kaolin has a number of features that must be considered separately.

1. First, we must analyze the values of g -factors of the resonance lines 1 and 2 which belong to the iron impurity ion. The Fe^{3+} ion has the configuration d^5 . The spin of the ground state is $S = 5/2$. For the most frequently encountered EPR spectra of Fe^{3+} , the typical g -value is close to 2.

On the other hand, a resonance line with the g -value close to 4.3 has been analyzed in a number of studies (12–15) of the EPR spectrum of iron ions in silicate glasses. There is no long-range order in the glasses as well as in the kaolin powder investigated by us. In kaolin, lines 1 and 2 were observed by the authors of (10, 11, 16). In (17) a detailed analysis of the EPR spectrum of iron ions in amorphous materials is given. In (17) it is assumed that the spectrum consisting of two resonance lines with $g \cong 2$ and $g \cong 4.3$ belongs to different nonequivalent magnetic centers of the Fe^{3+} ion. The centers differ in the value of the low-symmetry component of the crystalline field acting on the magnetic ion. The authors of (17) assume that the line with $g \cong 2$ corresponds to a center for which the low-symmetry component of the crystalline field is much less than the Zeeman energy. The line with $g \cong 4.3$ corresponds to a center for which the low-symmetry component of the crystalline field is much larger than the Zeeman energy. Both cases are considered in items 2 and 3 in more detail.

2. If the electric field of the nearest environment of the magnetic ion Fe^{3+} is of the cubic symmetry or the low-symmetry component is much less than the Zeeman energy, then the Hamiltonian of the zero approximation will be in the form

$$H_0 = g_0 \cdot \beta \cdot \mathbf{H} \cdot \mathbf{S}, \quad [2]$$

where β is the Bohr magneton, and g_0 is the g -value of the ground-state multiplet $S = 5/2$. The numerical value of g_0 is close to 2.0. The Hamiltonian of fine-structure splitting should be considered a perturbation. In this case, the EPR spectrum of the magnetic center consists of five lines. The central resonance line does not, as a rule, depend on the direction of the magnetic field and corresponds to a transition $+1/2 \leftrightarrow -1/2$. The other four resonance lines of the fine structure of the spectrum depend on the magnetic-field direction. In a “polycrystalline” sample, a single resonance line will be observed with the effective g -value equal to that of the resonance transition $+1/2 \leftrightarrow -1/2$ and having a value $g \cong 2$. The resonance lines of the other transitions of the fine structure of Fe^{3+} are averaged as a result of the orientation disordering and will contribute to the linewidth.

3. If the low-symmetry component of the electric field of Fe^{3+} nearest-neighbor environment is much greater than the Zeeman energy, then according to (17, 18), the Hamiltonian of the zero-order approximation should be in the form

$$H_0 = D \cdot (S_z^2 - S(S+1)/3) + D \cdot (S_x^2 - S_y^2)/3. \quad [3]$$

The Zeeman Hamiltonian [2] and the Hamiltonian of the fine-structure splitting [4],

$$H_1 = (E - D/3) \cdot (S_x^2 - S_y^2), \quad [4]$$

should be considered a perturbation. Here S_x , S_y , S_z are components of the spin operator; D , E are parameters of the zero splitting, which characterize the field of axial symmetry and the rhombic component of the field, respectively. The action of the Hamiltonian [3] splits the spin multiplet $S=5/2$ into three Kramers doublets with energies $\varepsilon_1=0$; $\varepsilon_2=4\sqrt{7} D/3$; $\varepsilon_3 = -4\sqrt{7} D/3$. It has been estimated (17) that the lower and upper doublets have highly anisotropic g -tensors, while the g -value of the middle doublet is isotropic and approximately equal to $g \cong 4.3$. In a polycrystalline sample, the axes of symmetry of different magnetic centers are randomly oriented in different directions with respect to the magnetic field. As a result, the EPR spectrum of the doublets with the anisotropic g -tensors is “smeared” over a wide range of magnetic fields and cannot be observed experimentally. Only resonance line 1 with $g \cong 4.3$ is observed.

4. The transition from the low-temperature spectrum to the high-temperature one occurs not in a jump-like manner, but gradually (Fig. 3). Therefore, the structural phase transitions cannot cause the change in the intensity of the EPR spectral lines.

5. In articles (10, 11, 16, 17) it is assumed that the spectrum consisting of two resonance lines with g -values $g \cong 2$ and $g \cong 4.3$ belongs to different nonequivalent magnetic centers of the Fe^{3+} ion. It is believed (11) that line 1 corresponds to Fe^{3+} ions which are impurities in the kaolinite structure and substitute the Al^{3+} ions. Line 2 corresponds to Fe^{3+} ions which are in the structure of another mineral component of kaolin. Besides, in the kaolinite structure, there are two nonequivalent positions for the trivalent ion. Despite the magnetic ion having the ability to occupy nonequivalent positions, it is hardly probable that the temperature changes could induce real displacements of Fe^{3+} ions from one nonequivalent position to another.

6. In the high-field part of resonance line 2 of the EPR spectrum of Fig. 3 ($T = 4.2, 9, 26$ K) one can see the maxima rather well. The maxima are typical of the EPR spectrum which is averaged over directions of the magnetic field. Figure 8 shows the structure of energy levels of the multiplet $S=5/2$ and the EPR spectrum for $T = 4.2$ K. The resulting form of line 2 averaged over magnetic field directions has five maxima. The central maximum corresponds to transition $1/2 \leftrightarrow -1/2$. The other maxima correspond to another four transitions and appear as a background of the averaged line 2. The two high-field maxima correspond to transitions $-1/2 \leftrightarrow -3/2$, $-3/2 \leftrightarrow -5/2$. The two close maxima corresponding to transitions $-5/2 \leftrightarrow -3/2$ and $3/2 \leftrightarrow 1/2$ are near the field $H \approx 1$ kOe. The maxima on the high-field part of curve 2 permit one to estimate the parameter of the zero splitting $D = D_0 = 0.09 \text{ cm}^{-1}$ ($D < h\nu$).

7. It should be noted that the three states of the Fe^{3+} magnetic ion are observed experimentally. In the first low-symmetry

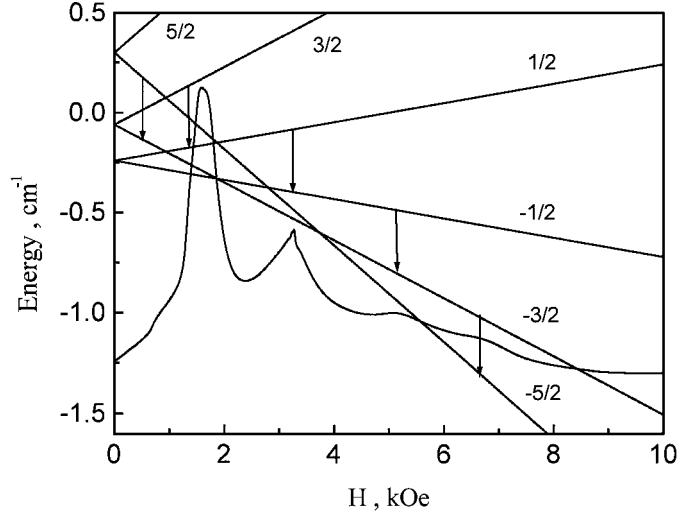


FIG. 8. Structure of the energy states of the spin multiplet $S=5/2$ and a form of the EPR spectrum at $T=4.2$ K. The resulting form of line 2 has five maxima. The central maximum corresponds to transition $1/2 \leftrightarrow -1/2$. The two high-field maxima correspond to transitions $-1/2 \leftrightarrow -3/2$, $-3/2 \leftrightarrow -5/2$. The two close maxima corresponding to transitions $-5/2 \leftrightarrow -3/2$ and $3/2 \leftrightarrow 1/2$ are near the field $H \approx 1$ kOe.

state, the parameter of spin Hamiltonian $D \gg h\nu = 0.3 \text{ cm}^{-1}$. The presence of line 1 testifies to the existence of such a state. $D_0 \approx 0.09 \text{ cm}^{-1}$ is characteristic of the second state. It is characterized by the form of line 2 at $T = 4.2$ K ($D = D_0 < h\nu$). The third state is highly symmetric and it is defined by the spin Hamiltonian parameter $D \ll D_0 < h\nu$. The form of line 2 at $T = 288$ K corresponds to this state.

The change in the form of line 2 with the temperature increase is not connected with the temperature dependence of the parameter of zero splitting D . Let us discuss this assertion. In the case of decrease in D , the width of line 2 should decrease with the rise of temperature. That is what we observe experimentally (Fig. 3). However, in such a case, the maxima of transitions $-1/2 \leftrightarrow -3/2$, $-3/2 \leftrightarrow -5/2$ should displace to the central transition $1/2 \leftrightarrow -1/2$ with the increase of temperature. In fact, the temperature increase results in a decrease of the intensity of contribution of the state with $D = D_0 \approx 0.09 \text{ cm}^{-1}$ in the absence of the displacement of corresponding maxima.

8. According to the temperature dependence of the EPR spectrum obtained in this paper, in kaolin the Fe^{3+} ions are distributed over states having different values of the low-symmetry component of the crystalline field. At low temperatures, the states with the low-symmetry component which is much more than the Zeeman energy are mainly occupied. When the temperature is increased, the excited states with the low-symmetry component which is much less than the Zeeman energy are occupied. Since the total number of magnetic ions is constant, the transition of ions to the excited states results in the decrease of the intensity of line 1 as the temperature is increased. Line 2 becomes more intense in this case (Figs. 3 and 6).

We thus pay attention to the following three characteristics. First, the low-temperature states are characterized by the low-symmetry properties, while the excited states are typical of the properties of much higher symmetry. Second, a region exists in which the low- and high-symmetry spectra coexist. Third, a decrease of the intensity of the low-symmetry spectrum when the temperature is increased and a corresponding increase of the intensity of the high-symmetry spectrum are observed. Such characteristics are inherent in the systems with the multimimum potential. The best studied system with the multimimum potential is the Jahn–Teller ion of a divalent copper ion in an octahedral environment. In such systems, the temperature-induced changes in the intensity of spectra, which correspond to the low- and high-symmetric states, are due to changes in the population of vibronic states (6, 7). It should be noted that Fe^{3+} is an S-ion, and the appearance of the Jahn–Teller effect for this ion is hardly probable. In the present case, the ion plays the role of a paramagnetic probe enabling one to observe the unusual dynamics of the ligand environment. The coincidence of the temperature changes of the EPR spectrum of Fe^{3+} in kaolin with similar temperature changes in systems with the multimimum potential provides grounds to assume that the magnetic center under consideration possesses similar properties. In systems with multimimum potentials, parameter E_0 [1] characterizes the height of barrier between the minima.

9. The attention should be paid to an unusual temperature change in the width of line 2. It is seen from Fig. 5a that for $T = 4.2$ K the line 2 is of unusual form typical of Fe^{3+} ion in powder provided that $D < h\nu$. Figure 9 shows the experimental line of the EPR spectrum in comparison with a theoretical model of line 2.

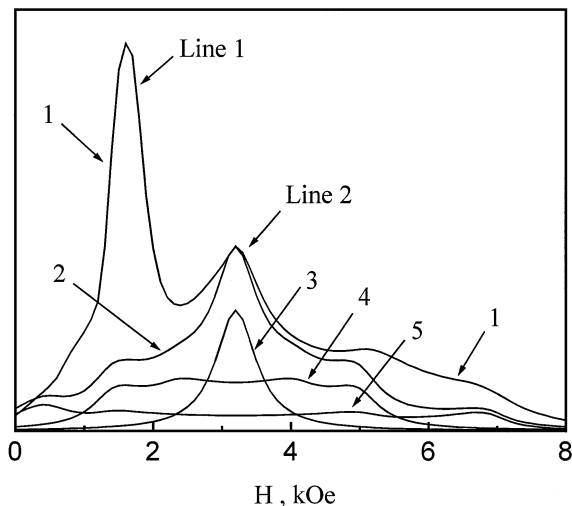


FIG. 9. The experimental line of the EPR spectrum in comparison with a theoretical model of line 2. A comparatively narrow central peak of line 2 is defined by the resonance transition $1/2 \leftrightarrow -1/2$ (curve 3). The resonance lines corresponding to transitions $-1/2 \leftrightarrow -3/2$, $-3/2 \leftrightarrow -5/2$, $3/2 \leftrightarrow 1/2$ are averaged and form a relatively broad absorption “band” (curves 4 and 5). Line 2 is a superposition of contributions from all quantum-mechanical transitions.

of line 2. The theoretical model of the line has resulted from the orientational averaging of the EPR spectrum with respect to the direction of the external magnetic field. The averaging has been done for Fe^{3+} ion with the spin Hamiltonian described by parameters $g = 2.0$, $D = 0.09 \text{ cm}^{-1}$. Spin Hamiltonian parameter E giving a lower, compared to parameter D , contribution to anisotropy of the spectrum is taken to be zero.

According to Fig. 9, a comparatively narrow central peak of line 2 is defined by the resonance transition $1/2 \leftrightarrow -1/2$. The resonance line corresponding to that transition does not practically depend on external magnetic field orientation. Thus, the orientational disordering of the magnetic centers has no influence on the resonance line of the transition (curve 3 of Fig. 9).

As a result of the orientational averaging with respect to external magnetic field direction the resonance lines corresponding to transitions $-1/2 \leftrightarrow -3/2$, $-3/2 \leftrightarrow -5/2$, $3/2 \leftrightarrow 1/2$ are averaged and form a relatively broad absorption “band” (curves 4 and 5 of Fig. 9). Line 2 is a superposition of contributions from all quantum-mechanical transitions.

The width of the absorption band formed by transitions $-1/2 \leftrightarrow -3/2$, $-3/2 \leftrightarrow -5/2$, $3/2 \leftrightarrow 1/2$ is proportional to spin Hamiltonian parameter D . As a result, the larger parameter D , the wider line 2.

CONCLUSIONS

Within the framework of the proposed model of the excited-state population, it is possible to explain the character of the temperature dependence of the integral intensity of the EPR spectrum resonance lines, the width of resonance for line 2, and the rest of the features of the EPR spectrum.

At helium temperature, the ligands of the environment are “frozen” at the bottom of the potential well (or wells) which correspond to the largest value of the low-symmetry component of the crystalline field. Simultaneously, the anisotropy of the crystalline electrical field is maximum, and therefore line 1 is the most intense. As the temperature is increased, a number of magnetic centers pass to the excited vibronic states. The excited states of magnetic centers are less anisotropic than the ground states. In the case of the Jahn–Teller ion of copper, this property is connected with the averaging of deformation as a result of fast “hops” from one potential well to another. The resonance line 2 of the EPR spectrum results from the population of weakly anisotropic excited states (Fig. 3). Increasing the number of magnetic centers in the excited states leads to a decrease of the number of magnetic centers in the ground state. This is the cause of the decrease in intensity of resonance line 1 when the temperature is raised.

The unusual temperature dependence of the width of resonance line 2 (Fig. 7) is due to the change in distribution of magnetic centers over the excited states.

At high temperatures, the greater part of the magnetic centers is found in the excited states for which $D \ll D_0 < h\nu$. The EPR spectrum of these centers is characterized by the g -value of the

transition $1/2 \leftrightarrow -1/2$. The orientational averaging of the rest of transitions does not broaden the resonance line.

At low temperatures, a major portion of the magnetic centers is in states close to the ground state. The lower the excitation energy, the higher the value of the low-symmetry component of the crystalline field and the farther the resonance lines of transitions $\pm 5/2 \leftrightarrow \pm 3/2$ are located from the line of the transition $1/2 \leftrightarrow -1/2$. As a result of the orientational averaging over directions of the axes of symmetry, the contribution of the transitions $\pm 5/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 1/2$ at low temperatures will result in the broadening of resonance line 2 (Figs. 3 and 7).

The temperature-induced change in the EPR spectrum of the Fe^{3+} complex in kaolin is similar to that of the Fe^{3+} ion in nitroso- β -naphthol and polyaniline (5). This coincidence of the properties of the EPR spectra of the magnetic centers, despite the substantial difference in the ligand environment of the Fe^{3+} ion, evidences the presence of an effect which is common to those different substances.

In this article, it is shown that the investigated magnetic ion plays the role of a magnetic probe. This magnetic probe is an essential part of kaolinite, and this fact can be used for investigating the magnetic properties of kaolinite-clay.

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