Nanocrystals of Montmorillonite in Composites of Ultrahigh-Molecular Weight Polyethylene

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The results of the X-ray diffraction analysis of ultrahigh-molecular weight polyethylene with montmorillonite crystals have shown the Debye lines to be wide and low-resolved for all the diffraction angles. During the investigation of Fe^{3+} EPR spectum for montmorillonite single crystals, the effect of crystalline – field multiminimum potential has been revealed in the temperature range from 77 to 300 K. It has been also revealed that the position of Fe^{3+}– ion in the electric field is not central. The results of the EPR and X-ray diffraction analysis done on montmorillonite and kaolinite nanocrystalls have shown that the spectra are well – resolved and can be used in future studies of the texture in nanocomposites of ultrahigh – molecular weight polyethylene with kaolinite and montmorillonite crystals.

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INTRODUCTION

Spectroscopy investigations of nanocrystals of montmorillonite and kaolinite in composites of ultrahigh-molecular weight polyethylene done by methods of electron paramagnetic resonance (EPR) and the X-ray diffraction analysis have shown that the EPR method possesses unique potentialities. Crystal orientation is, as a rule, investigated by the X-ray diffraction analysis. However, the fact that this method was helpless and the EPR method was prospective in investigation of montmorillonite nanocrystals is the reason for the EPR technique development undertaken in this work. It is shown in this paper that the X-ray diffraction analysis can't give us the information on orientation of montmorillonite crystals in polymeric matrix. This is because the Debye lines are broad, low intensive and low-resolved for all angles of diffraction. On the other hand, the EPR method turned out to be fruitful due to the anisotropy line 1 [1–8] of intensity increasing with temperature decrease. The resolution of spectral lines increases accordingly.

EXPERIMENTAL RESULTS AND DISCUSSION

Montmorillonite and kaolinite structures refer to one and the same subclass of silicates. Their crystal structures are therefore very similar. Figure 1 illustrates the structure of kaolinite $Al_2[Si_2O_5](OH)_4$. But in montmorillonite and kaolinite structures, the unit cell parameters and symmetry differ very much.

Kaolinite $Al_2[Si_2O_5](OH)_4$ – crystalline structure consisting of two-layer packets containing one tetrahedral silicon-oxygen layer of composition $[Si_{2n}O_{5n}]^{2n-}$ and one octahedral alumo-oxygen-hydroxylic layer of composition $[Al_{2n}(OH)_{4n}]^{2n+}$. Both layers form a packet by means of common oxygen atoms from the silicon-oxygen layer. The kaolinite space group is C_i^1 ($P\bar{1}$) with the unit cell parameters $a_0 = 5.14\,\text{Å}$; $b_0 = 8.93\,\text{Å}$; $c_0 = 7.37\,\text{Å}$; $\alpha = 91.8°$; $\beta = 104.5°$; $Z = 2$. The Fe^{3+} content of kaolinite is 0.5%, depending on the deposit of origin.

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 magnetic Fe^{3+} ion substitutes the Al^{3+} ion isovalently. It is seen from Figure l that the magnetic Fe^{3+} ion has two nonequivalent positions.
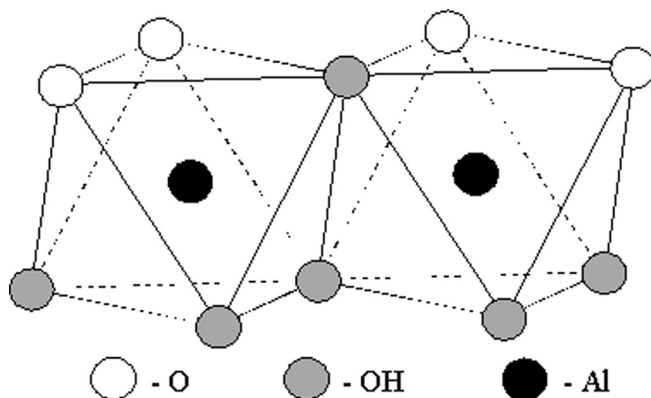
FIGURE 1 Structure of kaolinite $Al_2[Si_2O_5](OH)_4$. Nearest environment of Al^{3+} ions.

Montmorillonite: $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$, (M = monovalent cation; x = degree of isomorphous substitution). The montmorillonite space group is monoclinic syngony C_{2h}^3–C2/m with the unit cell parameters $a_0 = 5.17$ Å; $b_0 = 8.97$ Å; $c_0 = 9.95$ Å; $\beta = 99°54'$; Z = 2. The Fe^{3+} content of montmorillonite is 0.8%, depending on the deposit of origin.

The nearby environment of Fe^{3+} ions is in the form of octahedrons of two types. The magnetic Fe^{3+} ion substitutes the Al^{3+} ion isovalently. The magnetic Fe^{3+} ion has two nonequivalent positions.

The X-ray diffraction analysis of the kaolinite and montmorillonite crystals orientation was done at T = 295 K. A spectrograph was used making it possible to investigate the diffuse scattering of low-intensive X-rays in a wide range of the X-ray scattering angles ($\theta = 5$–$80°$) with a high resolution of diffraction maxima due to the application of the Debye method and a soft CrK_α-radiation, $\lambda = 2.29092$ Å.

For the diffraction from the initial kaolinite powder, the maximum intensity is observed for diagonal planes of the $(1\bar{1}\bar{1})$ type and for basal planes of the (001) type. The lines are well resolved and can be used in subsequent investigation of nanocrystal orientation in composites of polymers.

Results of the X-ray diffraction analysis of ultrahigh-molecular weight polyethylene with montmorillonite crystals have shown that the Debye lines are broad, low intensive and low-resolved for all angles of diffraction. For diagonal planes of the $(1\bar{1}\bar{1})$ type and for basal planes of the (001) type, the intensity practically merges with that of halo – a diffraction band from the amorphized phase of this structure.

Difference in crystallographic symmetries of the studied materials makes a definite contribution to the obtained results of X-ray diffraction analysis of ultrahigh-molecular weight polyethylene with kaolinite and montmorillonite crystals. Comparison of crystallographic symmetries of the mentioned structures shows that kaolinite unit cell is of a higher symmetry than that of montmorillonite. Therefore, denser reflections from basic symmetry planes of kaolinite are resolved. This is explained by a higher repetition of rays reflected from the symmetry planes. For montmorillonite, the condensation of reflections from basic symmetry planes is little distinguished above the intensive halo. This spectrum of the diffraction X-ray consists of very faint lines.

Unordinary temperature dependence of Fe^{3+} EPR spectrum in organic substances of different composition and structure has been revealed [1,2]. In paper [3] and in this paper, similar peculiarities of Fe^{3+} EPR spectrum have been revealed in typical inorganic minerals, such as kaolinite $Al_2Si_2O_5(OH)_4$ and montmorillonite $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$. Such EPR spectra are typical of the effect of multiminimum potential of the crystalline field the magnetic Fe^{3+} ion is in.

In montmorillonite $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$, multiminimum potential effect was revealed at high temperatures. The EPR spectrum of both lines is well resolved at T = 77–300 K.

The Fe^{3+} EPR spectrum of montmorillonite $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$ was investigated by using a spectrometer with the microwave field frequency $v = 9.756 \pm 0.001$ GHz at T = 77–300 K. Primary attention was paid to the spectrum of the impurity Fe^{3+} ion, a component of montmorillonite $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$ mineral. The form of the EPR spectrum is shown in Figure 2. The spectrum of the impurity Fe^{3+} ion consists of two resonance lines. Line 1 is anisotropic, it is described by the effective g-factor $g_1 = 4.13 \pm 0.16$. Resonance line 2 is described by the effective g-factor $g_2 = 2.15 \pm 0.1$.

Fe^{3+} ion is an S-ion, its ground state is described by the spin S = 5/2. EPR spectrum is described by Hamiltonian (1) [8]:

$$H_0 = D \cdot (S_z^2 - S(S+1)/3) + D \cdot (S_x^2 - S_y^2)/3 \tag{1}$$

Here S_x, S_y, S_z – are components of spin operator, D – parameter of initial splitting. Its characterizes the field of axial symmetry.

When the temperature is decreased, the intensity of line 1 increases, that of line 2 decreases. The Fe^{3+} EPR spectrum of kaolinite behaves similarly. That's why, one should investigate the orientation of kaolinite and montmorillonite nanocrystals at T = 77 K and lower.

In the studied substance – montmorillonite $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$, being in electrical field, the position of Fe^3 ions is
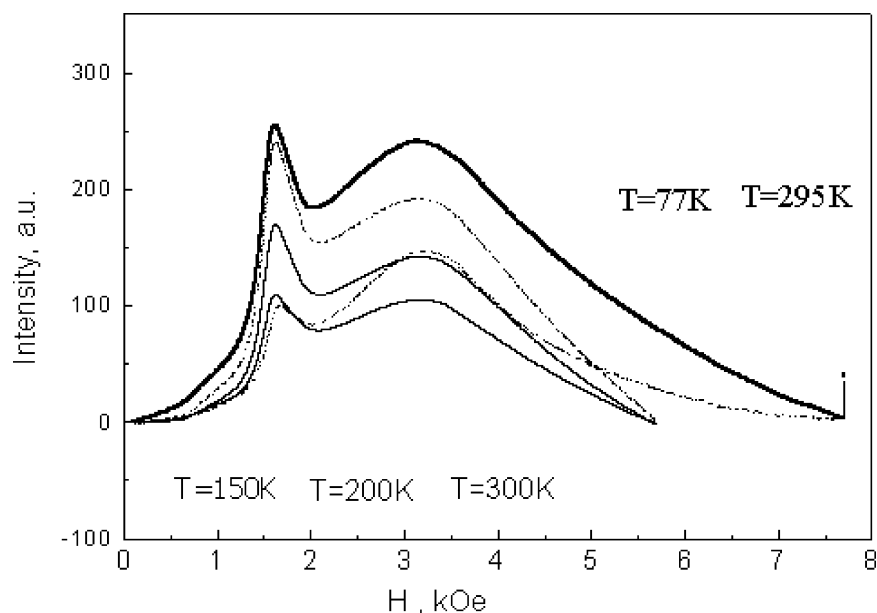
FIGURE 2 EPR spectrum in monmorillonite: T = 77, 150, 200, 295 and 300 K.

noncentral. Such position of magnetic ions results in the formation of multiple minima for the potential of crystalline field the Fe^3 ion is in. And the noncentral position of the magnetic ion results in the existence of the dipole moment.

Investigations of the influence of dipole moment on the Fe^{3+} EPR spectrum of monmorillonite $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$ in microwave electrical fields were done by using an X-band radiospectrometer. In the spectrometer, there is a rectangular resonator with 2 half-waves. An investigated sample is placed into the maximum of microwave magnetic field of the resonator. In this case, the electrical field is minimal. With measuring ampoule of small diameter, the electrical field value is close to zero.

Dependence of electrical field E on distance is determined by Eq. (2):

$$E_z = E_0 \sin(m\pi/a)x \sin(n\pi/b)y \, e^{jwt-yz} \tag{2}$$

where m and n are integers, a and b – sides of resonator section. By using differential relations between x and y – components of the electromagnetic field arising from the above Maxwell equation, we can find value of the electrical field E.

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In the experiment, value of x was pre-assigned by diameter of ampoules. There were ampoules of two diameters. Ampoule 1 was of a larger diameter. And the electrical field the sample was higher than in the case of ampoule 2. Figure 2 illustrates EPR spectra of Fe^{3+} ions in montmorillonite crystals placed in the ampoules. Broad line stands for EPR spectra measured in ampoule 1 of larger diameter for $T = 77$ K and $T = 295$ K. Narrow line – those for ampoule 2 of lesser diameter and $T = 150, 200$ and 300 K. In Figure 2, the difference in width and shape of lines for the two ampoules is evident. For samples in ampoule 1 of larger diameter, the line width (Fig. 2, $T = 77$ K and 295 K) is much larger than those for samples in ampoule 2 ($T = 150$, 200 and 300 K). This corresponds to a higher electrical microwave field for ampoule 1, as compared to that for ampoule 2. The line shapes are also rather different. By this difference in width and shape of lines one can determine value of the magnetic dipole moment.

It has been shown that the investigated magnetic ion Fe^{3+} substituted Al^{3+} ion in kaolinite [3] and montmorillonite, plays the role of a magnetic probe. This a magnetic probe is the integral part of kaolinite and montmorillonite single crystals, and this fact can be taken into consideration when investigating the orientation of nanocrystals in composites of polymers by the EPR method.

REFERENCES

[1] Vasyukov, V. N., Dyakonov, V. P., Shapovalov, V. A., Aksimentyeva, E. I., Szymczak, H., & Piechota, S. (2000). *Low Temperature Physics*, *26*, 265.
[2] Vasyukov, V. N., Shapovalov, V. A., Dyakonov, V. P., Dmitruk, A. F., Aksimentjeva, E. I., Szymczak, H., & Piechota, S. (2002). *Intern. J. Quantum Chem.*, *88*(4), 525.
[3] Vasyukov, V. N., Shapovalov, V. V., Schwarz, S. A., Rafailovich, M. H., Sokolov, J. C., & Shapovalov, V. A. (2002). *J. Magn. Resonance*, *154*, 15.
[4] Burzo, E., Chipara, M., Ungur, D., & Ardelean, I. (1984). *Physica Status Solidi*, *B124*, K117.
[5] Singh, R. (1984). *J. Phys. D: Appl. Phys.*, *17*, L57.
[6] Wickman, H. H., Klein, M. P., & Shirley, D. A. (1963). *J. Chem. Phys.*, *42*, 2113.
[7] Dowsing, R. D. & Gibson, J. F. (1969). *J. Chem. Phys.*, *50*, 294.
[8] Klyava, Ya. G. (1988). *EPR spectroscopy of disordered solids*. Riga: "Znanie".