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Characteristics of Nanocomplexes with iron Fe^{3+} in Glass Ionomer Cement Powder by ESR method

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The study is part of nanomedical biotechnology and is carried out by probing these systems using the Electronic Spin Resonance (ESR) method. The paper investigates Glass Ionomer Cement powder widely used in dental practice Glass Ionomer Cement C–Plus Triplekit–TM. To assess the quality of Glass Ionomer Cement and use ESR radiospectroscopy in the range from low ($T = 4.2$ K) to room ($T = 300$ K) temperatures. A new characteristic of compounds with nanocomplexes of magnetic iron ions Fe^{3+} is applied.

Key words: Electronic Spin Resonance (ESR), nanocrystals, crystal field potential, intensity of ESR lines.

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1. Introduction

Substances containing magnetic iron ions Fe^{3+} are widely used. The study of such substances with different structural symmetry requires a different approach. Research of single-crystal substances by the method of Electronic Spin Resonance (ESR) are widely known [1]. In the inestigation of powdered substances [2], as a result of orientational averaging of randomly oriented nanocomplexes with magnetic ions, the determination of magnetic properties requires the use of new methods. In this case the effect of the multi-minimum potential of the crystal field is used, which manifests itself in the ESR spectra with Fe^{3+} ions and Cu^2 [3–7]. Such a manifestation occurs when exploring the temperature transformation of the ESR spectra with Fe^{3+} ions and Cu^2 [3–7] in the range from low ($T = 4.2$ K) to room ($T = 300$ K) temperatures. In these works [3–7], research of organometallic compounds with ions of the iron group was carried out, which showed that the effect of a multi-minimum potential is common for substances, regardless of the type of symmetry of the structure.

2. Experimental results and discussion

The composition of Glass Ionomer Cement CX–Plus Triplekit–TM includes kaolinite $Al_2[Si_2O_5](OH)_4$ with impurity iron ions Fe^{3+}, which are part of the mineral kaolinite. Impurity paramagnetic Fe^{3+} ions in kaolinite isovalently replace Al^{3+} ions. The iron content of kaolinite is typically around 0.3%. The studied magnetic ion Fe^{3+} in kaolinite nanocrystals is located in an octahedron consisting of two oxygen anions O and four OH groups (Fig. 1). The nearest environment of the magnetic center of iron has a coordination number of 6.

The study was carried out on a radio spectrometer with a frequency of 10 GHz in the range from low ($T = 4.2$ K) to room ($T = 300$ K) temperatures. The spectrum consists of two lines belonging to the iron ion Fe^{3+} (Fig. 2, 3) in Glass Ionomer Cement CX–Plus Triplekit–TM. The spectrum does not depend on the orientation of the external magnetic field. Fig. 2 demonstrates the ESR spectrum of ions iron Fe^{3+} in Glass Ionomer Cement at temperatures: $T = 3.7$, 46, 64 K. As the temperature increases, the intensity of

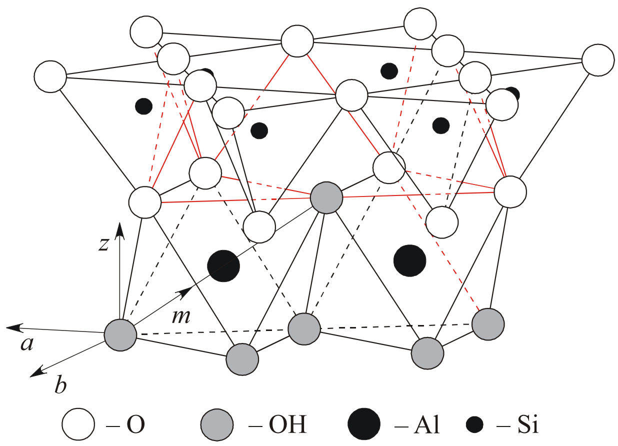

Figure 1. Unit cell of kaolinite $Al_2[Si_2O_5](OH)_4$: *a, b* — crystallographic axes; *m* is the magnetic axis; *Z* is the axis perpendicular to the plane (*ab*).

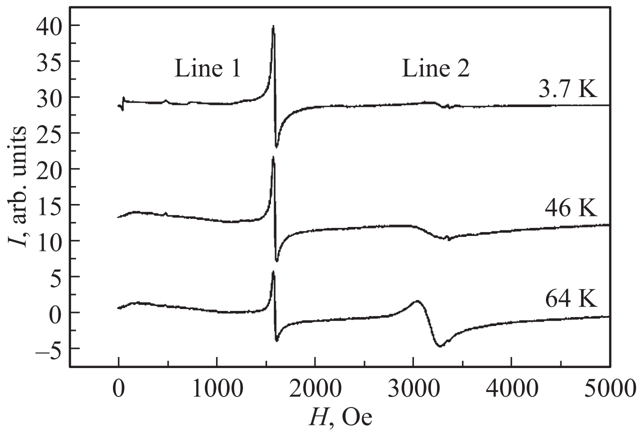

Figure 2. Temperature change in the spectrum of ESR ions iron Fe^{3+} in Glass Ionomer Cement. With increasing temperature: $T = 3.7$, 46, 64 K the intensity of resonance line *1* decreases, while the intensity of line *2* increases. For each temperature, the sum intensities of lines *1* and *2* is a constant value.

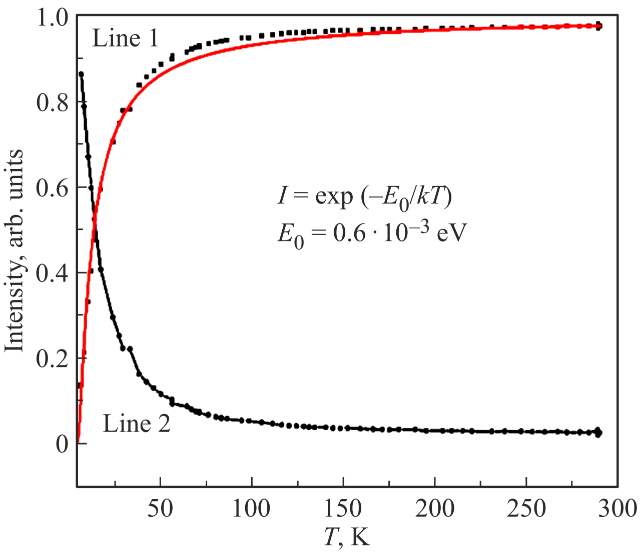

Figure 3. Temperature dependence of the reduced integral intensities of lines *1* and *2* of the spectrum of ESR ions iron Fe^{3+} in Glass Ionomer Cement.

resonance line *1* decreases, while the intensity of line *2* increases. The intensities of lines *1* and *2* are transferred at a constant total intensity of these lines. The value of the g factor of line *1* at a temperature $T = 4.2$ K is $g_1 = 4.13 \pm 0.16$. The value of the g factor of line *2* at a temperature $T = 4.2$ K is equal to $g_2 = 2.15 \pm 0.1$.

Fig. 3 presents the redistribution of the intensities of line *1* with $g \cong 4$ and line *2* with $g \cong 2$ ESR spectra of Fe^{3+} ions in the range from low ($T = 4.2$ K) to room ($T = 300$ K) temperatures. The nature of the redistribution of intensities is determined by the height of the barrier potential of the crystal field $E_0 \cong kT$ (Fig. 3). Barrier height E_0 of the crystal field potential is determined from experimental studies of the temperature dependences of the ESR spectra. For each temperature, the sum of the reduced intensities of lines *1* and *2* is a constant value equal to *1*. The barrier height E_0 depends on the structure of the nearest environment of the Fe^{3+} ions. The parameters of the immediate environment depend on the technology of using the Glass Ionomer Cement CX−Plus Triplekit−TM and can be fixed by the barrier height of the crystal field potential $E_0 \cong kT$ (Fig. 3).

Dependencies shown in Fig. 3 can be described by the relationship

$$I = \exp(-E_0/kT)$$

where k is the Boltzmann constant, E_0 is the height of the barrier of the adiabatic potential of the crystal field

$$E_0 = 0.6 \cdot 10^{-3}\,\text{eV} \quad (4.8\,\text{cm}^{-1}).$$

The properties of the material with kaolinite are subject to changes under mechanical action. Therefore, the properties of the material used in dental practice change during operation.

A study of such a change in the properties of the material under external influence was carried out. Composites with kaolinite nanocrystals have been analysed. Kaolinite crystals are thin plates $0.2 \times 0.2 \times 0.01\,\text{mm}^3$ in size [8]. The problem of investigating the location of kaolinite crystals in a polymer matrix is very relevant. Works [9–11] are devoted to its study. One of the promising methods for obtaining polymeric materials with a given orientation of filler crystals is solid-phase extrusion [12]. In the latter, orientational drawing of the material under high hydrostatic pressure is carried out. A polymer composite containing 27 wt% kaolinite has been studied. Samples for research were made by the method of plunger extrusion [13]. As a result of solid-phase extrusion, cylindrical specimens were produced. The extrusion degree of stretching was determined by the ratio λ of the cross-sectional areas of the workpiece (container channel) and die opening. Samples with $\lambda = 7$ were studied.

The orientation of crystalline kaolinite lamellae in a polymer composite was explored by X-ray diffraction and ESR spectroscopy. The dependence of the ESR spectrum on the orientation of the magnetic field was analysed in a plane parallel to the axis of a cylindrical sample. The dependence of the position of the peak of line *1* on the orientation angle of the magnetic field is shown in Fig. 4.

The main symmetry axis of the magnetic center for an octahedral environment, as a rule, coincides with one of the fourfold axes of the ligand octahedron. On Fig. 1 such a magnetic axis is denoted by the vector **m**. Analysis of the experimental angular dependence shown in Figs. 4 allows us to conclude that the Z axis of each kaolinite plate is oriented predominantly perpendicular to the axis of the extrudate. Those, planes (ab) of kaolinite plates are oriented mainly along the axis of the extruded sample.

The results of X-ray diffraction studies showed that the planes (a) of kaolinite plates acquire a predominant direction parallel to the sample axis. The Z axis turns out

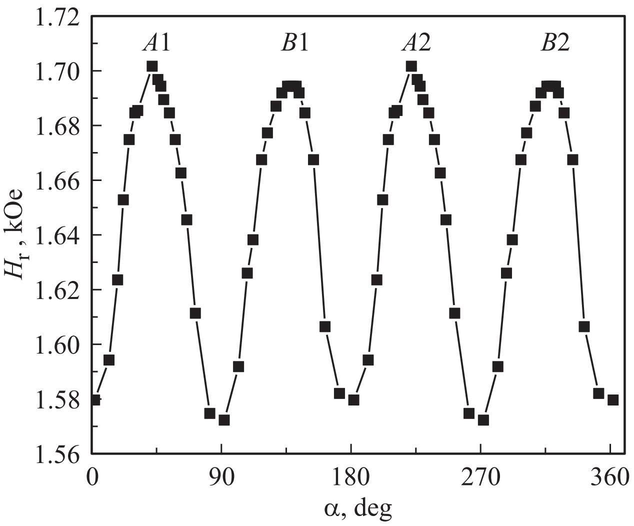

Figure 4. Angular dependence of the resonant fields of line *1* of the ESR spectrum at $T = 4.2$ K in a plane parallel to the cylinder axis.

to be located along the end layer of the sample, which coincides with the ESR data.

3. Conclusion

This research can be used to assess the quality of Glass Ionomer Cement CX–Plus Triplekit–TM used in dental practice. For this, ESR radiospectroscopy is used. The Fe^{3+} ion, which characterizes its nearest environment, is used as a probe. The parameters of this environment are fixed by the height of the potential barrier of the crystal field $E_0 \cong kT$ (Fig. 3), in which the Fe^{3+} ion is located. Under the mechanical action that occurs during treatment, kaolinite plates are ordered. This is possible due to the presence of a developed faceting plane of the kaolinite crystal. The nature of the orientation of kaolinite plates is determined by the direction of the deformation gradient and its magnitude. At the same time, the properties of the material used in dental practice and the quality of dental treatment change accordingly.

Conflict of interest

The authors declare that they have no conflict of interest.

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