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Specific aspects of the response to electric field of the natural pyrite electronic system

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The paper presents the results of studying the response of *n*— and *p*-type natural pyrite to single electric voltage pulses 50−300 V in amplitude. The sample resistance was found to decrease with increasing voltage amplitude. A dependence of the studied materialsŕesistances on the pulse polarity was revealed. The data obtained are consistent with the results of previous studies that evidence the presence in natural pyrite of intrinsic field caused by nonuniform impurity distribution in the bulk.

Keywords: pyrite, pulsed electric field, resistivity, nonuniform impurity distribution, diffusion and drift currents.

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At present there is a high interest in studying natural semiconductor compounds with a view to their use in various electronic devices [1–4]. One of the relevant research areas is studying the possibility of using natural minerals as thermoelectric energy converters. This is largely induced by the desire to involve into the field of thermoelectric materials science relatively low-cost materials widespread in nature. Semiconductor compounds based on which low-cost thermoelectric converters can be manufactured are sulfides, namely, binary compounds of sulfur with various metals. They exhibit quite high thermo-EMF coefficients [5,6], however, it is necessary to find ways to reduce their resistivity. The most common representative of the sulfide family is pyrite FeS_2. Results of previous studies show [6,7] that, depending on the deposit location, pyrite are of either *n*— or *p* conductivity type, which is because of differences in impurity compositions. At the same time, there exist pyrite samples in which ionization of impurities induces, in the temperature range preceding the onset of intrinsic conductivity, a rapid increase in the specific electrical conductivity [8], which has a favorable effect on the material thermoelectric efficiency. However, in the low-temperature region there is required a certain action able to reduce electrical resistance of the sample. This makes necessary to comprehensively study the natural pyrite physical properties, e.g. the processes occurring under the impact of electric field capable of ionizing impurity atoms.

Hence, the goal of this work is to study polarization-relaxation phenomena in samples of natural pyrite FeS_2 and to reveal the laws of electrical resistivity variation with the magnitude and polarity of single DC voltage pulses applied to samples with different types of conductivity.

In this research there was studied the response to external electric field of twelve samples of both the *n*— and *p*-type natural pyrite. For this purpose, an electrical voltage pulse was applied to a sample fixed in the measuring cell; after removing the voltage, the contacts were switched from the sample to the device measuring the electrical resistance. The experimental setup layout is given in Fig. 1. Measuring cell *1* provided temperature monitoring and control for sample *2* fixed between spring-type clamping contact *3* and stationary contact *4*. The DC voltage pulse was fed to the sample from power supply *6* via keyswitch *5*. The sample electrical resistance was measured upon the end of the electrical pulse by using the set of instruments *7* comprising a stabilized power supply and millivoltmeter.

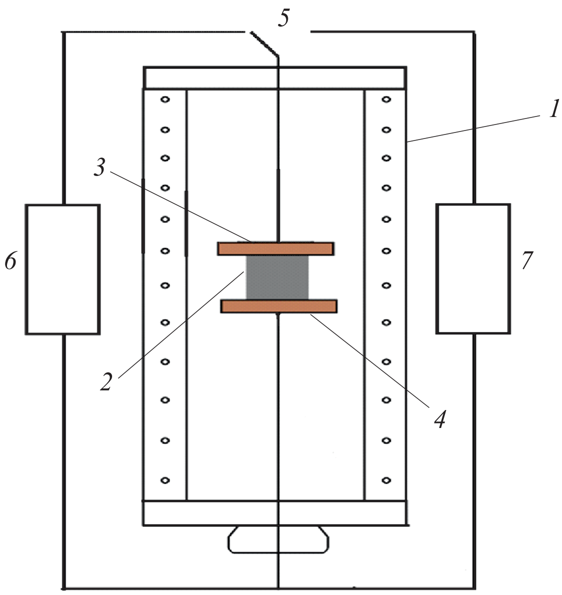

Figure 1. Layout of the experimental setup. *1* — measuring cell, *2* — sample under study, *3* — clamping contact, *4* — stationary contact, *it 5* — keyswitch, *6* — DC power supply, *7* — a set of instruments for determining the DC resistance.

The pulse duration was $\Delta t_{imp} \approx 10$ s; this value ensured minimization of the effect of sample heating by the current passing through it. The amplitude of voltage applied to the sample varied within $U = 50-300$ V. It was established that, within 1 min after the electrical pulse completion, the sample resistance continues decreasing to $\rho_{\min}$, after which increases to the initial value in several hours. In view of this, the experiment was repeated (with a higher voltage) only after complete relaxation of the sample.

Fig. 2 presents the results of studying two samples (samples 3 and 7 having the lowest and highest initial resistivity, respectively). The data obtained shows that $\rho_{\min}$ decreases with increasing applied pulse voltage.

This may be due to the electric-field-induced activation of an increasing number of impurity atoms; in addition, this fact evidences the existence in the studied pyrite samples of a smeared energy spectrum of impurity states whose presence was also detected in work [8] devoted to studying temperature dependences of electrical resistivity of FeS_2. Thus, in the described experiment, the role of external factor inducing activation of charge carriers is most likely played not by temperature but by a voltage pulse applied to the sample. The voltage pulse induces activation of charge carriers from impurity centers and traps, as a result of which the resistivity at a given temperature decreases. Practically, the effect of reducing the sample resistance by an electric voltage pulse is interesting because it makes possible an increase in the material electrical conductivity and, thereby, helps increase its thermoelectric efficiency.

Besides, the experimental data presented in Fig. 2 may be another argument confirming the presence of intrinsic field in the natural pyrite samples which are characterized by a significant thermo-EMF coefficient dispersion depending on the probe location. This is most likely due to the nonuniform distribution of impurity in the sample bulk, which promotes diffusion of free charge carriers and, hence, emergence of electric field stopping the diffusion. The laws

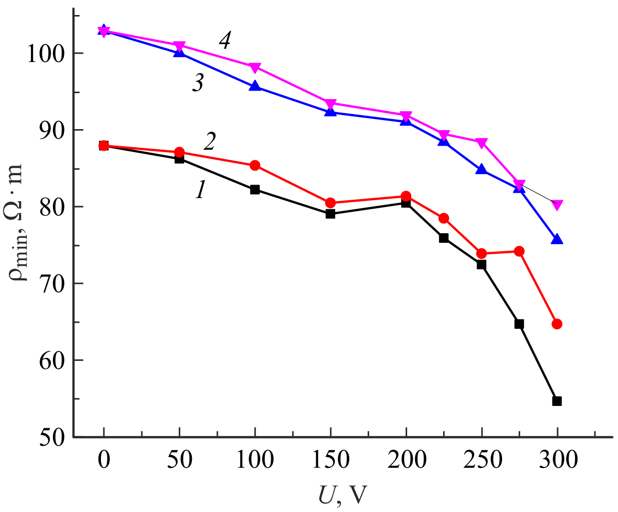

Figure 2. Dependence $\rho_{\min}(U)$. *1*, *2* — sample 3; *3*, *4* — sample 7. *1*, *3* — negative polarity; *2*, *4* — positive polarity.

of variation with temperature in the intrinsic field of the natural pyrite samples were studied in [8]. The presence of intrinsic field manifests itself also in the experimental results obtained in this study. As shown in Fig. 2, there was observed a resistivity dependence on the polarity of a pulse applied to the sample. The negative polarity was assumed to be that at which a greater decrease in resistivity was detected. Most probably, this depends on the alignment or misalignment of the external and internal field directions. As shown in [8], the latter varies in a complicated fashion depending on temperature, which is a consequence of temperature dependence of the physical quantities included in the expression describing the balance of diffusion and drift currents:

$$eD_p \text{grad} p = pe\mu E, \tag{1}$$

where e is the electron charge, D_p is the hole diffusion coefficient, p and μ are the hole concentration and mobility, respectively, E is the intrinsic electric field strength. Based on the Einstein equation accounting for the relationship between the charge carrier diffusion coefficient and mobility, it is possible to obtain for U the following expression:

$$U = Ex = kT \text{grad} p\, x/pe, \tag{2}$$

where x is the interprobe distance, T is the temperature, k is the Boltzmann constant.

This voltage can either coincide or not coincide in direction with the external one. In the first case, it will enhance the effect of decrease in resistance, while in the second (opposite) case the effect weakening is to take place, which is just what is observed in the experiment.

In conclusion, notice that the effects of the resistivity dependence on the magnitude and polarity of voltage applied to the sample can be used to increase the natural pyrite thermoelectric efficiency.

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Conflict of interests

The authors declare that they have no conflict of interests.

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