The EPR spectra of the W$^{5+}$ (5d$^0$) complexes in defective natural scheelite monocrystals were investigated. The principal values of the g-tensor, their directions, and also the hfs constants were determined. An analysis of the electronic state of W$^{5+}$ and probable distortions of the tungsten-oxygen tetrahedron in defective and irradiated scheelite monocrystals was carried out.

An investigation of paramagnetic defects of the type WO$_4^{2-}$ (W$^{5+}$ ions in a tetrahedral oxygen environment) in scheelite (CaWO$_4$) monocrystals is of interest in connection with the structural representations of these complexes and also with the determination of certain parameters of the electronic state of W$^{5+}$. The paramagnetic complexes of pentavalent tungsten in scheelite can come into being as centers of charge compensation, defects of radiation origin, structural defects in the growth of the crystals, etc. An EPR study of these defects was carried out by the authors of [1-3]. In particular, it was shown that when CaWO$_4$ monocrystals were irradiated at 77 K, paramagnetic centers, which were identified by the trapping of an electron by the tungsten-oxygen tetrahedron and by the appearance of paramagnetic W$^{5+}$ (5d$^0$) in the distorted tetrahedral coordination [2], are observed. A hole-type paramagnetic center on the oxygen, which weakly interacts with the two neighboring equivalent tungsten ions, is simultaneously observed in these same crystals. In connection with the fact that both spectra appear together after irradiation and simultaneously disappear at the annealing temperature of $-132^\circ$C at approximately the same rate, the authors suggest that these centers are probably the result of a single process in which the electrons paired in the original state are unpaired.

Irradiation of scheelite with neutrons also leads to the formation of similar defects which were identified by the trapping of an electron by the tungsten-oxygen tetrahedron [3].

The paramagnetic centers in defective natural scheelite monocrystals were investigated in this work.* The EPR spectra were investigated at 300-77 K at a frequency $\nu = 9200$ MHz. EPR spectra of two types were observed in the samples: the first consisted of a group of lines corresponding to an effective g-factor of less than 2.0023, and the second consisted of a group of lines with a value of the g-factor around that of a free electron. An investigation of the angular relationship of the spectra of the first group showed that three paramagnetic centers can be distinguished which, from now on, will arbitrarily be designated as A, B, and C. Each of them, in accordance with the tetragonal symmetry of the unit cell of scheelite, has four magnetically nonequivalent sites, an electron spin $S = \frac{1}{2}$, anisotropy of the g-factor, and hyperfine structure of the one nucleus with spin $I = \frac{1}{2}$. All four complexes of each paramagnetic center merge into one position when the direction of the magnetic field vector is parallel to axis $C_4$, and the total spectrum is simplified and has the form shown in Fig. 1. The intensities of the principal component and the component of the hyperfine structure (hfs) for centers A, B, and C are related in the ratio 1 : 0.15, which indicates an interaction occurs between the unpaired electron and the nuclear moment of W$^{5+}$, which has a spin $I = \frac{1}{2}$ and a natural distribution of 14.4%.

* Dark scheelite samples from the Ural Gumbeik deposit were the objects of this investigation. From spectral analysis, traces of the following are found in them: Ti, Fe, Mg, Si, and also weak EPR spectra of Mn$^{2+}$, Eu$^{2+}$, and Gd$^{3+}$ were recorded.

Fig. 1. EPR spectra of natural scheelite with the orientation of the magnetic field $H \parallel C_4$ and $T = 77^\circ K$: a) original sample, b) sample annealed at 300°C, c) annealed sample after $\gamma$-irradiation. Lines A, B, and C are the paramagnetic complexes of $W^{5+}$. The principal line and hfs lines from the $W^{183}$ nucleus for each complex are designated by the same letter. The additional hfs for type C $W^{5+}$ from the neighboring tungsten atoms is designated in the figure as $C'$. $A_1$, $A_2$, $B_1$, and $D_1$ are hole-type paramagnetic centers $WO_4$.

The experimentally found values and directions of the principal values of the $g$-tensors, angles $\theta$ and $\varphi$, and the hyperfine structural constants are given in Table 1 ($\varphi$ is the angle between the projection of the direction of $g_1$ onto the plane $(001)$ and the alignment of $[100]$). For comparison, the parameters of the previously investigated defect paramagnetic centers in irradiated scheelite [1-3] are also given. These data show that centers A, B, and C are caused by the trapping of an electron by the tungsten-oxygen tetrahedron forming the paramagnetic ion $W^{5+}$ ($5d^1$), which is similar to the results found for irradiated CaWO$_4$ monocrystals. A slight nonorthogonality of the principal directions of the $g$-tensor was noted for the centers we investigated, in particular for B and C.

The additional hfs from ions with nuclear spin $I = \frac{1}{2}$ (Fig. 1) is another characteristic of the spectra of A, B, and C. The additional hfs can be attributed to the interaction of the unpaired electron with the four equivalent $W^{183}$ nuclei located in the next neighboring position.

All the paramagnetic centers A, B, and C are stable at room temperature; the spectrum of A is observed at 77 and 300°C, and spectra of B and C only at 77°C.

The initial ratios of the intensities for these centers are approximately $1 : 0.4 : 0.03$. When the samples are heated to 300°C (1 h in air), the intensity of the spectra of A and B decreases considerably, and the spectrum of C disappears. When the sample was subsequently irradiated in a Co$^{60}$ $\gamma$-radiation source ($10^7$ rad) at 77°C, the