The Hg₃In₂Te₆ compound is crystallized into a sphalerite-type lattice with stoichiometric vacancies in the cationic sublattice; this feature is responsible for the high radiation hardness of this material [1]. A high photosensitivity makes this semiconductor promising for optoelectronic applications [2, 3]. Being a direct-gap semiconductor with a band gap of $E_g = 0.74$ eV, Hg₃In₂Te₆ has significant technological advantages over other materials for photodetectors in optical-fiber communication lines [4].

Doping is one of the ways of obtaining materials with new properties. Therefore, the investigation of the state and behavior of impurities of transition metals with an unfilled 3$d$ shell (in particular, Fe) in Hg₃In₂Te₆ crystals is an urgent problem of the physics and materials science of semiconductors.

Hg₃In₂Te₆ crystals were doped with iron to $10^{19}$ cm⁻³ during growth by the Bridgman method.

When replacing Hg²⁺ and In³⁺ cations in the Hg₃In₂Te₆ lattice, the iron impurity acquires the charge states Fe²⁺ and Fe³⁺, respectively. The stability of the newly formed bonds depends on their formation enthalpy $\Delta H$, which is negative [5]. The larger the value of the enthalpy $\Delta H$, the stronger the bond is. Comparison of the $\Delta H$ values for Hg–Te, In–Te, and Fe–Te bonds (−31.6, −96.2, and −77.8 kJ mol⁻¹, respectively) shows that the Hg–Te bond is the weakest, and a gain in energy is possible when mercury is replaced with iron. Therefore, the Fe²⁺ charge state in Hg₃In₂Te₆ is preferred in comparison with Fe³⁺. The Fe²⁺ impurity ion has a radius of 0.75 Å (according to Pauling [5]), which is much smaller than the radius of replaced Hg²⁺ ion: 1.1 Å (according to Pauling); this difference leads to lattice strain around impurity atoms.

Substitutional impurity atoms with a smaller radius form defects with local levels in the band gap. According to the data of [6–8], transition-metal impurities form states in the band gap, which manifest themselves in the additional absorption of light, both during the generation of free carriers and upon intracenter transitions. In this context, we investigated the photoconductivity and optical absorption spectra of Hg₃In₂Te₆(Fe) crystals.

Figure 1 shows the room-temperature photoconductivity spectra of undoped and iron-doped Hg₃In₂Te₆ samples. The long-wavelength edge of the photoconductivity spectrum [$I = f(h\nu)$] of the undoped material is due to interband optical transitions. The value $h\nu_{I=0.5} = 0.74$ eV for curve 1 is related to direct allowed transitions; it determines the optical width of the Hg₃In₂Te₆ band gap.
The photoconductivity spectrum of the iron-doped sample (Fig. 1, curve 2) contains a pronounced threshold in the low-energy region, after which the photoconductivity decreases with a decrease in the photon energy. Additional absorption near the intrinsic absorption edge causes electronic transitions from impurity levels near the top of the valence band to the conduction band. The energy of absorbed photons satisfies the inequality $h\nu \geq E_g - E_i$, where $E_i$ is the impurity ionization energy and $E_g = 0.74$ eV. The impurity ionization energy estimated from the edge shift (Fig. 1) is $E_i \approx 0.05$ eV; i.e., the impurity level is located approximately 1 eV above the top of the valence band, and the impurity photoconductivity is due to electronic transitions from the ground state of the Fe$^{2+}$ ion to the conduction band: Fe$^{2+} + h\nu \rightarrow$ Fe$^{3+} + e_c^-$, with a change in the charge state of the impurity center. Thus, the ground state of the Fe$^{2+}$ ion forms a deep level at $E_c - (E_g - E_i) = E_c = 0.69$ eV.

The optical density spectra were investigated in the photon-energy range from 0.2 to 0.74 eV at room temperature. Let us first analyze the optical density spectra $D = f(\nu)$ near the intrinsic absorption edge (Fig. 2). Comparison of the spectra $D = f(\nu)$ for the undoped and doped samples shows that doping of Hg$_3$In$_2$Te$_6$ crystals with iron leads to the additional absorption of light and a red shift of the absorption edge. Since the samples under study were insufficiently thin, the absorption-edge measurements did not allow us to reliably determine the band-gap width; however, the continuations of straight-line portions of the spectra $D = f(\nu)$ converge to the same point at $\nu = E_g = 0.74$ eV. This fact indicates that doping with iron does not change the band gap of Hg$_3$In$_2$Te$_6$.

The spectrum $D = f(\nu)$ for the doped sample (Fig. 2, curve 2) demonstrates a decline in the region $\nu < 0.68$ eV, which is adjacent to the long-wavelength absorption edge. This feature indicates the presence of a deep (relative to the conduction band) level. Since the concentration of ionized impurity centers (according to the Hall-effect data) is relatively low ($\sim 10^{13} - 10^{14}$ cm$^{-3}$), the step in the spectral optical density curves near the absorption edge is only slightly pronounced. Additional absorption, which manifests itself in the same spectral range as the photoconductivity, is related to electronic transitions between the impurity levels and conduction band.

It is noteworthy that, possessing an impurity level near the valence band, Hg$_3$In$_2$Te$_6$(Fe) crystals exhibit electronic conductivity in a wide temperature range, as is evidenced by thermopower data (Fig. 3, curve 1). This is due to the fact that the concentration of donors exceeds that of acceptors. The impurity conductivity activation energy (Fig. 4, curve 1) depends on the degree of impurity compensation.

To change the ratio of donor and acceptor concentrations and, correspondingly, the degree of compensation, the Hg$_3$In$_2$Te$_6$(Fe) samples were subjected to heat treatment at 460°C in helium. The temperature dependence of the thermopower demonstrates a transition from electron to hole conductivity as a result of annealing (Fig. 3, curve 2). The thermal ionization energy of the impurity in the annealed crystal was found from the slope of the dependence $\log \sigma = f(10^3/T)$ (Fig. 4, curve 2) to be 0.05–0.06 eV; this value is in good agreement with the optical ionization