FIG. 1

minimum or maximum electric conductivity is obtained, are determined by the affinity of the impurity to oxygen. Impurities having an ionization potential U_{imp} which is smaller than that of selenium, U_{Se}, form electrically neutral molecules with oxygen and decrease the electric conductivity of the selenium, whereas impurities with $U_{imp} > U_{Se}$ do not interact with the oxygen and, forming local levels, increase the conductivity. Figure 1 shows the plots of log (σ_{min}/σ) and log (σ_{max}/σ) against U_{imp}; here σ is the electric conductivity of pure but not oxygen-free selenium, σ_{min} and σ_{max} are the extremal values of the electric conductivity as functions of the concentration.

The thermal conductivity of amorphous selenium increases linearly with temperature, experiencing a jump ($\sim 40\%$) at the vitrification point ($\sim 31°C$). This jump is connected with the appearance of rotational vibrations in the individual links of the long chains of selenium. By varying the intermolecular coupling (by introducing different impurities) it is possible to vary the vitrification temperature, and thereby extend the technical usefulness of amorphous selenium.

It was established that up to $80°C$ the heat in crystalline selenium is transported by acoustic phonons, and above this temperature it is carried also by the photons.

Since there is no saturation of the bonds on the ends of the selenium chains, unpaired electrons are produced. These were investigated by the EPR method, and a signal with g = 2.0035 ± 0.0005 and ΔH_m = 5—Oe was observed in the selenium. In the initial pure material, there was no EPR absorption, regardless of whether selenium was in the form of a powder or a monolithic piece, although the presence of chains was not subject to any doubt. In all cases, the signal was produced only in the presence of acceptor impurities (oxygen, iodine, bromine), a large ratio of the surface of the volume, and after preliminary heat treatment.

Figure 2 shows the dependence of I/I_{st} on the heat treatment temperature T_{tr}. The maximum concentration of the EPR centers is $\sim 10^{17}$ cm^{-3}. An analysis of the dependence of I on T_{tr} shows that the process of EPR center formation has an activation character. The aggregate of the data allows us to conclude that the EPR absorption in selenium most probably caused by states with charge transfer, produced as a result of donor-acceptor interaction of the chains of selenium with the acceptor molecules of oxygen and the halides. It is also seen from Fig. 2 that the signal becomes indistinguishable after heat treatment at $T_{tr} \gtrsim 600°C$—an irreversible decay of the paramagnetic centers is produced as a
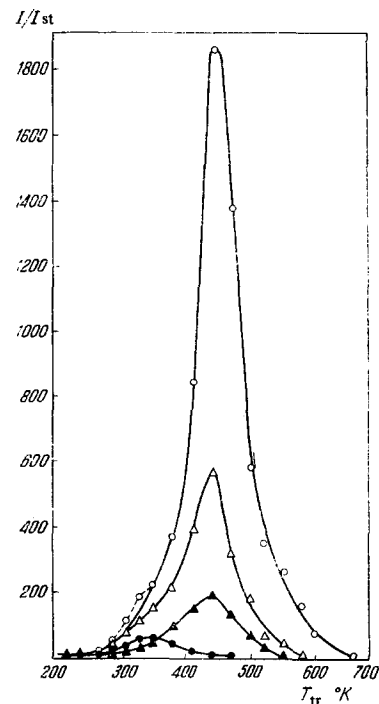

FIG. 2. Dependence of the EPR signal intensity in selenium on T_{tr}. O — Se B-2, powdered, p = 10^{-4} mm Hg: Δ — Se B-2, granule, p = 10^{-4} mm Hg; ● — Se B-2, p = 760 mm Hg; ▲ — Se B-5, p = 10^{-4} mm Hg.

result of the chemical binding of the acceptor with the selenium. The character of the variation of the line-width with changing T_{tr} indicates the presence of exchange narrowing due to the increased local concentrations of the paramagnetic centers as a result of their uneven distribution in the sample. During the cooling of the liquid selenium, regions with more or less ordered packing of the molecules are apparently produced in it spontaneously and their aggregate forms a definite supermolecular structure. The minimum dimension of such formations is determined by the nature of the selenium itself as a polymer. Only under this assumption are large local concentrations of paramagnetic centers and their uneven distribution in the selenium possible.

The concentration of the oxygen in the selenium was determined by the EPR and IR spectroscopy methods, and turned out to be ~ 0.1 wt.%.

The proposed existence of supermolecular formations and states with charge transfer explains many properties of selenium.

G. B. Abdullaev, Z. A. Aliayarova, G. A. Asadov, É. N. Zamanova, and A. L. Shabalov. Electric Properties of Certain Chalcogenides in Contact with Metals.

Interest has increased recently in solid-state phenomena connected with negative resistance. Negative conductivity was observed by many authors in thin oxide films of crystalline and vitreous semiconductors[1-4]. Most authors connect the appearance of negative differential resistance with double-injection[5] and microscopic heating[6].

We have studied the electric properties of the relatively little investigated chalcogenide semiconductors

and of their contact with various metals. Such compounds are impurity semiconductors, having a defective structure, p-type conductivity, a forbidden-band width $\Delta E \sim 019-2$ eV, and a carrier density $10^{18}-10^{20}$ cm^{-3}.

The contact between such semiconductors and certain metals has interesting switching effects. The gist of the effect is shown graphically in Fig. 1. When current passes through the contact in forward direction (current flows from the crystal to the junction), hysteresis is observed. In the inverse direction, the current increases in proportion to the applied voltage, up to a certain value I_{cr}, at which the resistance of the contact increases strongly and the current decreases jumpwise by several orders of magnitude. Such a switching is irreversible and occurs within a time shorter than 1 μsec.

The junction resistance remains high for any change of inverse voltage, up to the breakdown value. There is only one way of taking the contact out of the high-resistance state, namely by passing through it current in the forward direction, after which the junction again has a low resistance to the current flowing in the inverse direction.

An interesting property of the junction is that it "remembers" its states during a long time even at zero bias. Even more unusual is the fact that the switching current depends on the maximum value of the forward current flowing through the contact. By passing through the junction a current of definite magnitude in the forward direction, it is possible to prescribe beforehand the value of the switching current I_{cr}. Figure 2 shows the dependence of the switching current on the current flowing in the forward direction.

The electric properties of the junction were investigated in a wide range of temperatures. Figure 3 shows the dynamic characteristic of the junction at different temperatures. As seen from the oscillograms, the region of negative resistance decreases with increasing temperature. The switching effect is observed up to 400°C, after which the junction acquires the usual rectifying properties and retains them up to 500°C. At a temperature of 120°C, the junction resistance becomes low, and this can be attributed to the structural transition of the semiconductor from one modification to another. In junctions comprising a metal with certain chalcogenides, a bilateral controlled relay effect was observed. Figure 4 shows the current-voltage charac-

FIG. 3

FIG. 4

teristic of such a junction. The junction has at first high resistance to both current directions, and when a certain critical voltage U_{cr} is reached in the former direction, the resistance of the junction decreases sharply and the current increases jumpwise, after which the junction has low resistance for both current directions. In the inverse direction, when the current reaches a certain critical value I_{cr}, the junction resistance increases abruptly and the current decreases jumpwise, with the junction returning to the high-resistance state.
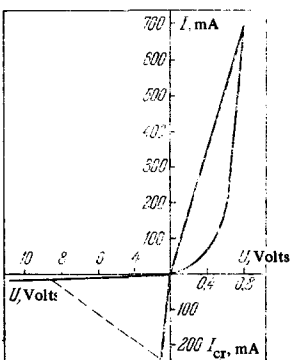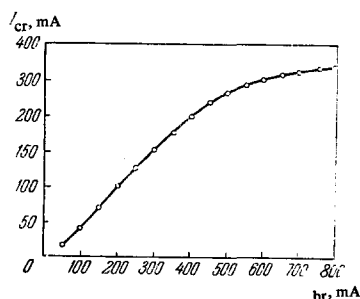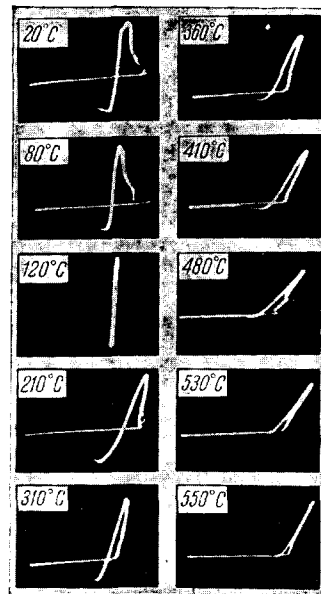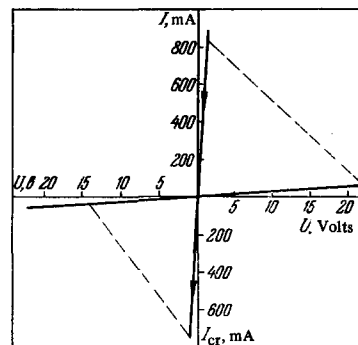

FIG. 1

FIG. 2

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