POLARIZATION MECHANISM OF TlInSe$_2$ <Li$^+$> SINGLE CRYSTAL IN DC – ELECTRIC FIELD

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Polarization and depolarization processes have been investigated in lithium – intercalated chain structure TlInSe$_2$ single crystals at different applied dc-electric fields and 120 K. We calculated the time constant of the contact capacitance charging $\tau = 2s$; contact capacitance $C = 1.5 \cdot 10^{-11}$F; the region of charge concentration $d_c = 6 \cdot 10^{-4}$ cm, and the mobility of localized charges $\mu_f = 3 \cdot 10^{-2}$ cm^2 / Vs. It was established that an "injection" polarization is also observed against the background of ionic polarization in the dc- electric field region under study.

The problem of intercalated crystals is one of the most urgent problems in modern solid-state physics. Initially it arose as the problem of intercalation of layer crystals.

It is known that foreign ions, atoms and molecules which do not only change the parameters of crystals, also impart radically new properties to them, can be introduced into the interlayer spaces of layer crystals. Crystals with a chain structure are also interesting objects of intercalation. In such crystals, Van der Waals "slits" are formed over two mutually perpendicular planes, which favours intercalation of foreign particles over them.

This report deals with an investigation of polarization and depolarization processes in chain- structure TlInSe$_2$ single crystal of p-type conductivity, intercalated with lithium ions.

Intercalation was carried out by the method of a pulling electric field applied along the chains of TlInSe$_2$ single crystal [1].

Electrical measurements were conducted in the dark at a temperature of T = 120 K. The specimen contacts were produced from an In-Ga eutectic mixture and applied to the lateral butt-ends along the crystal [$\bar{1}$10] direction.

As a result of Li$^+$ intercalation, the degree of anisotropy of the electrical conductivity of TlInSe$_2$ single crystals increases more than twofold. At 120 K the resistivity of TlInSe$_2$ <Li$^+$> single crystals along the [$\bar{1}$10] crystallographic direction amounted to approximately 10^{12} Ωcm.

When studying the electrical properties of TlInSe$_2$ <Li$^+$> single crystals a decreasing current relaxation typical of most of the high-resistance semiconductors and due to polarization of the specimen, was found in a dc- electric field. We investigated time-dependent dark current decays at different applied electric fields (forward currents), as well as short-circuit currents, i.e. depolarization currents (back currents) flowing after the external electric field is turned-off and electrodes are short-circuited via the load resistance ($R_L << R_{cr}$). The relaxation processes were recorded by means of a fast-response recording potentiometer with an appropriate time scanning. Upon turning-on the voltage a sharp initial jump of current I_0 and its subsequent decay were observed. The decaying branches of both forward and back current experience a certain oscillation that attenuates in amplitude with time. Then the current oscillation disappears and a steady state current level I_{st} is established in about 6 to 8 after the initial jump I_0. In about the same time the depolarization current drops from its

maximum value to zero. The depolarization currents are due to the internal electric field of reversed polarity in relation to the external field, set up in the specimen. This internal field responsible for the electric memory of the specimen grows with time as a charge is accumulated in the crystal and reaches saturation after a steady-state current level I_{st} is achieved.

Polarization of the specimen in a dc electric field can take place due to the separation of intrinsic charge carriers and charge carriers injected from the electrode. In weak electric fields (where the injection level is very low) the main current carriers are represented by the intrinsic charge carriers, which separate in the electric field and accumulate near the electrodes. In strong electric fields (where the injection level is rather high) the leading part in the charge transfer is played by the carriers already injected into the crystal, if their concentration N_i exceeds that of intrinsic carriers. Elsewhere [2] criteria for the separation of these polarization mechanisms have been suggested. In the region of weak electric fields the current and charge values at different applied voltages and their action times can be calculated with the formulas

$$I = I_0 \exp\left(-\frac{eN\mu St}{LC_c}\right),$$
(1)

$$Q = UC_c - \frac{LC_c I}{eN\mu S},$$
(2)

where S is the contacting area of the specimen, L is its thickness, μ is the mobility of charge carriers, N is their concentration and C_c is the close-to-contact capacitance. In the case of a high injection level ($N_i \gg N$) it has been established that

$$I = UC_c \frac{\tau}{(t+\tau)^2},$$
(3)

$$Q = UC_c - \sqrt{\frac{C_c L^3 I}{d_c \mu}},$$
(4)

where $\tau = L^3 / \mu d_c U$ is the contact capacitance charging constant and d_c is the charge concentration region of the specimen.

Thus, when studying the experimental dependences I(t), I(U), Q(t), and Q(U), one can establish the polarization mechanism by correlating these dependences with theoretical expressions (1) through (4). According to report [2], a certain voltage

$$U_0 = \frac{6SL^2}{C_c d_c \mu},$$
(5)

exists, below which the leading part is played by polarization due to intrinsic carriers, whereas at $U > U_0$ an injection mechanism of polarization begins to prevail. An analysis of our experimental data has shown that the transient forward currents and the charges accumulated in the voltage region from 100 to 500 V are approximated with the use of (3) and (4).

Fig.1 depicts the dependence of Q on $\sqrt{I}$, obtained experimentally at U = 100 V. As seen, this dependence falls well on a straight line, in compliance with (4). Based on a procedure set forth in another publication [3], we calculated the parameters τ, C_c, d_c, and μ, which proved to be equal to 2 s, $1.5 \cdot 10^{-11}$F, $6 \cdot 10^{-4}$ cm, and $3 \cdot 10^{-2}$ cm^2 / Vs, respectively. The

knowledge of these parameters enabled us to evaluate with formula (5) the value of U_0 that proved to be equal to 10 V. The value of U_0 ($U_0 < U$) points to the fact that it is actually the injection mechanism that is mainly responsible for the polarization in the voltage region from 100 to 500 V.
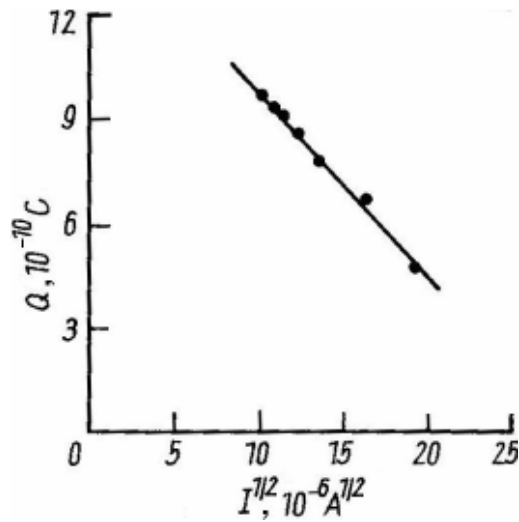

Fig.1. Dependence of accumulated charge on $I^{0.5}$ (U = 100 V).

Fig.2 shows the experimental Q(t) dependences at different voltages. The dashed curve in this figure is the theoretical dependence Q(t) plotted for one of the applied voltages (100 V) according to the following formula [3]:

$$Q = UC_c \frac{t}{t + \tau}. \tag{6}$$

There is a satisfactory agreement between the experimental data (curve 1) and theory (curve 1´). The dependence $Q \sim U^n$, where n = 0.5 is typical of the specimen under study. In the electric-field region under study the current-voltage characteristics (CVC´s) of $TlInSe_2$ $<Li^+>$ single crystals were close to linear dependences.

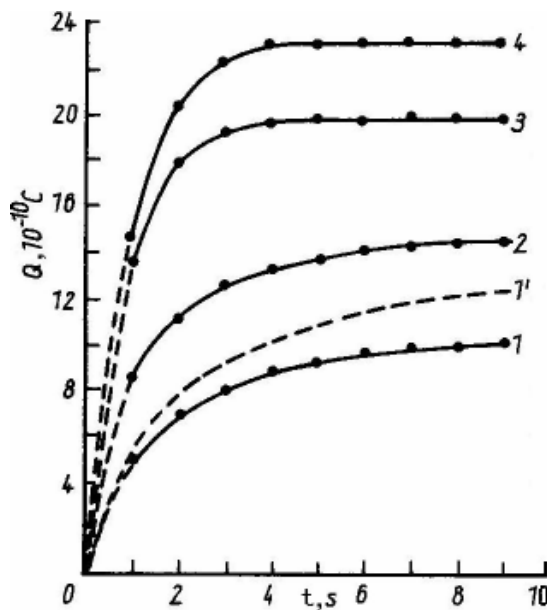

Fig.2. Time dependence of polarization charge at different voltages U:
(1) 100, (2) 200, (3) 400, (4) 500 V. The dashed line is the theoretical Q(t) curve.

Fig.3 displays CVC's plotted on the basis of initial currents I_0 (curve 1) and steady-state currents I_{st} (curve 2). Curve 3 shows the appropriate dependences of the initial values of depolarization currents upon turning-off the voltage. As seen from the figure, $I_0 \approx I_{st} + I_{sc}$. If we had to do with a pure injection mechanism of polarization [3], it would have been expected that $I_0 \sim U^2$ and I_{st} was independent of U.
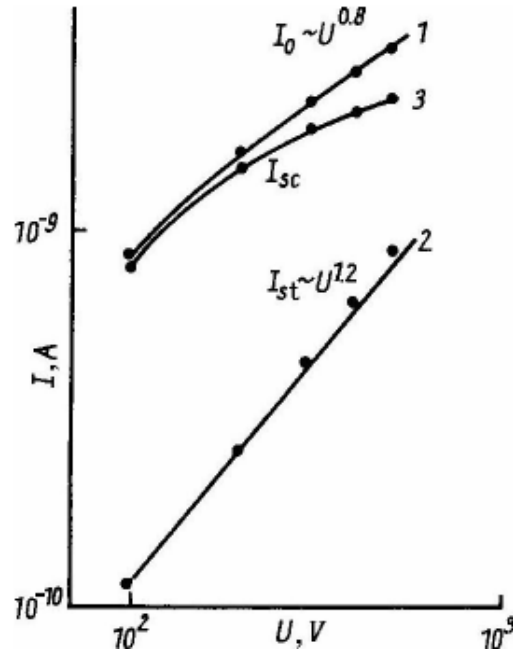

Fig.3. CVC's of TlInSe$_2$ <Li$^+$> single crystals, plotted on the basis of initial (1) and steady-state (2) current values as well as initial values of the depolarization current (3). L = 0.15 cm, S = 10^{-2} cm^2, T = 120 K.

However, we failed to observe that, inasmuch as we had to do with a case where the concentrations of intrinsic (not injected) charge carriers could not be ignored. The point is that between the chains of the TlInSe$_2$ crystals under study there are intercalated Li$^+$ ions, which are rather mobile in the voltage region mentioned above and make a certain contribution to the conductivity of the crystal.

Being separated in the electric field, they form a bulk charge near the cathode, which also leads to a decreasing current relaxation in the specimen. As a result, the accumulation of both intrinsic (holes, Li$^+$ ions, etc.) and injected charge carriers near the electrodes is responsible for the polarization of TlInSe$_2$ <Li$^+$> single crystals as well as for the conservation of the internal electric field upon turning-off the external field, i.e. for the electric memory. In other words, an "injection" polarization is also observed against the background of ionic polarization in the electric field region under study, i.e. we have to do with mixed polarization.

At illumination of polarized sample TlInSe$_2$ <Li$^+$> single crystal there is observed short-circuit current. Fig.4 gives spectrum of short-circuit current in TlInSe$_2$ <Li$^+$> single crystal.

Thus it has been revealed that, in lithium- intercalated TlInSe$_2$ single crystals the existence an electric memory is observed. Intercalation of TlInSe$_2$ with lithium ions brings about the setting up of strong internal local fields sensitive to external effects, namely to electric fields, irradiation with quantum energies in the spectral sensitivity region of crystal. These results give perspective for the use of these objects as various transducers and detectors.
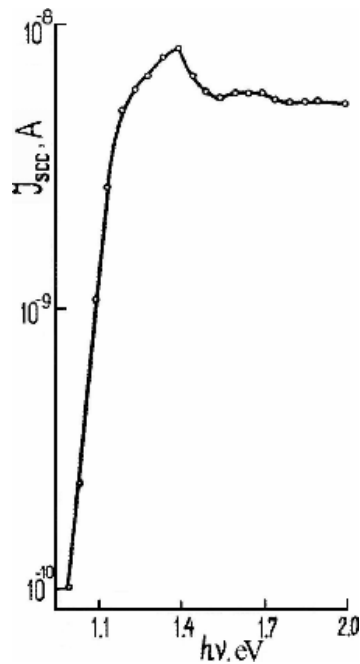
Fig.4.Spectral dependence of short-circuit current in TlInSe$_2$ <Li$^+$> single crystal.

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SABİT ELEKTRİK SAHƏSİNDƏ TlInSe$_2$ <Li$^+$> MONOKRİSTALINDA POLYARİZASİYA MEXANİZMİ

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Sabit elektrik sahəsində müxtəlif gərginliklərdə, T = 120 K-də zəncirvari quruluşlu TlInSe$_2$ <Li$^+$> monokristalında polyarizasiya və depolyarizasiya prosesləri tədqiq edilmişdir. Aşağıdakı parametrlər təyin edilmişdir: kontaktın yüklənmə vaxtı τ = 2s; kontaktın tutumu C_c=1.5·10^{-11}F; kristalda yükün yığılması oblastı d_c=6·10^{-4} cm, lokalizə olunmuş yük daşıyıcılarının yürüklüyü μ_f = 3·10^{-2} cm^2 / V·s.

МЕХАНИЗМ ПОЛЯРИЗАЦИИ МОНОКРИСТАЛЛА TlInSe$_2$ <Li$^+$> В ПОСТОЯННОМ ЭЛЕКТРИЧЕСКОМ ПОЛЕ

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В цепочечных монокристаллах TlInSe$_2$, интеркалированных ионами лития, изучены процессы поляризации и деполяризации при различных напряженностях постоянного электрического поля и при T = 120 K. Определены такие параметры, как время зарядки контакта τ = 2c; контактная емкость C_c=1.5·10^{-11}Ф; область сосредоточения заряда в кристалле d_c = 6 ·10^{-4} cm, а также подвижность локализованных носителей заряда μ_f =3·10^{-2} cm^2 / В·c. Установлено, что в изученной области электрических полей в TlInSe$_2$ <Li$^+$> на фоне ионной поляризации имеет место также инжекционная поляризация.