

SOME ELECTRICAL AND THERMAL PROPERTIES OF HgI₂ SINGLE CRYSTALS

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Electrical and thermal conductivity of mercuric iodide single crystals in the tetragonal phase and the region of transition to the orthorhombic phase have been investigated. Slowly decaying charging transients and a simultaneously arising inhomogeneous electric field in the sample have been observed. The decrease of the current density with time is caused to a small extent by the accumulation of the space charge near the electrodes; the main cause, however, is a change in the electrical conductivity, a consequence of the migration of defects acting as deep donors towards the cathode region.

НЕКОТОРЫЕ ЭЛЕКТРИЧЕСКИЕ И ТЕРМИЧЕСКИЕ СВОЙСТВА МОНОКРИСТАЛЛОВ HgI₂

В работе приведены результаты исследований удельной электропроводности и удельной теплопроводности монокристаллов иодида ртути, находящегося в тетрагональной фазе и близости перехода в ромбическую фазу. В образце монокристалла наблюдались медленно затухающие переходные процессы с одномеренно возникающим неоднородным электрическим полем. Причиной понижения плотности тока со временем в некоторой степени является пространственная зарядка, накопленного вблизи электродов. Главной причиной однако является изменение электропроводности, обусловленное перемещением дефектов, действующих в качестве глубоких доноров в область катода.

1. INTRODUCTION

In the past few years mercuric iodide attracted the attention of many investigators, due especially to its potential suitability for γ and X-ray spectroscopy [1, 2], although some of its other properties, such as photoconductivity, may also be said to be a matter of interest [3—5]. Great attention has been paid to the investigation of some of its physical properties, mainly optical ones in the tetragonal modification existing below 133 °C. Nevertheless, its electrical properties are not well understood. Sporadic information on the electrical conductivity

can be found in some papers, e.g. [4, 5]. Bube [6] published the temperature dependence of d.c. dark conductivity and photoconductivity of crystals prepared by different methods. Results of thermostimulated current measurements are in papers [6—8]. Recently the temperature dependence of the drift mobility of electrons and holes [9] and the photodielectric effect [10] have been investigated. More detailed information on the electrical properties of pure and doped crystals and of the effect of impurities on the phase transition from the tetragonal to the orthorhombic modification was published in [11]. As far as we know, no measurements of the thermal properties of HgI₂ have been published yet.

Meanwhile no generally accepted concept of the mechanism of dark electrical conductivity exists. Usually electronic mechanisms were suggested; however, the possibility of ionic conduction could not be plausibly ruled out. According to [6] the conductivity is intrinsic, in [12] HgI₂ was found to be an n -type semiconductor. Data of Minder et al. [9] on the mobility of electrons and holes lead to the conclusion that a region of intrinsic conductivity can be observed, in which the electronic component exceeds that of the holes due to the small mobility of the holes [11].

In order to achieve a better understanding of electric and dielectric properties of HgI₂, measurements of d.c. and a.c. conductivity, of charging and discharging currents and of the potential distribution were performed and completed by an investigation of the effect of the electric field on the thermal conductivity of the material in the vicinity of electrodes.

II. EXPERIMENTAL

HgI₂ single crystals were grown by a slow evaporation of the solvent from the solution of analytical grade HgI₂ in analytical grade acetone as described in an earlier paper [11]. The size of the crystals was usually a few mm, in the best cases approximately 5 × 5 × 3 mm³. Because of the brittleness of the crystal, the samples approximately 1 mm thick were prepared by cleaving or they were used "as grown" without any mechanical treatment. Electrodes were painted on the opposite faces of the samples, using colloidal graphite. Some attempts to use metal electrodes were not successful due to the great reactivity of the material at higher temperatures. The fast sublimation at temperatures above 100 °C made any effective heat treatment impossible. The measurements were performed in an argon atmosphere, some of them in air. The results were in both cases the same. Measuring in vacuo was unsuitable due to the enhanced sublimation of the samples. All measurements were performed in dark.

D.c. conductivity was measured with 10 volts usually at a temperature increasing at a rate of 2 °C/min. A.c. conductivity measurements were performed in the frequency range 10 Hz—50 kHz by measuring the in phase component of the

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current flowing through the sample by means of a lock-in amplifier having a zero phase error. Measurements of charging and discharging currents and of the potential distribution were made using the partly adapted apparatus described in [13], complemented by supply and registration circuits. For potential distribution measurements a Pt probe was used. The spatial resolution was 1 μm and the reproducibility 2 μm .

Thermal conductivity was measured by the pulse method [14], using a line heat source. The response to the heat pulse was measured by means of a thermocouple on the opposite face of the sample.

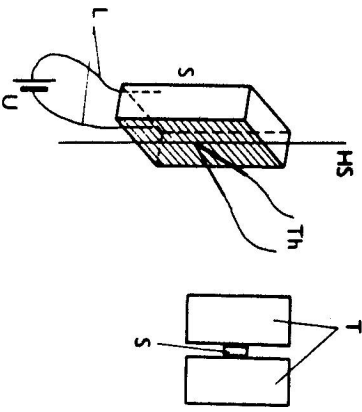


Fig. 1. The arrangement used for the measurement of thermal conductivity of the electrode region in a polarized sample.

The influence of the electric field on thermal conductivity was investigated in the arrangement shown in Fig. 1. An isolated line heat source HS (Manganan \varnothing 0.071 mm), welded together with a copper-constantan (\varnothing 0.05) thermocouple junction Th, was pressed to one electrode. The sample was polarized or short-circuited through the leads L. 0.2 A current pulses lasting 100 ms were used for heating. The warm-up of the heat source was about 0.5 $^{\circ}\text{C}$. The decrease of its temperature was registered by means of the thermocouple Th. The sample was held between Teflon blocks T. For this arrangement thermal conductivity can be calculated using the expression [15]

$$\lambda = A \frac{Q}{2\pi T\tau}$$

where A is a constant resulting from the geometry of the arrangement, Q is the heat quantity supplied to the sample, T is the difference in temperatures at the time τ and before switching on the heat pulse. For measurements of thermal conductivity changes it is sufficient to measure the voltage of the thermocouple at a proper time. Usually the time instant 0.5 sec was used.

The temperature range of electric and thermal conductivity measurements was from RT to 150 $^{\circ}\text{C}$. The effect of polarization on the thermal conductivity was investigated at 50 $^{\circ}\text{C}$ and 100 $^{\circ}\text{C}$. Measurements of current transients were made in the range from -15.5 $^{\circ}\text{C}$ to +126 $^{\circ}\text{C}$, measurements of potential distribution from 27 $^{\circ}\text{C}$ to 126 $^{\circ}\text{C}$.

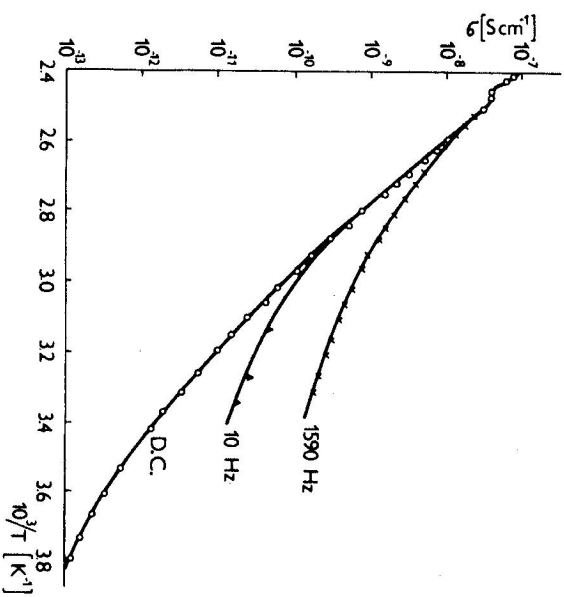


Fig. 2. Temperature dependence of d.c. and a.c. conductivity of pure Hg₁.

III. RESULTS

III.1. Electrical conductivity

The temperature dependence of the dark d.c. and a.c. electrical conductivity at 10 Hz and 1590 Hz is shown in Fig. 2. The frequency dependence of the a.c. conductivity measured at constant temperatures is shown in Fig. 3. The magnitude of a.c. conductivity at temperatures at which it exceeded the d.c. conductivity was badly reproducible from sample to sample. Its spread exceeded one order of magnitude. The conductivity can be approximated by a power law

$$\sigma \sim \omega^n$$

with n decreasing from 0.37 to 0.15 with increasing temperature.

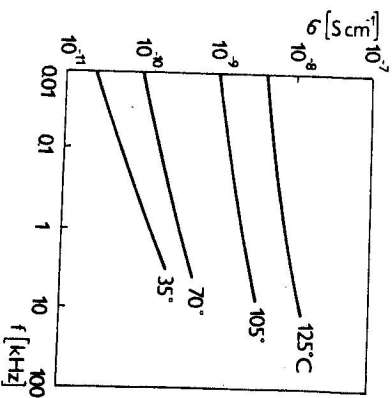


Fig. 3. Frequency dependence of a.c. conductivity.

III.2. Transient currents

The charging current measured in a sample exhibiting enhanced a.c. conductivity decreased monotonously and within hours it did not attain a constant value. Currents measured with 6 volts at different temperatures are shown in Fig. 4. For times greater than ~ 10 —100 sec the current follows the power law $i \sim t^{-n}$ with n

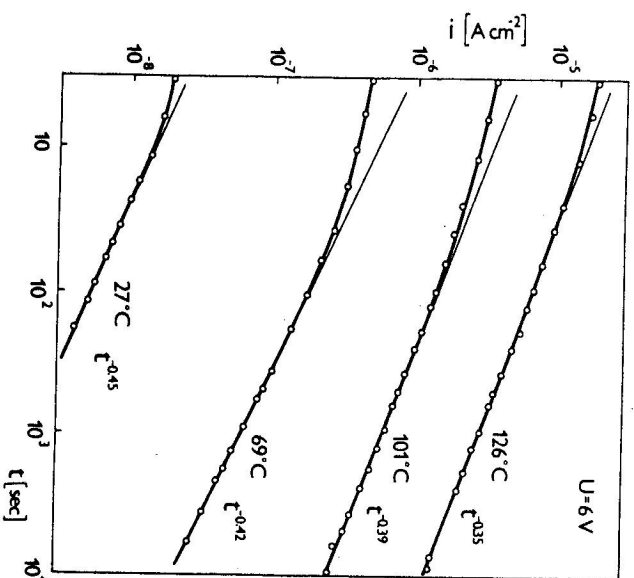


Fig. 4. Time dependence of charging currents. Sample 1, 1 mm thick.

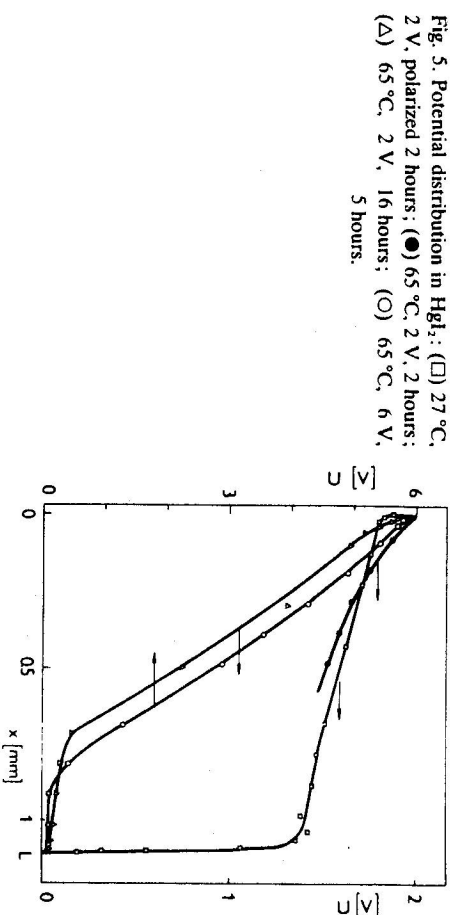


Fig. 5. Potential distribution in HgI_2 : (\square) 27°C, 2 V, polarized 2 hours; (\bullet) 65°C, 2 V, 2 hours; (Δ) 65°C, 2 V, 16 hours; (\circ) 65°C, 6 V, 5 hours.

close to 0.4, slightly decreasing with increasing temperature. For shorter times the value of n was smaller.

After shorting the sample polarized shortly (1—30 sec), the discharging current roughly corresponded to the charging transient, it had a similar magnitude, rate of decay and opposite polarity. However, when the sample had been polarized, e.g., for one hour, the discharge transient had an initial magnitude much smaller than the current before short-circuiting. It scarcely reached 1% of the initial magnitude of the charging transient and it decayed very slowly.

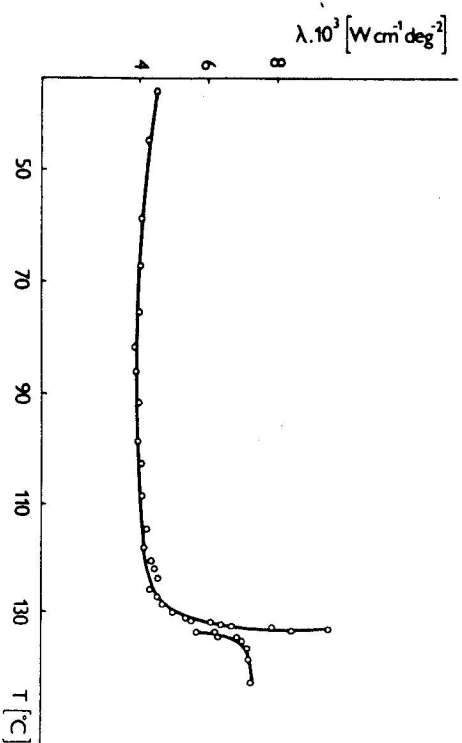


Fig. 6. Temperature dependence of thermal conductivity of HgI_2 .

III.3. Potential distribution

Due to the great time constant of charging the input of the electrometer (30 pF) across the great resistance of the probe, only a quasistatic potential distribution could be measured. The requirement of a negligible loading of the probe by the input resistance ($10^{15} \Omega$) limits the measurements to temperatures at which the conductance of the sample is greater than approximately 10^{-11} S . Some results are shown in Fig. 5. They have not been corrected for the difference of contact potentials HgI_2 | Graphite — HgI_2 | Pt. It was approximately — 110 mV at room temperature.

III.4. Thermal conductivity

The temperature dependence of thermal conductivity is seen in Fig. 6. It shows a peak near the phase transition point and no significant changes below the relatively narrow transition region. Above the transition point there is an unusual increase, caused mostly by an increase in heat capacity. The smooth course of the dependence below the transition region created a wide temperature range for investigations of thermal conductivity changes under polarization.

III.5. The effect of polarization on thermal conductivity

Figs. 7 and 8 show the changes of thermal conductivity of the surface layer of two samples, caused by polarization. Curves 1 correspond to the positive polarity of the electrode at which the heat source was placed, curves 2 to the negative one. The dashed line in Fig. 8 was obtained under negative polarization before heat

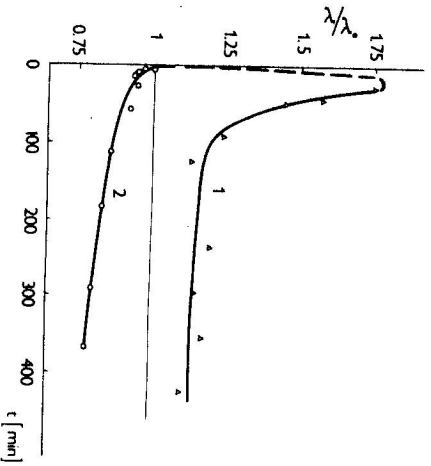


Fig. 7. Time dependence of thermal conductivity of the electrode region, (Δ) anode, (\circ) cathode. $U = 10 \text{ V}$.

treatment, the full curves after annealing the sample at 100°C for 150 hours (curve 2) and for 175 hours (curve 1).

IV. DISCUSSION

The time dependence of the charging current and the inhomogeneous electric field arising in the sample had some peculiarities. Within a relatively short time after applying the voltage to the electrodes the potential distribution in the sample was typical for partly blocking electrodes, with potential drops at the electrodes. After some time the voltage drops at the electrodes decreased and two regions of different but nearly uniform field strength, extending deeply into the bulk, arose. The depth of the low field region at the cathode decreased with time and the field strength decreased in both parts of the sample. The greater the voltage on the electrodes was, the faster was this process.

The measured potential distributions recall some static distribution curves, calculated by Macdonald [16] for two blocking electrodes and material containing one mobile charge carrier. With applied voltages much greater than kT/e a depletion or even exhaustion region may arise near one electrode and an accumulation region at the other. Nevertheless the similarity between the above and our case is misleading. A space charge, which would cause such potential

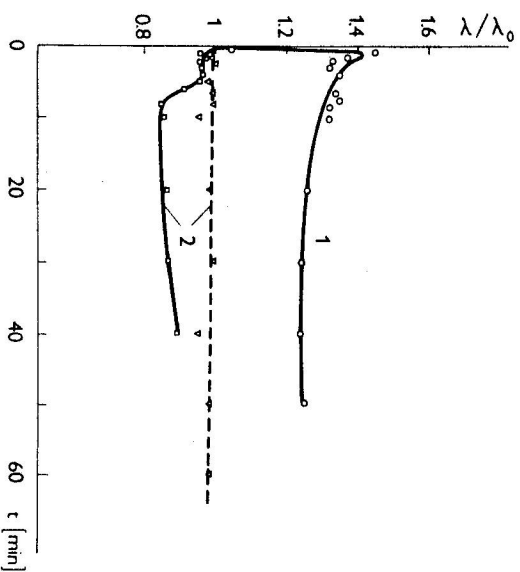


Fig. 8. Time dependence of thermal conductivity of the electrode region (\circ) anode, (\square) cathode, dashed line before heat treatment, curve 1: annealed at 100°C for 175 hours; curve 2: annealed at 100°C for 150 hours.

distribution and the observed fall of the charging current would lead to an open circuit voltage at the electrodes, measured immediately after switching off the voltage, nearly equal to the polarizing voltage. However, this has not been observed, after a polarization lasting 3 hours with 6 volts at 64 °C the open circuit voltage of 300 mV was measured. This suggests that a space charge is not the cause of the inhomogeneous field in this material.

The observed potential distribution cannot be explained by an injection of electrons or holes from the electrodes, as with the mobilities and mean free lifetimes found by Minder and coworkers [9] the mean free path of the charge carriers would be hardly a few μm .

The inhomogeneous field in the bulk can be explained as a result of different conductivities in the two parts of the sample. The conductivity of the highohmic part, calculated from the instantaneous field strength and the current density is shown in Fig. 9. It is in good agreement with the d.c. conductivity (Fig. 2) at high temperatures and it suggests that the bending of the "d.c." conductivity dependence at lower temperature may result from measuring at not steady temperatures. The activation energy in this region is 1.02—1.04 eV, which is in accord with one half of the optical gap found by Bube [6] (2.08—2.04 eV) for solution grown

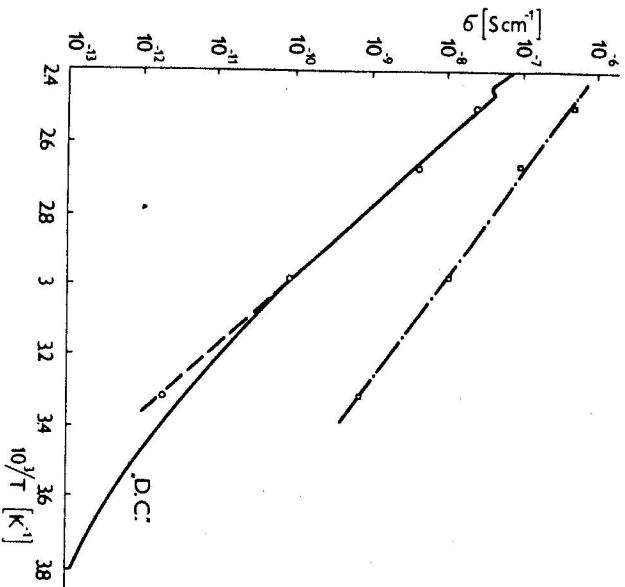


Fig. 9. Temperature dependence of d.c. conductivity (full line) (O) of the highohmic part of the sample, (□) of total conductivity.

crystals. This supports the conclusion [11] that the conductivity above room temperature is intrinsic.

The temperature dependence of the conductivity of the highohmic part of the sample and of the total conductivity calculated from the initial magnitude of the charging currents, measured 0.5 sec after switching on the voltage, is shown in Fig. 9 together with the d.c. conductivity from Fig. 2. The sample had a great anomalous conductivity, therefore the total conductivity exceeds the a.c. results from Fig. 2. The activation energy of total conductivity is 0.66 eV. It is interesting to note the agreement with the activation energy of the mean peak in the TSC spectrum (0.67 eV) found by Bube [6] and with the activation energy of dark conductivity of polycrystalline samples (0.7 eV) [17]. Peaks at similar energies were found also in photopolarization and in photoconductivity quenching spectra (0.69 eV) by Zolotar'ov et al. [18].

The enhanced conductivity near the cathode is obviously of the same origin as the not well reproducible frequency dependent a.c. conductivity. The slight frequency dependence of the a.c. conductivity excludes the possibility of a simple extrinsic electronic mechanism, caused by donors or acceptors, for which an independence of frequency would be expected. Similarly, were the excess conductivity ionic, it should not depend on frequency. In case of electrodes blocking one or more charge carriers the resulting dependences would be in the range $\omega^{1/2}$ — ω^2 and the corresponding charging current would decay with the exponent $n \geq 1/2$, or exponentially [19, 20]. For a hopping mechanism an n between 0.5 and 1, preferentially close to 1 would be expected. However, for such a mechanism the mobilities are too high [9].

The charging and discharging currents, the a.c. conductivity as well as the potential distribution may be better explained as an ageing effect. If the crystal contains mobile positively charged defects, e.g. anion vacancies, impurity cations, some products of photolysis or of thermal degradation, these defects may contribute to the conductivity both directly and indirectly, by creating deep donor levels in the gap of the host material. If a voltage is applied to the electrodes, the defects migrate towards the cathode. No significant space charge results, since it may be compensated by electrons present in the sample. Thus a region depleted or exhausted of excess charge carriers and thus of reduced conductivity may easily arise. The total conductivity of the sample decreases in spite of the increasing conductivity of the cathode region. If the electrodes are blocking for the donors, the process may be reversible. Details of the proposed model and its consequences will be published elsewhere [21].

Information on the type of excess charge carriers can be obtained from measurements of thermal conductivity changes caused by polarization. Generally a diffuse space exists below the surface of solids [22—24]. The concentrations of charge carriers change if a voltage is applied to the sample. The presence of atomic

or ionic impurities usually does not affect or reduce thermal conductivity [25], whereas free electrons or holes contribute to it [26]. Figs. 7 and 8 show a marked increase of thermal conductivity of the vicinity of the anode, which could be caused either by an increase in the concentration of electrons or by a decrease in the concentration of positively charged ionic defects, or by both. Were the dominating factor a drop in the concentration of ions, the increase of thermal conductivity would be monotonous. For an increase of the concentration of electrons excited from mobile donors, the change should have a maximum, caused by a fast response of the concentration of electrons and the following gradual depletion, due to the migration of donors towards the cathode.

For the opposite polarity the changes should be less marked, as the effect of a possible increase in concentration of less mobile holes if the electrode is at least partly blocking for them may or may not cancel the influence of the increasing concentration of ions and of the decrease in the concentration of electrons. The initial rapid drop of curve 2 in Fig. 7 could result from the response of concentrations of electrons and holes and the following slow drop from the increase in the concentration of ions. Thus we conclude that the anomalous contribution to conductivity is caused by an excitation of electrons from mobile defects acting as deep donors. Further experiments have shown that the effect of polarization on thermal conductivity develops upon annealing in the dark at an increased temperature (100 °C) for some days at least (Fig. 8). This suggests that the donor centres result from thermal degradation (breakdown of stoichiometry).

V. CONCLUSIONS

Our results confirmed the intrinsic character of the d.c. conductivity of HgI₂ above room temperature. Besides this the crystals possess a badly reproducible anomalous contribution to conductivity, causing the frequency dependence of a.c. conductivity, a slow decay of the current, flowing after the application of a potential and giving rise to an inhomogeneous electric field in the sample. Above room temperature at voltages exceeding a few volts the space charge contribution to these effects is small. The existence of an anomalous contribution to conductivity complicates the interpretation of results at lower temperatures, since the application of suitable measuring methods is difficult if not impossible. The measurements have shown that the decrease of the slope of the $\ln \sigma_{a.c.}$ vs $1/T$ plot (see Fig. 9) is at least partly the consequence of the anomalous contribution to the conductivity.

Interesting is the possible connection between the observed contribution to conductivity, caused by centres acting as deep donors, and the photosensitivity of the vicinity of the cathode, observed by Bube [6]. His measurements also showed an appreciable photoconductivity for frequencies below the absorption edge in solution grown crystals. Bube suggested that the divergences from the properties

of crystals grown by other techniques arise from impurities or from imperfect stoichiometry. From our results it follows that impurities cannot cause these effects, as the necessary concentration would be too high.

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