

HOW TO DISTINGUISH BETWEEN UNIFORM AND SPACE CHARGE POLARIZATION IN HIGH-RESISTIVITY GLASSES — A THERMALLY STIMULATED DEPolarIZATION ANALYSIS

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A modification of the standard thermally stimulated depolarization (TSD) method is suggested, which makes it possible to distinguish directly between the uniform and the space charge polarization due to ionic motions in high-resistivity glasses. Possibility of estimating the net surface charge as well as of determining the accumulated bulk charge distribution is involved. Applicability of the method proposed is restricted to glasses with a dielectric relaxation time $\tau_d = \rho\epsilon$ exceeding ~ 10 min. near 300 K. The experimental procedure is demonstrated using the $\text{GeS}_{1.5}$ glass.

КАК УСТАНОВИТЬ РАЗЛИЧИЯ МЕЖДУ ОДНОРОДНОЙ ПОЛЯРИЗАЦИЕЙ И ПОЛЯРИЗАЦИЕЙ ПРОСТРАНСТВЕННЫМ ЗАРЯДОМ В СТЕКЛАХ С ВЫСОКИМ УДЕЛЬНЫМ СОПРОТИВЛЕНИЕМ НА ОСНОВЕ АНАЛИЗА ТЕРМИЧЕСКИ СТИМУЛИРОВАННОЙ ДЕПОЛЯРИЗАЦИИ

В работе представлена модификация стандартного метода термически стимулированной деполаризации, который позволяет непосредственно установить различия между однородной поляризацией и поляризацией пространственным зарядом, обусловленной движением ионов в стеклах с высоким удельным сопротивлением. Рассматривается возможность вычисления чистого поверхностного заряда, а также определение распределения накопленного объёмного заряда. Использование предлагаемого метода ограничено стеклами, имеющими время диэлектрической релаксации $\tau_d = \rho \cdot \epsilon$ свыше ~ 10 мин. при температуре 300 К. Экспериментальный метод демонстрируется на стекле $\text{GeS}_{1.5}$, которое использовалось в экспериментах.

1. INTRODUCTION

The slow dielectric relaxation phenomena observed in a variety of vitreous ionic conductors are governed by ionic diffusion [1, 2]. There are in the glasses essentially two effects which restrict ion migration. The first of them might be, e.g.,

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the displacement of vacancies in the impasses [3], an effect closely related to a dispersion of low frequency permittivity, the latter being a bulk limited phenomenon like the Maxwell—Wagner loss [1]. Apart from the bulk polarization electrode polarization arises as a consequence of piling-up moving ions at the electrodes. Assuming completely blocking electrodes, space charge relaxation is expected at low frequencies, this being the case treated, e.g. by Tomozawa and Doremus [4]. Since any real metallic electrode is incompletely blocking for ions, the slowest relaxation observed arises from a transfer of ions through the interface [5]. In most cases all the mentioned contributions interfere in such a manner that the bulk-limited relaxation cannot be correctly extracted from the total dielectric loss spectrum. Some difficulties connected with electrode reactions seem to be overcome when using stainless steel electrodes [4].

According to our previous results concerning the dielectric polarization phenomena in glasses of the system Ge—S, the thermally stimulated depolarization (TSD) method might become a convenient alternative of the dielectric loss measurement. Two dielectric relaxation phenomena were detected in Ge—S glasses by the TSD [6]. The former was found to be bulk-limited, whereas the latter seemed to be rather an electrode-limited phenomenon.

In the present paper a modified TSD procedure is proposed and verified to obtain the possibility of direct separation of both the bulk and the electrode polarization. Moreover, the amount of the charge trapped on the surface can be estimated. Using $\text{GeS}_{1.5}$ glasses, one finds both types of polarization to be linear with applied voltage and so a linearly check is certainly insufficient for the identification of TSD peaks. Applying evaporated metallic electrodes, electrothermally induced changes of the contacts were observed, their origin being briefly discussed in the paper.

II. EXPERIMENTAL METHOD

Following the model suggested by Boksay and Lengyel [3], displacement of vacancies in the impasses resembles to some extent the orientational polarization in alkali halides doped with divalent alkali cations, for instance the polarization due to an exchange of the vacancy with the impurity. To obtain some kinetic parameters of reorientation of "impurity-vacancy" complexes, Buccì et al. [8] suggested the ionic thermocurrent method (ITC), which was primarily based on thermally stimulated depolarization of a previously polarized capacitor with the dielectric under investigation. Some advantages of the ITC method over that of the dielectric loss measurement were discussed by Perlman and Unger [9].

) Ionic conductivity in $\text{GeS}_{1.5}$ glasses has been recently established by ionic transference number measurements [7].

Next, we shall consider a modified TSD method, which should permit us to detect the parameters of the polarization in glasses discussed by Boksay and Lengyel [3] as well as to elucidate the polarization phenomena associated with space charge relaxation. The standard TSD procedure starts from the polarization of a glass sample (thickness L , unit area) at a properly chosen temperature T_p for a time t_p . The sample is then cooled down under applied dc bias U_p to the

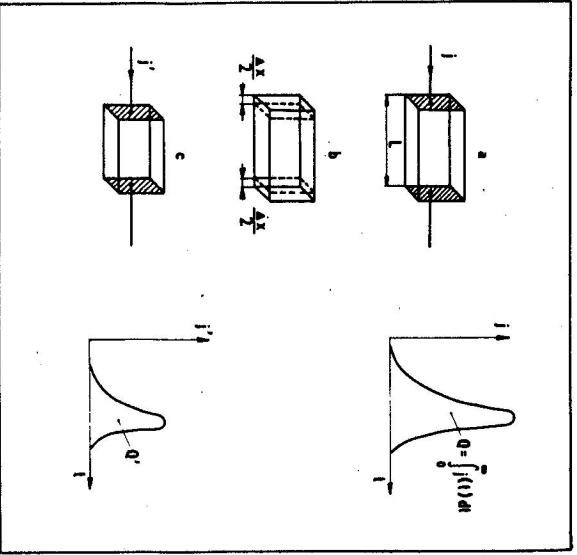


Fig. 1. A schematic picture of the modified TSD method.

temperature T_s , at which temperature the electrodes are shortcircuited. After a storage time t_s the system is heated at a constant heating rate $v = dT/dt$. During this period the depolarization current $j = dP/dt$ is flowing in the external circuit due to the displacement of bound charges (Fig. 1a). The integrated charge Q corresponds evidently to the amount of polarization P . Now, if one reduces the volume V of the polarized sample prior to depolarization to $V - \Delta V = (L - \Delta x) \cdot 1$ (Fig. 1b), the current j' will be registered giving the net charge Q' in Fig. 1c.

The bound charge density is related to polarization by

$$dQ/dV = dQ/dx = -\text{div } P,$$

as it is well known from elements of electrostatics. In the case of a uniform dielectric polarization — $\text{div } P = \text{const.}$ and therefore

$$\frac{Q - Q'}{\Delta x} = \frac{Q}{L}. \quad (1)$$

Is this not the case, then one deals definitely with space charge polarization. In the latter case the amount of the charge gathered on the surface Q_s can be estimated. To perform this, one should be able to remove electrodes leaving the bulk undisturbed, in which case $Q - Q' = Q_s$ is valid.

Thus, a method has been suggested which enables one to distinguish directly between uniform and space charge polarization in high-resistivity glasses. Applicability of the proposed method is of course limited to the glasses with a dielectric relaxation time $\tau_g(T_s) > t_s$.

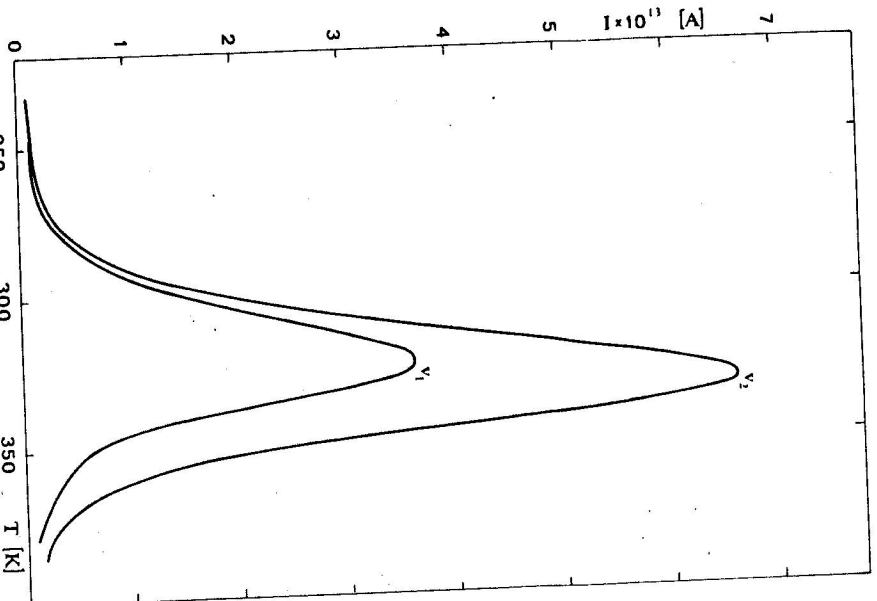


Fig. 2. TSD of GeS_3 glass (peak 1) polarized by $U_p = 340$ V ($T_p = 330$ K, $t_p = 2$ min.). The heating rates of $v_1 = 0.085$ Ks^{-1} and $v_2 = 0.17$ Ks^{-1} respectively, were used.

III. EVIDENCE FOR BOTH UNIFORM AND SPACE CHARGE POLARIZATION — GLASSY $\text{GeS}_{1.5}$

III. 1. Experimental

For TSD measurements bulk samples ($\Phi = 7.5$ mm, $L = 1$ mm) of $\text{GeS}_{1.5}$ glass were cut from ingots, obtained when cooling ampoules with melt freely in air. Dag dispersion in alcohol as well as evaporated Pd, Pb, Au, Cu were used as electrodes. Depolarization currents were registered by an electrometer VIB-RON 33C connected with an X-Y recorder.

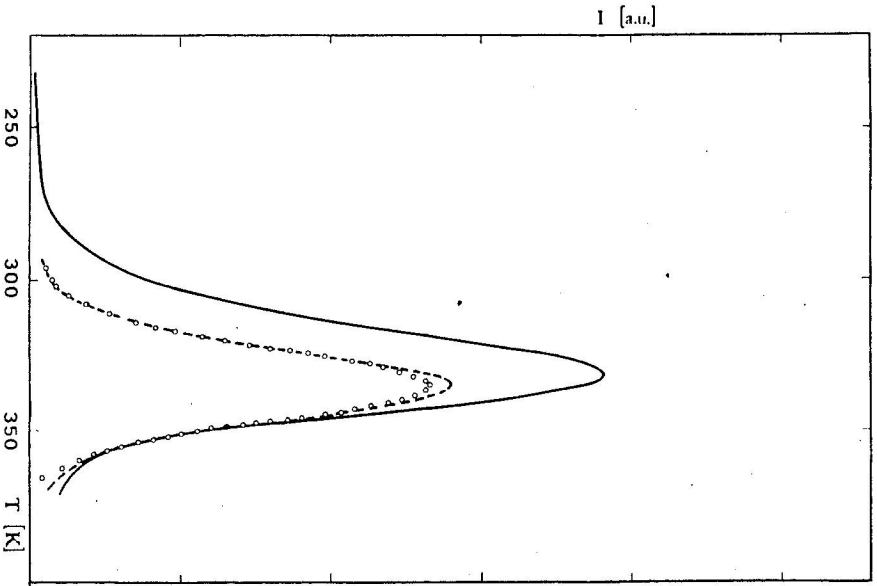


Fig. 3. The standard TSD is represented by the full line, for further details see text.

III. 2. Results

In our preliminary report on dielectric polarization phenomena in glasses of the system Ge-S [6] essentially two distinct TSD peaks were resolved in the complete spectrum of depolarization currents. The low temperature peak (peak I) with a maximum temperature $T_{max} \sim 330$ K replotted in Fig. 2 was shown earlier to be little affected by the electrodes, whereas the peak positioned at elevated temperatures was assigned to electrode polarization [6]. Now, we are able to prove directly the origin of both peaks by the procedure described in the preceding section.

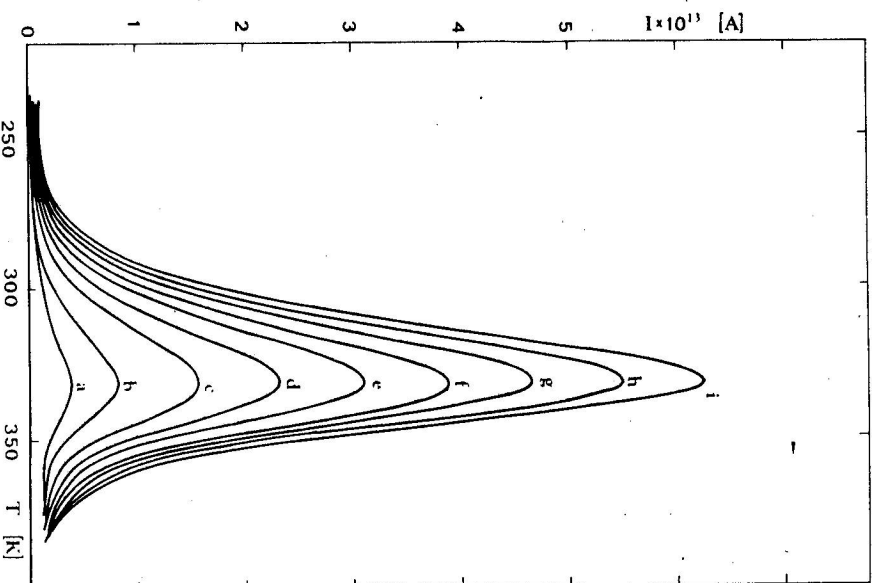


Fig. 4. TSD of $\text{GeS}_{1.5}$ glass with a bias voltage as follows: a — 20 V, b — 40 V, c — 80 V, d — 120 V, e — 160 V, f — 200 V, g — 240 V, h — 280 V, i — 320 V. For polarization conditions cf. Fig. 2, $\nu = 0.17 \text{ Ks}^{-1}$.

Let us turn our attention to Fig. 3, where the dashed line corresponds to the TSD of an originally 1 mm thick sample with dag electrodes polarized at 330 K, the system being stored shortcircuited at $T_s \sim 300$ K for 18 min. It is clear that during this time the fast components of the total TSD spectrum (full line in Fig. 3) vanished, nevertheless, a sufficient amount of charge persists to allow the following experiment. The sample is polarized again under identical conditions and cooled down with an applied bias of up to ~ 300 K, at which temperature 10 μm thick glass layers below both electrodes are removed and new electrodes applied during $t_p = 18$ min. In this way the relative change of the volume of the polarized sample $\Delta V/V = \Delta x/L$ is equal to 0.02, the respective thermogram is depicted in Fig. 3 by circles. In the case of a uniform polarization the charge Q' represented by the area

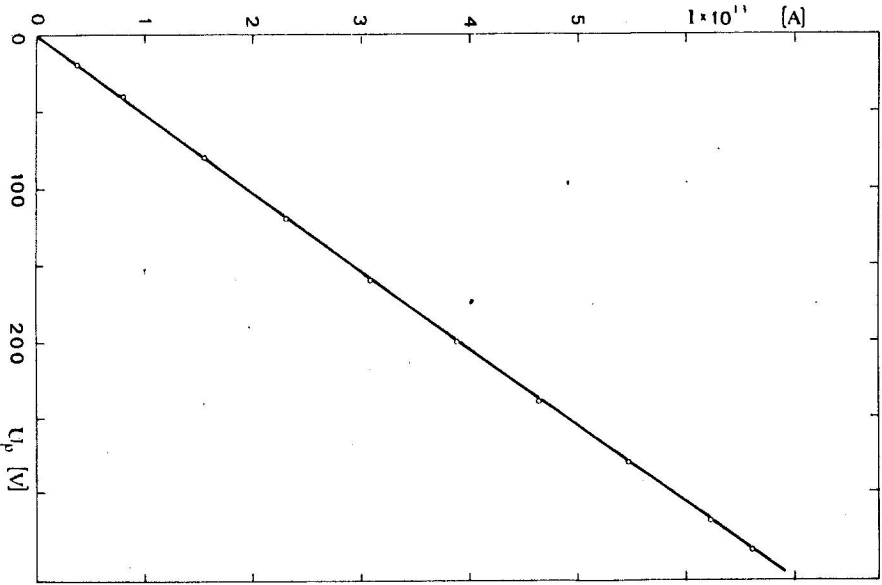


Fig. 5. The maximum current as a function of the bias voltage U_p — peak I.

under the thermogram is expected to be only 2% less than the charge Q obtained without contact manipulation (area under the dashed line). As evident from an inspection of Fig. 3, both $I(T)$ thermograms coincide within the experimental error, so that we have concluded that equation (1) is fulfilled.

We hope to have provided a direct evidence that the 330 K peak in $\text{GeS}_{1.5}$ results from a uniform dielectric polarization. As expected, the peak position is independent of bias (Fig. 4), the peak height being a linear function of bias voltage U_p — see Fig. 5.

Polarizing the system metal — glassy $\text{GeS}_{1.5}$ — metal at a temperature T_p above 330 K, another pronounced relaxation process is observed — peak II in Fig. 6. The

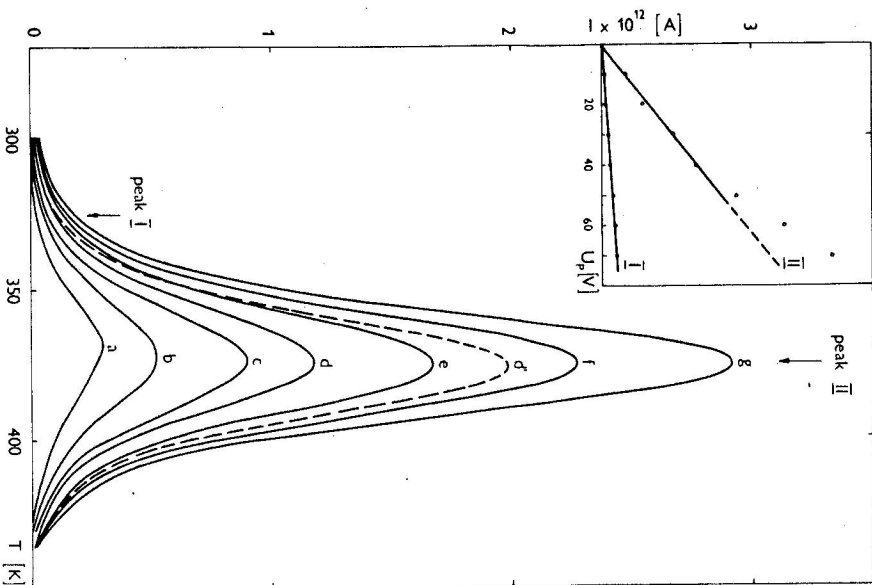


Fig. 6. TSD of a system Pd-glassy $\text{GeS}_{1.5}$ -Pd ($n = 0.17$ Ks $^{-1}$) with U_p as follows: a — 10 V, b — 20 V, c — 30 V, d — 40 V, e — 50 V, f — 60 V, g — 70 V, the polarization conditions being: $T_p = 380$ K, $t_p = 5$ min.

temperature T_{max} at which the current is a maximum is not well defined, that means the latter is a function of T_p, t_p , loading resistance, electrode material. The modified TSD procedure described in the introductory section was applied to this peak to reveal its origin in a convincing manner. The results obtained with dag electrodes applied to a 1 mm thick sample are shown in Fig. 7. The full and dashed line were obtained without contact manipulation for storage times 1 min. and 18 min., respectively. Both curves deviate one from another within the limits of experimental accuracy, in other words, the polarization manifested by peak II is conserved at ambient temperature. After the removal of 10 μm thick layers from both faces of the polarized sample and application of new contacts ($t_p = 18$ min.), the $I(T)$ thermogram represented by circles in Fig. 7 was measured. One finds for

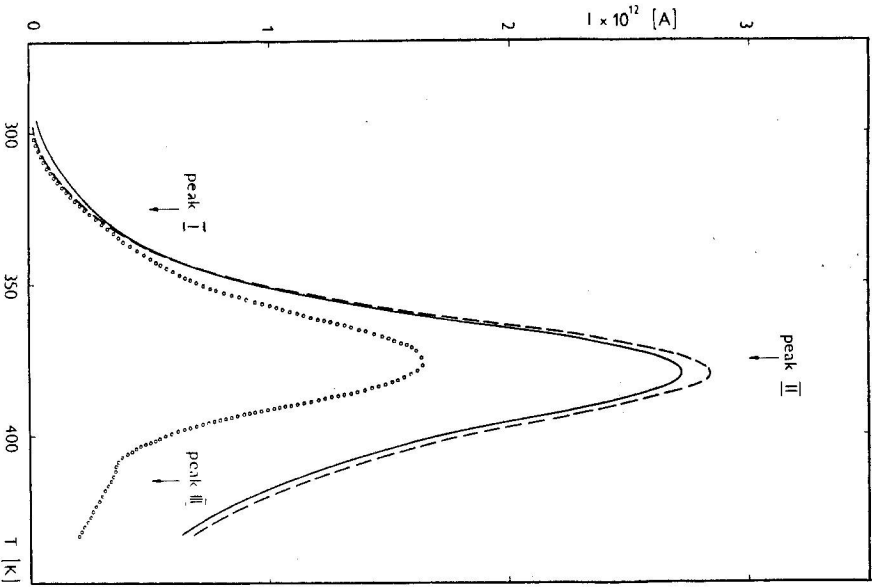


Fig. 7. The modified TSD procedure applied to the complete $I(T)$ thermogram — dag electrodes.

the peak II

$$\frac{Q - Q'}{Q} \gg \frac{\Delta x}{L}$$

so space charge relaxation is the most probable explanation for the origin of peak II.

To estimate that portion of the space charge which is accumulated on the surface, in the course of another experiment only the dag electrodes of the polarized sample were removed and replaced by new ones at ambient temperature ($t_p = 18$ min), after which procedure a thermogram essentially identical with that denoted by circles in Fig. 7 was registered. This finding implies that about 40% of the net accumulated charge were gathered on the surface and probably discharged. The rest is expected to be distributed nearly uniformly throughout the bulk.

Strictly speaking, a poorly resolved peak III in Fig. 7 suggests the presence of an additional relaxation process at still higher temperatures, its origin is not clear as yet.

To obtain a more complex information on the behaviour of the space charge peak at about 380 K, the dependence of the peak height on bias voltage U_p was investigated using different contact materials. The results are summarized in Fig. 8. Interestingly, at low bias voltages linear dependence $I(U_p)$ is found for all the contacts used. The deviations from this behaviour observed with metallic contacts are due to irreversible changes in the metal — glass interface, e.g. the curve 'd' in Fig. 6 was obtained with the same bias as curve 'd', the former being obtained during the last measuring cycle. The irreversible changes in the peak height cannot be explained by electrode metal diffusion mainly for two reasons:

1. As evident from the inset of Fig. 6 no significant deviations from linearity of peak I could be detected measuring both peak I and peak II simultaneously.
2. The penetration depth of the metal under the applied field should be of the order of hundreds of μm in order to be compatible with the peak height increase observed. For an approximative calculation the diffusion data of Süpitz et al. [10] for Au in amorphous As_2Se_3 were adopted, the mobility μ being expressed as

$$\mu_{Au} = 3.5 \exp\left(-\frac{1.0 \text{ eV}}{kT}\right) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}.$$

Then at $T_p = 380$ K, assuming the net electromigration time $t = 1$ hour and the electric field intensity $E = 10^3 \text{ V/cm}$, an Au electrode would pass a distance of $\Delta = \mu Et = 10^{-2} \mu\text{m}$.

Thermally induced changes in the glass structure are improbable below 450 K (the highest temperature reached in the course of the TSD measurements), since the crystallization temperature T_x of our $\text{GeS}_{1.5}$ glass was found to be 820 K at a heating rate of 20 K/min. the corresponding glass transition temperature being

640 K. We have concluded, therefore, that some insulating layer is developed below the electrodes during successive polarization events, which might consist, e.g., of a few layers of neutralized ions. In the case of porous dag electrodes these products are probably removed under the assistance of residual atmosphere and so the equilibrium can be restored at the temperature region of the TSD measurements.

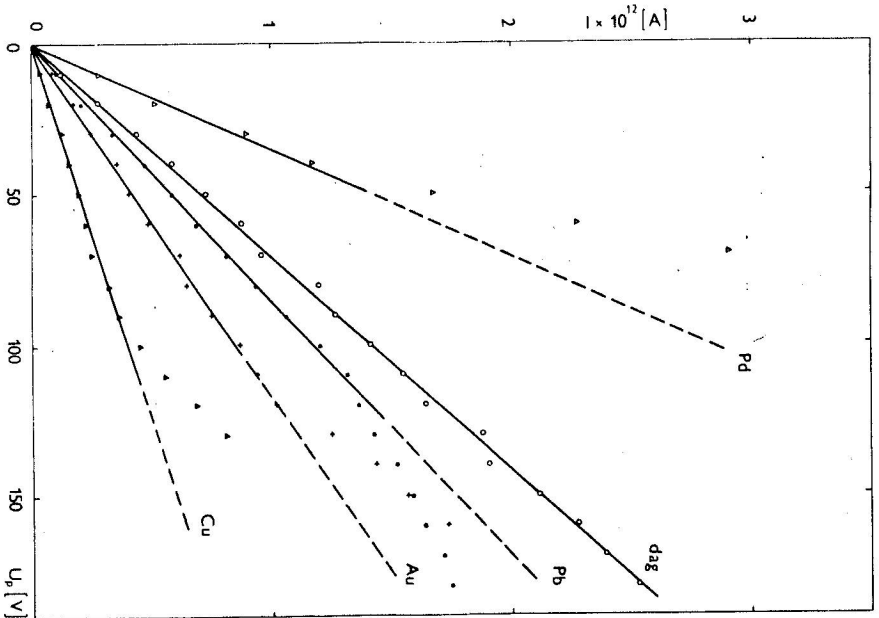


Fig. 8. The maximum current as a function of the bias voltage U_b — peak II.

IV. DISCUSSION

First, let us turn our attention to the question in what aspects the suggested method might be more profitable in investigating dielectric relaxation in glasses

when compared with the widely used dielectric loss measurements. The main advantage is the possibility of separating different tightly overlapping polarization processes without any special requirements as to the electrode material. Moreover, using a suitable sectioning technique the profile of the static space charge distribution [11] within the bulk as well as the amount of the charge accumulated on the surface can be determined.

It is desirable to point out that from the $I(T)$ thermogram belonging to a uniform polarization some macroscopic parameters characteristic of the glass, such as activation energy or jump frequency, can be deduced [6]. Since at least one of these parameters is expected to be distributed, there are some complications involved in the analysis of thermograms similarly as in polymers [12]. On the other hand, by means of a multistage depolarization one can judge which of the two kinetic parameters is distributed [12] and in some cases even the shape of the distribution function becomes available [12, 13].

From a microphysical point of view, little can be said about the mechanism of the uniform polarization from the TSD data. Namely, a question arises, whether one deals with either thermal or a priori vacancies in terms of the theory of Boksay and Lengyel [3]. To answer this question, the temperature dependence of the polarization is required [3], such dependence being not accessible by the TSD technique. This will become evident if one keeps in mind that the glass is to be polarized within a limited temperature range. For the reason we are confined to the calculation of low frequency permittivity dispersion ($\epsilon_s - \epsilon_\infty$) = $P/\epsilon_0 E$, without giving interpretation of the activation energy of depolarization.

V. CONCLUSIONS

Taking $\text{GeS}_{1.5}$ glass as an example, direct evidence for both uniform and space charge polarization has been obtained by the modified TSD method. About 40% of the total space charge was found to be accumulated on the surface, whereas the remaining charge seems to be distributed nearly uniformly throughout the bulk. It is surprising that both polarizations change linearly with bias voltage, so that a linearity check is of little importance whenever space charge effects are to be proved. Obviously, the modified TSD approach might be potentially useful when investigating space charge effects in crystalline dielectrics.

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