# Short-circuit effect in plastic deformation of ZnS and motion of charged dislocations

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(Submitted May 10, 1975)
Zh. Eksp. Teor. Fiz. **69**, 1362–1371 (October 1975)

A description is given of the influence of electrical boundary conditions on the plastic properties of a ZnS single crystal. An investigation is reported of the deformation currents and potential difference between the surfaces of a sample, which result from plastic deformation. The observed phenomena fit well the idea of motion of charged dislocations. The results are given of a determination of the linear dislocation charge density in ZnS.

PACS numbers: 61.70.Mf

## 1. INTRODUCTION

Investigations of plastic flow in II–VI crystals have demonstrated a strong dependence of the plastic properties of these materials on the deformation conditions. Monochromatic illumination can strongly increase [1] and reduce [2] the plasticity of these compounds. Moreover, a considerable hardening of ZnSe crystals occurs on application of electric fields. [3] We shall report a study of the influence of electrical boundary conditions on the plastic properties of ZnS crystals. We shall also give the results of a study of the mechanism of this phenomenon and of the determination of the dislocation charge in ZnS.

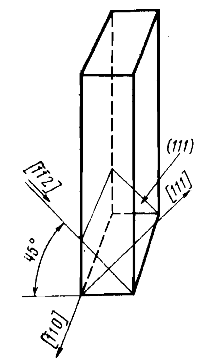


FIG. 1. Orientation of ZnS samples.

## 2. METHOD

We used ZnS single crystals which were grown from the melt but not doped. These crystals had the sphalerite (cubic) structure with a high density of growth stacking faults. In these faults the cubic lattice was rotated by 60° about the [111] axis perpendicular to the plane of the fault. This gave rise to an apparent sixfold symmetry relative to the [111] axis. [4] The total concentration of stacking faults was about 10% of the volume of a crystal. The dark electrical resistivity of ZnS was $\rho_d \approx 10^{10}\ \Omega\cdot$cm at room temperature and it increased to $\rho_{d0} \approx 10^{12}-10^{13}\ \Omega\cdot$cm after 24-h storage, which indicated a long photoconductivity relaxation time. Our ZnS samples were cut from single crystals by a diamond saw, ground with abrasive powders, and polished with a diamond paste. The dimensions were $5 \times 4 \times 1.5$ mm or $4 \times 3 \times 1$ mm (Fig. 1).

Samples were subjected to uniaxial compression parallel to the longest edge. They were deformed at a constant rate, which was varied from one to 100 $\mu$/min between runs. Examination of slip bands indicated that the slip (glide) plane was (111) which was the plane of the stacking faults. Samples were compressed with quartz plungers in a light-tight chamber. Before deformation each sample was kept for about 24 h in darkness to increase its dark resistivity. The leakage of charge through air was reduced by filling the deformation chamber with silicone oil or by placing a drying agent inside the chamber.

The electrical boundary conditions on the surfaces of ZnS samples were varied in the course of deformation in two ways: I) in the first method, the deformation chamber was filled with mercury so that the sample was under a layer of this metal and the potential was the same on all the side surfaces, II) in the second method, metal contacts were deposited on the wide faces ($5 \times 4$ or $4 \times 3$ mm), and these could be short-circuited by conductors outside the deformation chamber so that the potentials of the two large faces became equal. The contact material was In + Hg liquid amalgam or In, which produced an ohmic contact when soldered ultrasonically. Since the samples were thin high-resistivity (≈ 10) plates, we were able to ignore the edge effects and assume that the electric field in the sample was E = 0 for both short-circuiting methods.

All the measurements were carried out at room temperature. Experimental errors were represented in our graphs by the size of the points along the two coordinate axes.

## 3. EXPERIMENTAL RESULTS

1. Figure 2 is the deformation diagram of a ZnS sample. This sample was kept in darkness for 63 h before deformation. The rate of deformation was $v_d$ = 20 $\mu$/min = const so that the time axis t represented also the total strain $\epsilon$. During deformation the sample was immersed in silicone oil. It is clear from Fig. 2 that the initial stage was elastic deformation, which then changed to easy plastic flow (method I). At the moments 2 and 4 the mercury level in the chamber was suddenly lowered and the circuit joining the surfaces was broken. It is clear from Fig. 2 that the short-circuiting of the surfaces resulted in a strong softening so that plastic flow occurred at lower stresses $\sigma$: we found that $\Delta\sigma/\sigma \approx 40\%$ breaking of the short circuit resulted in hardening and recovery of the initial deforming stress. Such a change

  

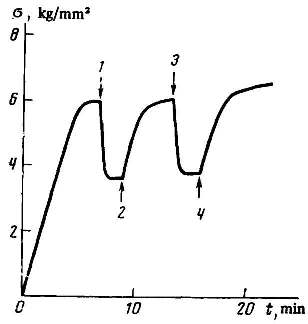


FIG. 2. Deformation diagram of a ZnS sample. Here, $\sigma$ is the mechanical stress in the sample, t is the time, $v_d = 20\ \mu$/min. The short-circuiting took place at moments 1 and 3 and the circuit was opened at moments 2 and 4.

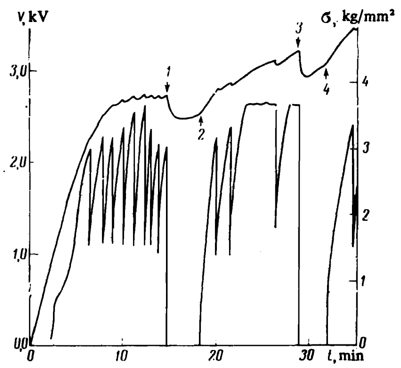


FIG. 3. Deformation diagram (upper trace) and time dependence of the potential difference between the surfaces of a ZnS sample (lower trace). Here, V is the potential difference, $\sigma$ is the mechanical stress, and $v_d = 10\ \mu$/min. The sample was kept for 15 h in darkness. The deformation took place in air. The dimensions of the sample were 4X3X1 mm.

in the deforming stress could be observed repeatedly for the same sample. The same phenomenon occurred also when the large faces were short- or open-circuited by external conductors (method II). The effect was independent of the material used to short-circuit the surfaces.

The sudden change in the deforming stress $\Delta\sigma$ increased with the electrical resistance of the sample. Therefore, large values of $\Delta\sigma$ were obtained after a prolonged storage of ZnS in darkness. The resistance of that sample whose deformation diagram is plotted in Fig. 2 was $R_s \approx 10^{13}\ \Omega$. Deformation of samples not immersed in silicone oil resulted in a periodic electric discharge through air between the surfaces and this gave rise to peaks in the plastic flow diagram.

2. Since the short-circuiting of surfaces of a sample simply altered the potential difference between these surfaces without affecting other physical conditions during deformation, it was natural to assume that a potential difference appeared between the surfaces and the change in this potential difference by short-circuiting resulted in the observed perturbation of the deformation diagram. We checked this hypothesis by connecting a S50 electrostatic voltmeter (input resistance $R_{in} \approx 10^{15}\ \Omega$ and input capacitance 4 pF) between the wide faces of a sample which had contacts made of the In + Hg amalgam.

Figure 3 shows the results of simultaneous recording of the deformation diagram and of the potential difference between the large faces of a ZnS sample. It is clear from Fig. 3 that plastic deformation (deviation of the deformation diagram from the "elastic" slope) produced a potential difference between the surfaces and this difference rose rapidly with the rate of plastic deformation. The potential difference was not due to the piezoelectric effect, which could be observed only in the case of rapid changes of the load: $d\sigma/dt \gtrsim 1\ \mathrm{kg \cdot mm^{-2} \cdot sec^{-1}}$ since the polarization charge produced by the piezoelectric effect leaked away through the sample and measuring circuit in a time t = RC, where R and C are the resistance and capacitance of the system formed by the sample and its measuring circuit. In our case $R \approx 10^{12}\ \Omega$, $C \approx 5$ pF, and $RC \approx 5$ sec. This was deduced from the following simple calculation. If Q is the polarization charge due to the elastic deformation of a piezoelectric, then

$$\dot{Q} = K\dot{\sigma} - I_c, \tag{1}$$

where K = const, which is governed by the geometry of the sample and by the piezoelectric moduli, and $I_c$ is the conduction current representing leakage of the charge through the external circuit in the sample. Since $I_c = Q/RC$, the solution of Eq. (1) subject to the condition $d\sigma/dt$ = const, gives

$$Q = K\dot{\sigma}RC + \mathrm{const} \cdot e^{-t/RC}. \tag{2}$$

Hence, we can see that if $\dot{\sigma} = 0$, the piezoelectric potential difference decays ($V_n = Q/C \to 0$) in a time t = RC, Moreover, the piezoelectric potential differences are not only small but their polarity is opposite to that observed in the plastic deformation case and they are always, even in the elastic stage, at least two orders of magnitude smaller than those observed in our study.

When the potential difference between the surfaces reached $\gtrsim 2$–$2.5$ kV, periodic discharge took place through air and this resulted in a sawtooth dependence of V on time and a similar sawtooth modulation of the deformation diagram as shown in Fig. 3. In this figure the moments 1 and 3 correspond to short-circuiting and the moments 2 and 4 to the breaking of the external circuit.

3. The application of a voltage between the surfaces with the aid of an external source (VS-23) resulted in hardening or softening of the sample, depending on the polarity of the applied voltage (Fig. 4). This effect was independent of the nature of the current contacts and, in contrast to the symmetric electroplastic effect in ZnSe, [3] its sign changed with the polarity of the applied voltage. Figure 5 gives the dependence of the change in the deforming stress $\Delta\sigma$ on the applied electric field. This dependence was linear and the same for the hardening $\Delta\sigma > 0$ and softening $\Delta\sigma < 0$ effects. The value of $\Delta\sigma$ was independent of the origin of the potential differ-

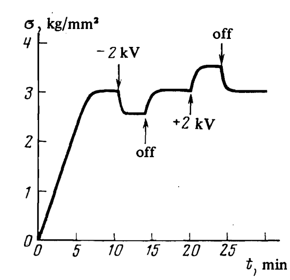


FIG. 4

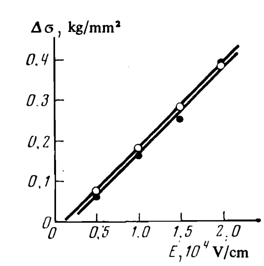


FIG. 5

FIG. 4. Influence of an external electric field on the deformation of a ZnS sample (4X3X1 mm) deformed at a rate $v_d = 10\ \mu$/min.

FIG. 5. Dependence of the change in the deforming stress $\Delta\sigma$ on the electric field E ($v_d = 10\mu$/min): ○) hardening; ●) softening.

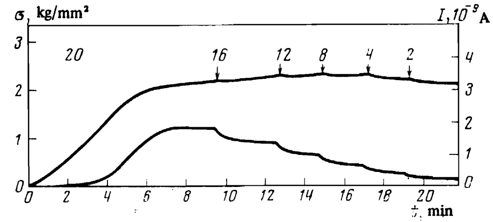


FIG. 6. Deformation diagram of a ZnS sample (upper trace) and time dependence of the deformation current I through the same sample (lower trace). The initial rate of deformation was 20 μ/min. The arrows indicate the moments of reduction in the rate of deformation to 16, 12, ..., 2 μ/min.

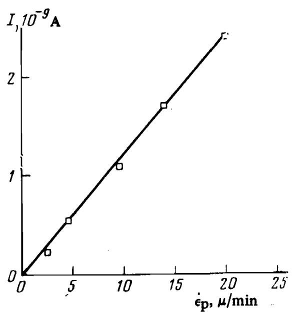


FIG. 7. Dependence of the deformation current through a ZnS sample on the rate of plastic deformation.

ence between the surfaces of the sample. An external voltage source (ES-23) produced the same change $\Delta\sigma$ at a given value of V as the internal potential difference.

4. Since the resistance R between the large faces covered with metal contacts had a finite value $R \sim 10^{12}\ \Omega$, a constant potential difference between the contacts could be maintained in the course of deformation if the sample was a constant-current source. In measuring this current we connected, in series with the sample, a TE-980 electrometer which was used as a nanometer. Since the internal resistance of the TE-980 electrometer operated in this way was $R_{int} = 10^7 \ll 10^{12}-10^{13}\ \Omega = R_S$, the charge emerging on the surface during deformation leaked away through this instrument. We used a two-pen plotter to record simultaneously the deformation diagram and the time dependence of the deformation current I.

The results of such measurements are shown in Fig. 6. It is clear from this figure that the appearance of plastic flow gave rise to a current in the external circuit which rapidly increased, within the plastic flow region, to a steady value and remained constant when the rate of plastic deformation was maintained without change. Changes in the rate of deformation had practically no influence on the deforming stress but they altered greatly the deformation current. It was found that the deformation current I was a linear function of the rate of plastic deformation $\dot{\epsilon}_p$ (Fig. 7), which was deduced from the deformation diagram as follows:

$$\dot{\varepsilon}_p = \dot{\varepsilon} - \dot{\sigma}/m, \quad (3)$$

where $\dot{\epsilon}$ = const is the total rate of deformation governed by the test machine; $\dot{\sigma}$ is the rate of change of the mechanical stresses deduced from the slope of the deformation diagram at a given moment; m is the effective elastic constant of the sample and of the test machine, deduced from the slope of the elastic part of the deformation diagram.

The ratio $I/\dot{\epsilon}_p$ was found to be independent of the nature of electrical contacts (In, liquid amalgam). The current between the (110) surfaces (Fig. 1) was found to be approximately two orders of magnitude less than the current between the large faces. Moreover, the direction of the current varied during deformation in a random manner so that the average value of the current along this direction was zero.

Since $I \propto \dot{\epsilon}$, measurement of the deformation current was found to be a very sensitive and convenient method for determining the rate of plastic deformation.

## 4. MODEL OF THE SHORT-CIRCUIT EFFECT AND CALCULATION OF THE DISLOCATION CHARGE IN ZnS

The first observations of electric charge "bursts" on the surfaces of deformed ionic crystals were made by A. V. Stepanov back in thirties.[5] Nowadays such phenomena in ionic crystals are attributed to the transport of charge by moving dislocations.[6]

The reported measurements of the deformation currents (Figs. 6 and 7) show convincingly that plastic flow causes transport of charge; we shall assume that dislocations whose motion produces plastic deformation are charged. The emergence of such dislocations on the surface of a sample produces an electric charge and establishes a potential difference between the faces of a sample (Fig. 3). The force acting per unit length of a charged dislocation is

$$\mathbf{F} = [(\mathbf{b}\sigma_{ij})\mathbf{l}] + q\mathbf{E}, \quad (4)$$

where **b** is the Burgers vector; $\sigma_{ij}$ is the stress tensor; **l** is a unit vector coinciding with the direction of a dislocation line; q is the linear charge density of a dislocation; **E** is the electric field in a sample. It is clear from Eq. (4) that a change in **E** alters the total force acting on a dislocation. The dislocation velocity can remain constant if the mechanical stress σ changes suitably. This alters the deforming stress σ on application of an external voltage V to a sample of ZnS (Figs. 4 and 5) and on short-circuiting of the surfaces of a sample (Figs. 2 and 3) if the deformation occurs at a constant rate.

Thus, the motion of charged dislocations can account for all the results reported above: the short-circuit effect (Fig. 2), appearance of a potential difference between the faces of a sample as a result of plastic deformation (Fig. 3), sudden changes in the deforming stress on application of an external field (Fig. 4), and the deformation current (Fig. 6).

We shall now obtain some quantitative estimates.

Since plastic flow produces a current through a sample, it is possible to calculate the electric charge carried by a single dislocation. In the case of a static current, we have

$$I = S\sum_i e_i n_i v_i, \quad (5)$$

so that the charge passing through the circuit is

$$Q = S\sum_i e_i n_i l_i, \quad (6)$$

where S is the cross section of the sample; $e_i$, $n_i$, $v_i$, and $l_i$ are the charge, concentration, and normal (to S) components of the velocity and displacement of dislocations participating in charge transport.

We shall now consider the contribution of the motion

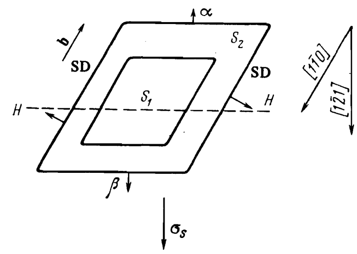


FIG. 8. Expansion of a dislocation loop in a (111) plane. Here, b is the Burgers vector, $\sigma_S$ is the projection of the shear stresses onto the (111) plane, NN is the trace of a plane normal to the direction of the measured electric field, and SD are segments of screw dislocations.

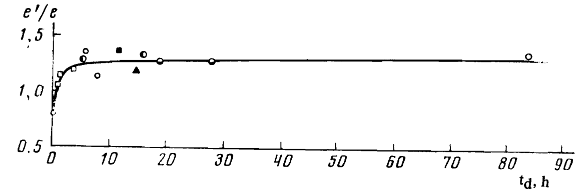


FIG. 9. Dependence of the charge of a dislocation line segment b= 3.82 Å long on the duration of storage in darkness. Here, e'=qb, e is the electron charge, $t_d$ is the duration of storage in darkness. The circles denote the charge calculated from the deformation current, the squares the charge calculated from the changes in the deforming stress, and the triangles the charge calculated from the short-circuit effect. The different shading of the experiment points represents samples cut from different boules.

of one dislocation loop to the charge transport. The minimum translation vectors in a (111) plane in sphalerite are vectors of the ⟨110⟩ type. Therefore, the vectors **b** and **I** of dislocations are oriented along these directions. This gives rise to two types of dislocation: screw and 60°. The 60° dislocations can be of two kinds: $\alpha$ and $\beta$ dislocations, characterized by the breaking of bonds of the Zn and S atoms, respectively, along the dislocation lines. For simplicity, we shall assume that the screw dislocations are either neutral or they carry a charge much smaller than the 60° dislocations, and that the $\alpha$ and $\beta$ dislocations have equal but opposite charges. This relationship between the charges of the $\alpha$ and $\beta$ dislocations is obtained if the cause of these charges is the bond ionicity or piezoelectric fields around the dislocations. [7]

Figure 8 shows the simplest dislocation loop in a (111) plane; this loop consists of two screw and two 60° ($\alpha$ and $\beta$) dislocations.

Plastic strain $\Delta\epsilon_p$ which occurs during expansion of this loop is

$$\Delta\varepsilon_p \propto b\Delta S, \tag{7}$$

where $\Delta s$ is the change in the loop area.

If the linear density of the charge of the 60° dislocations is q, it follows from Eq. (6) that the charge which passes through the measuring circuit as a result of the expansion of the loop is

$$\Delta Q \propto q\{l_\alpha(L_s-l_s)+L_s(L_\alpha-l_\alpha)\}\cos 30°=q\Delta S \tag{8}$$

($l_\alpha$, $l_\beta$, and $L_\alpha$, $L_S$ are the lengths of the 60° and screw components before and after expansion of the loop). It follows from Eqs. (7) and (8) that

$$\Delta Q/\Delta\varepsilon_p=I/\dot{\varepsilon}_p=Kq/b, \tag{9}$$

where K is a constant which is independent of the ratio of the contributions of the screw and 60° $\alpha$ and $\beta$ dislocations to the strain. This is true of a loop of any kind consisting of 60° and screw dislocation segments.

The motion of neutral screw dislocations also gives rise to an electric current, as observed by us, because such motion increases the length of the charged $\alpha$ and $\beta$ dislocations, which is equivalent to a spatial separation between opposite charges, i.e., to an electric current. The ratio in Eq. (9) can be used to calculate from the experimental results (Fig. 6 and 7) the linear density of the dislocation charge q without the knowledge of the ratio of the mobilities of the screw, $\alpha$, and $\beta$ dislocations. The constant K can be calculated from the orientation and dimensions of a sample. Circles in Fig. 9 represent the results of a calculation of the linear dislocation charge density on the basis of experimental results.

The power $P_0$ dissipated by the test machine in deforming a sample at a constant rate $\dot{\epsilon}$ under a mechanical stress $\sigma_0$ is

$$P_0=c_0\dot{\varepsilon}\sigma_0, \tag{10}$$

where $c_0$ is a constant calculated from the orientation and dimensions of a sample. In the presence of an electric field the test machine carries out an additional work to produce dislocation currents and this requires dissipation of an additional power

$$P_E=-c_1IE, \tag{11}$$

where $c_1$ is a constant governed by the dimensions of a sample. It follows from Eqs. (9) and (11) that

$$P_E=-c_1Kq\dot{\varepsilon}_pE/b. \tag{12}$$

On the other hand, if the rates of deformation of a sample in an electric field and in its absence are the same:

$$P_E=c_0\dot{\varepsilon}\Delta\sigma=-c_1Kq\dot{\varepsilon}_pE/b, \tag{13}$$

$$q=-c_0\Delta\sigma b\dot{\varepsilon}/c_1K\dot{\varepsilon}_pE. \tag{14}$$

The formula (14) gives a second method for calculating the dislocation charge from sudden changes in the deforming stress $\Delta\sigma$ observed at the beginning and end of application of an electric field. It is important to note that this result again does not include the ratio of the mobilities of the screw and 60° dislocations. The results of such a calculation are represented by squares in Fig. 9. We can see that they agree well with the value of e′/e calculated by measuring the deformation currents.

We shall now consider the quantitative aspects of the short-circuit effect. Let us assume that during the stage of easy plastic flow the rate of plastic deformation of an open-circuited sample is $\dot{\epsilon}_p$. This gives rise to dislocation currents [see Eq. (9)]

$$I=Kq\dot{\varepsilon}_p/b. \tag{15}$$

These currents charge the surface of a sample until the opposite conduction current becomes equal to the dislocation current

$$I=I_c=V/R=Kq\dot{\varepsilon}_p/b, \tag{16}$$

where V is the potential difference which appears between the surfaces and R is the resistance of the sample; since V = Ed (d is the thickness of the sample), it follows from Eqs. (16) and (14) that

$$\Delta\sigma=c_1K^2q^2\dot{\varepsilon}_p^2R/c_0db^2\dot{\varepsilon}, \tag{17}$$

where $\Delta\sigma$ is the change in the deforming stress due to the short-circuiting of the sample when E becomes equal to zero. Applying Eq. (17) and measuring $\dot{\epsilon}_p$, $\dot{\epsilon}$, R, and $\Delta\sigma$, we obtain one more method for calculating the dislocation charge. The results of such a calculation are represented in Fig. 9 by triangles.

It is clear from Eq. (17) that

$$\Delta\sigma \propto (\dot{\epsilon}_p)^2/\dot{\epsilon} \approx \dot{\epsilon}. \quad (18)$$

This dependence is indeed observed experimentally.

It is usually found that accumulation of plastic strain in ZnS reduces the resistivity. The dependence is not the same for all the samples but usually accumulation of a strain $\epsilon_p \approx 10-15\%$ reduces the resistivity by an order of magnitude. Moreover, a strong hardening appears at $\epsilon_p \approx 10\%$ and this alters the rate of plastic flow $\dot{\epsilon}_p$. It is clear from Eq. (17) that a reduction in R and $\dot{\epsilon}_p$ should weaken the short-circuit effect. Such a dependence of $\Delta\sigma$ on $\epsilon_p$ is indeed observed experimentally.

## 5. CONCLUSIONS

The agreement between the charge of the 60° dislocations calculated by three different methods (Fig. 9) shows that a simple model based on the idea of motion of charged dislocations describes satisfactorily all the phenomena observed by us. It follows from the results in Fig. 9 that $e'/e = 1.3 \pm 0.15$. This is 1.5–3 times greater than the estimate given in [8] where the dislocations charge is calculated from the change in the number of deformation-induced luminescence flashes and from the values of the accompanying changes in the potential. Bearing in mind the dependence of the dislocation charge on the storage in darkness found in the present investigation (Fig. 9), we can regard our results as being in reasonable agreement with those reported in [8]. The dependence of $e'/e$ on the storage in darkness clearly demonstrates the influence of illumination on the dislocation charge in ZnS. Such a dependence was observed by us and it is being investigated at present.

It should be mentioned that lack of allowance for the influence of electrical boundary conditions on the plastic properties of ZnS may result in considerable experimental errors in studies of the dislocation mobility, flow stress, etc. Moreover, this influence may alter the observed intensities and form of the spectrum of the photoplastic effect [1] in high-resistivity semiconductors since the photoconductivity shunts the electric potential difference. This may result in softening, i.e., in a change in the deforming stress which is opposite to the change observed in the photoplastic effect (hardening).

We are grateful to N. V. Klassen, S. Z. Shmurak, S. I. Bredikhin, and V. B. Shikin for valuable discussions of the results, and to E. K. Sal'nikov for his help in the experimental part of the work.

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Translated by A. Tybulewicz
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