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Temperature Effect on Space-Charge-Limited Currents in CdSe Single Crystals

By

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The dark steady-state $I-U$ characteristics of CdSe single crystals of high resistivity are measured. The temperature dependence of the $I-U$ characteristics is interpreted in terms of space-charge-limited currents (SCLC) with a single trap level. The parameters of levels located in a forbidden gap are determined by combining SCLC technique with thermally stimulated current and Hall mobility, μ, measurements. It was found that $\mu = \mu(T)$ is determined by the scattering due to clusters of imperfections. Depending on the location of the Fermi level relative to a single trap level a steep current increase at the end of the square law region can be caused by trap filling or field ionization. The article goes further into restrictions imposed on SCLC by the field ionization of traps.

Es wurden stationäre Dunkelstrom-Spannungs-Charakteristiken an CdSe-Einkristallen gemessen. Die Temperaturabhängigkeit der $I-U$-Charakteristik wird durch raumladungsbegrenzte Ströme (SCLC) mit einem einzelnen Haftstellenniveau erklärt. Aus der Kombination der SCLC-Technik mit thermisch stimulierten Strömen und der Hallbeweglichkeit μ wurden die Parameter der lokalisierten Niveaus ermittelt. Es wurde gefunden, daß $\mu = \mu(T)$ durch Streuung an ionisierten Defektagglomeraten bestimmt wird. Es wird gezeigt, daß der scharfe Knick im Endbereich des quadratischen Teiles der $I-U$-Charakteristik in Abhängigkeit von der Lage des Fermi-Niveaus bezüglich eines Haftstellenniveaus sowohl durch Füllung als auch durch Feldionisation der Störstellen hervorgerufen werden kann. Der Einfluß der Feldionisation der Haftstellen auf SCLC wird diskutiert.

1. General

The study of space-charge-limited currents (SCLC) is important from theoretical and practical point of view. In our previous work [1] from the analysis of SCLC dependence on electrode spacing the conditions have been analysed under which SCLC regime can be obtained and distinguished from the high electric field effect. In the present paper it is shown that investigation of the temperature dependence of SCLC gives much more information. Such investigation allows to prove the presence of SCLC regime and enables not only to distinguish SCLC and high electric field effects but also to determine the SCLC and ohmic conduction mechanisms. This requires the integrated study of $I-U$ characteristic and Hall effect temperature dependences. For instance, the SCLC regime with a single trap level takes place if a) the square law behaviour is observed over a wide temperature range, b) the temperature dependence of the voltage U_{1-2}, at which Ohm's law turns to the square law behaviour, satisfies the expression [2]

$$U_{1-2} = \frac{2\, e\, d^2}{3\, \varepsilon\, \varepsilon_0} \frac{n_0(T)}{\theta(T)}, \tag{1}$$

where e is the electronic charge, $\varepsilon\, \varepsilon_0$ the dielectric constant, n_0 the thermal free electron density, θ the reduction factor

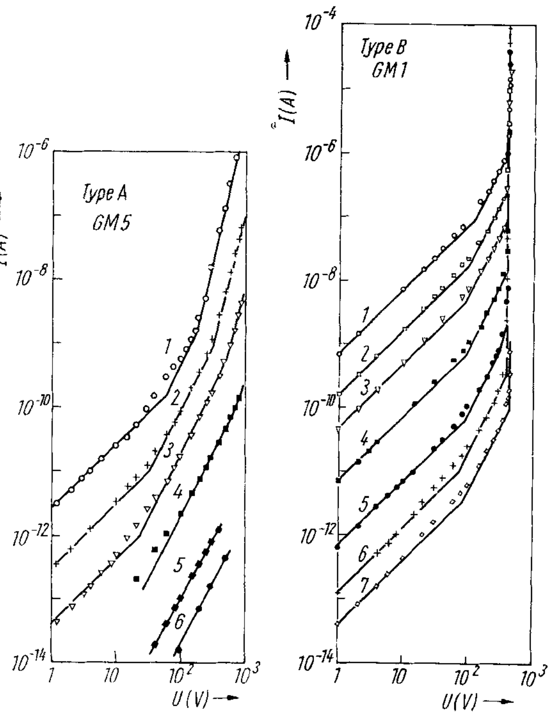
$$\theta = \frac{N_c}{g\,N_t} \exp\left(-\frac{E_t}{kT}\right) \qquad (n \ll n_t \ll N_t)\,, \tag{2}$$

where N_c is the effective density of states in the conduction band, N_t, E_t, and g the density, depth (here and throughout, the depth is reckoned from the bottom of the conduction band), and degeneracy factor of a single trap level, respectively; the other symbols have their usual meaning. Obviously, the thermal activation energy for U_{1-2} is equal to the difference between the activation energies for the ohmic and SCLC regions. The temperature dependence of the transition voltage U_{2-n}, at which a steep current increase occurs, can help to clear up the origin of this current increase. If, for instance, the current increase is caused by trap filling, then

$$U_{2-n}(T) = \frac{2\,e\,d^2\,N_t}{3\,\varepsilon\,\varepsilon_0} \frac{1}{1 + g\exp\left[-\dfrac{(E_f - E_t)}{kT}\right]}\,, \tag{3}$$

where E_f is the distance of the Fermi level from the bottom of the conduction band. Evidently, U_{2-n} is temperature independent if $E_f - E_t \gg kT$, and decreases slightly with temperature if $E_f - E_t \gtrsim kT$.

CdSe single crystals of high resistivity were chosen as the object of investigation. SCLC in CdSe single crystals have been first observed in [3]. However, until recently in the semiconductor considered SCLC are insufficiently investigated.



a b

Fig. 1. Dark steady-state I–U characteristics at different temperatures for CdSe single crystals. a) CdSe single crystal GM5 of type A. Curve 1: $T = 291$ °K, curve 2: $T = 272$ °K; curve 3: $T = 253$ °K; curve 4: $T = 230$ °K, curve 5: $T = 203$ °K, curve 6: $T = 190$ °K. Contact area $s = 1.3 \times 10^{-2}$ cm², $d = 750$ μm. b) CdSe single crystal GM1 of type B. Curve 1: $T = 291$ °K, curve 2: $T = 272$ °K, curve 3: $T = 257$ °K, curve 4: $T = 237$ °K, curve 5: $T = 219$ °K, curve 6: $T = 205$ °K, curve 7: $T = 191$ °K. $s = 1.6 \times 10^{-3}$ cm², $d = 300$ μm

2. Sample Preparation

CdSe single crystals were grown by the Boyd-Sihvonen method [4]. They had two pronounced parallel planes with the distance between them from 300 to 800 μm. This enables the preparation of sandwich-type specimens for the I–U characteristics and thermally stimulated current (TSC) measurements: The single crystals were equipped with rubbed-on In–Ga alloy electrodes and then mounted on a copper substrate. Such type of electrodes provides ohmic contacts to CdSe single crystals [5]. In the case of crystals used for the Hall mobility measurements the same type of electrodes was performed.

According to the nature of I–U characteristics at high electric fields (10^4 to 10^5 V cm^{-1}) the crystals were divided into two types: A and B (see Fig. 1). The crystals of type A have a resistivity from 10^{10} to 10^{11} Ω cm and of type B — of the order of 10^8 Ω cm.

3. Results

The dark steady-state I–U characteristics for CdSe single crystals were measured over the temperature range from 190 to 300 °K. At each applied voltage time was allowed for the current to reach steady-state value. In order to remove the excess charge, which was trapped in the crystal while previous measurements were performed, the specimen was short-circuited and heated to 300 °K before every run. I–U characteristics for sandwich-type specimens were independent of the pressure in the cryostat over the range from 7.6×10^2 to 10^{-5} Torr within the temperature range at which measurements were carried out. At lower electric fields I–U characteristics for both crystal types (A and B) are similar: For voltages $U < U_{1-2}$ Ohm's law holds and for $U_{1-2} < U < U_{2-n}$ the current shows the square law dependence on voltage over the whole temperature range. For crystals of type A the transition voltage U_{1-2} increases exponentially with temperature (the thermal activation energy for U_{1-2} $\Delta E_{U_{1-2}}$ varies from 0.12 to 0.17 eV) and for type B U_{1-2} is temperature independent. However, at high electric fields, i.e. for $U > U_{2-n}$, there is a pronounced difference between the I–U characteristics for different crystal types. For type A at high electric fields the current increases more sharply with voltage than in the square law region, and the voltage U_{2-n} at which the current deviates from the square law behaviour decreases exponentially with temperature, while for type B the current increases almost "vertically" with voltage and U_{2-n} depends slightly on temperature. For $U > U_{2-n}$ the I–U characteristics for both crystal types are stable and reproducible. In the present paper the results concerning the crystal GM5, representing type A, and the crystal GM1, representing type B, are only presented. I–U characteristics for these two crystals at different temperatures are shown in Fig. 1. For the crystal GM5 $\Delta E_{U_{1-2}} = 0.17$ eV (Fig. 2, curve 1) and for the crystal GM1 U_{1-2} is temperature independent with an accuracy of 0.01 eV (Fig. 2, curve 2).

Obviously, the values of Hall mobility μ and its temperature dependence are needed for a quantitative analysis of the temperature dependence of I–U characteristics. For this purpose the Hall effect has been measured under thermal equilibrium conditions on both crystal types over the temperature range from 247 to 342 °K using the technique described in [6]. It was obtained that CdSe single crystals are n-type and the electron mobility exponentially

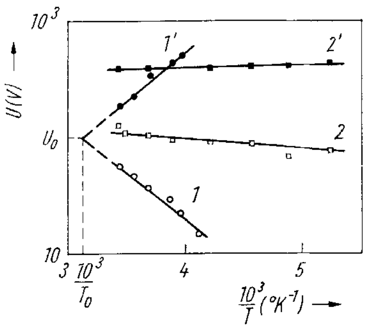


Fig. 2. Dependence of the transition voltage on temperature. $U_{1-2} = U_{1-2}(T)$: curve 1 — CdSe single crystal GM5, curve 2 — crystal GM1; $U_{2-n} = U_{2-n}(T)$: curve 1' — crystal GM5, curve 2' — crystal GM1

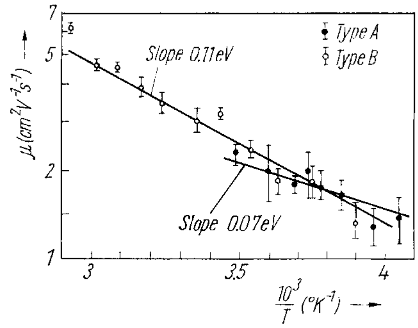


Fig. 3. Dependence of the electron Hall mobility on temperature. ● Hall mobility with evaluated mean-square error for CdSe single crystal GM5, ○ — for crystal GM1

increases with temperature over the temperature range studied. The values of 0.07 and 0.11 eV of thermal activation energy of mobility for the crystal GM5 and GM1, respectively, seem to fit the experimental data (Fig. 3). For both crystals the values of mobility are of the same order of magnitude.

4. Discussion

The temperature dependence of U_{1-2} and the fact that the square law behaviour is observed over the whole temperature range studied allow to assume that for both types of CdSe single crystals for $U > U_{1-2}$ the SCLC regime with a single trapping level takes place. The depth and density of this trapping level calculated from the temperature dependence of reduction factor (see (2)) are: $E_t = (0.38 \pm 0.02)$ eV, $N_t = (2.2 \pm 0.5) \times 10^{14}$ cm^{-3} (Fig. 4, curve 1') for the crystal GM5 and $E_t = (0.35 \pm 0.02)$ eV, $N_t = (1.3 \pm 0.7) \times 10^{13}$ cm^{-3} (Fig. 4, curve 2') for the crystal GM1. In this calculation the values of $m_e =$

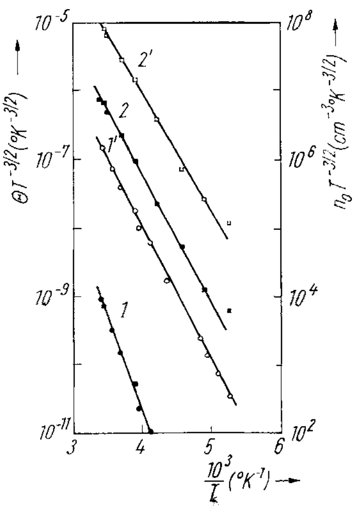


Fig. 4. Temperature dependence of θ and n_0. $n_0(T)$: curve 1 — CdSe single crystal GM5, curve 2 — crystal GM1; $\theta(T)$: curve 1' — crystal GM5, curve 2' — crystal GM1

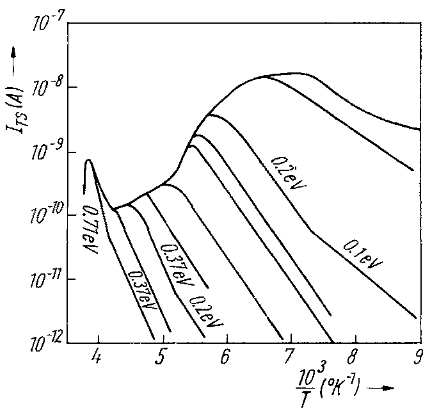


Fig. 5. Decay of thermally stimulated currents for CdSe single crystal GM5

$= 0.13\ m_0$ (m_e is the effective electron mass) [7, 8], $\varepsilon = 10$ [9, 10], and $g = 2$ were used and it was assumed that at temperatures lower than those at which the Hall effect was measured, the temperature dependence of μ determined was satisfied, too. When the trap depth is determined it is clear that in the case of crystal GM5, the activation energy for n_0 being (0.55 ± 0.02) eV (Fig. 4, curve 1), the experimental value of $\Delta E_{U_{1-2}}$ coincides with that predicted by the SCLC theory. As for the crystal GM1 the same relation between the temperature dependences of n_0/θ and transition voltage U_{1-2} is satisfied: The thermal activation energy for n_0 ($\Delta E_{n_0} = (0.37 \pm 0.02)$ eV, see Fig. 4, curve 2) coincides well with the trap depth, where the transition voltage U_{1-2} is temperature independent. When the values of the Fermi level location at the lowest and highest temperatures used in experiment of 0.4 and 0.44 eV are added to these data it seems reasonable to assume that over the temperature range studied the thermal free carrier density n_0 originates from the single trapping level. For the crystal GM5 another model is needed in order to explain the temperature dependence of thermal free carrier density. When the main part of carriers, thermally excited from the discrete level, the density of which is N_D and the depth E_D, is trapped at a single level E_t, then [11, 12]

$$n_0 = \frac{N_c}{g}\left(\frac{N_D}{N_t}\right)^{1/2} \exp\left(-\frac{E_D + E_t}{2\,kT}\right) \quad \text{at} \quad p_{D\,0} \approx n_{t\,0} \gg n_{t_i 0}\,, n_0\,, \tag{4}$$

where $p_{D\,0}$ is the thermal hole density on N_D, $n_{t\,0}$ and $n_{t_i 0}$ are the thermal electron densities on N_t and on the more shallow levels, respectively. From (4) one gets $E_D = (0.72 \pm 0.04)$ eV and $N_D = 1.5 \times 10^{13}\ cm^{-3}$. The parameters of the above two levels (E_D and E_t) satisfy both the experimental values of U_{1-2} (cf. Fig. 2, curve 1, with (1)) and the validity condition of (4) over the temperature range studied (Fermi level shifts from 0.59 to 0.61 eV), but they are needed to be checked by means of some other independent method. For this purpose the decay of TSC [13, 14] was measured on crystal GM5. This TSC method was chosen because it provides more reliable data — it enables to remove the influence of shallower traps on the initial TSC increase. The results of measurement shown in Fig. 5 indicate the discrete spectrum of levels in the forbidden gap. The depths of these levels determined from the slopes of initial TSC increase are: 0.1, 0.2, 0.37, and 0.71 eV. The levels 0.37 and 0.71 eV are consistent with those obtained from the temperature dependence of SCLC and ohmic conductivities. This coincidence justifies the application of the above model to dark ohmic conduction and confirms the conclusion that for $U > U_{1-2}$ SCLC regime occurs. The TSC data in turn can be complemented by results deduced from SCLC and ohmic conductivity. Since the more shallow level ($E_{t_i} = 0.2$ eV) well defined in TSC does not affect either the ohmic condoctivity or SCLC, its density is less than $2.6 \times 10^{15}\ cm^{-3}$ [15]. This was evaluated from $n_0 = n_0(T)$ and $\theta = \theta(T)$.

The steep current increase at the end of the square law region may be caused by carrier injection from the contacts, high electric field or heating effects. An analysis of these effects follows.

1. *Trap filling* — For crystals of type B the current increase for $U > U_{2-n}$ is caused by trap filling since the extremely sharp and temperature independent current rise with voltage together with the slight dependence of transition voltage U_{2-n} on temperature are an indication of trap-filled limited regime [2].

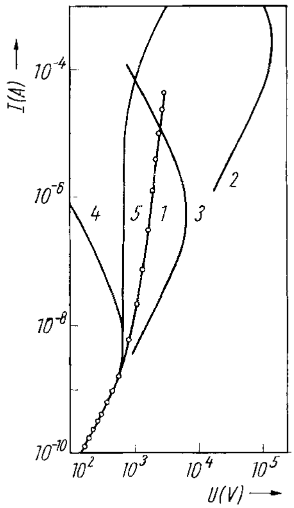


Fig. 6. Dark steady-state I–U characteristics for CdSe single crystal GM5 at high electric fields at $T = 260$ °K. Curve 1: experimental I–U characteristic; curves 2, 3, 4: theoretical I–U characteristics for different heat transfer conditions [18] for $R/R_{\mathrm{air}} = 10^{-4}, 1, 10^3$, respectively ($R_{\mathrm{air}} = 3 \times 10^{-3}$ W^{-1} °K, $s_1 = 3.4 \times 10^{-2}$ cm^2); curve 5: theoretical I–U characteristic in the case of field ionization [19]

For the crystal GM1 this conclusion is confirmed by the close agreement of the trapping level parameters determined using two independent methods — from the temperature dependence of θ and from trap-filled voltage U_{2-n}, because in the latter case one gets $E_t = (0.37 \pm 0.01)$ eV and $N_t = 5 \times 10^{12}$ cm^{-3}. For crystal GM5 trap filling does not occur because it gives a considerably underestimated value of N_t ($N_t = 8 \times 10^{12}$ cm^{-3}) and contradicts the temperature dependence of U_{2-n}.

2. *Joule's heating* — The influence of Joule's heating due to the passage of SCLC on I–U characteristic can be estimated when the values of the thermal resistance of the heat sink $R = (s_1 h)^{-1}$ are known, where s_1 is the crystal surface area and h the heat transfer coefficient, proportional to the heat conduction of surroundings [16]. Since in the case of heat transfer through the air at normal pressure h_{air} for CdSe single crystals was evaluated in [17], the I–U characteristics for different heat transfer conditions were computed according to [18] and the results concerning crystal GM5 are shown in Fig. 6. If heat transfer is considered to proceed only through the copper substrate (Fig. 6, curve 2) or only through the air atmosphere at normal pressure (Fig. 6, curve 3), the voltage at which the current starts to increase due to crystal heating is considerably greater than U_{2-n} (Fig. 6, curve 1). This voltage will conform to U_{2-n} if it is assumed that $R/R_{\mathrm{air}} = 10^3$ (Fig. 6, curve 4), what is entirely inconsistent with the experiment, since the CdSe single crystal is mounted on a copper substrate, covered with In–Ga alloy, and the I–U characteristics are independent of pressure in the cryostat. Furthermore, in the case of Joule's heating the crystal should be destroyed by thermal runaway after the current increase, by one order of magnitude relative to SCLC while actually the stable and reproducible increase of the current for $U > U_{2-n}$ covers five orders of magnitude. For the crystal GM1 the same conclusions are valid. Hence, Joule's heating plays no role in our experiment.

3. *Field ionization of trapping level* — For crystals of type A we propose the following way for determination of the reason of current rise for $U > U_{2-n}$. Since U_{2-n} decreases exponentially with temperature and U_{1-2}, on the contrary, increases exponentially with temperature, then at some temperature T_0, which can be determined from extrapolation, the square law region will disappear and the ohmic current will turn at once to the current steeply increasing with voltage, i.e. $U_{1-2} = U_{2-n} = U_0$. Hence, at T_0 the parameter

$$d_0 = \left(\frac{3\,\varepsilon\,\varepsilon_0\,U_0\,\theta}{2\,e\,n_0}\right)^{1/2}$$

[1] must conform to the electrode spacing if the field ionization effect takes place. For the crystal GM5 with $T_0 = 320$ °K and $U_0 = 10^2$ V (Fig. 2) the value $d_0 =$

$= 820\ \mu m$ is in good agreement with the electrode spacing ($d = 750\ \mu m$). From this we consider that in the case of crystal GM5 field ionization of trapping level takes place at high electric fields. When field ionization of trapping level is taken into account there is no qualitative disagreement between the theoretical I–U characteristic and the experimental one, as it was for Joule's heating effect. This is demonstrated by the I–U characteristic (Fig. 6, curve 5) computed under the assumption that the ionization probability for a single trapping level is equal to zero for $\mathscr{E} \leqq \mathscr{E}_0$ ($\mathscr{E}$ is the electric field) and unity for $\mathscr{E} \geqq \mathscr{E}_0$ [19]. In the experimental curve (Fig. 6, curve 1) the flatter current increase with voltage for $U > U_{2-n}$ is, from our point of view, due to the fact that actually the ionization probability for a local level monotonously increases from zero to unity with electric field.

The analysis carried out allows to go further into the restriction imposed on SCLC by field ionization of traps. Not only the parameter d_0 [1] but also T_0 must be considered as restriction criterion. If field ionization of traps takes place the SCLC region is reduced by the extension of electrode spacing (for $T =$ const) as well as by the increase of temperature (for $d =$ const). The latter fact indicates that the method of SCLC measurement at rised temperatures [20] can not be always applied.

The investigation performed allows to make some comments concerning the carrier scattering mechanism in CdSe single crystals. The small absolute values of mobility and its exponential increase with temperature can not be explained by scattering on uniformly distributed ionized imperfections but can be accounted for by scattering due to clusters of imperfections [21, 22]. In the latter case $\mu \sim A_1\ N^{1/3} \cdot T^{-(1/2 \div 5/6)}$, where N is the sum of free and trapped electron densities, A_1 is a quantity depending on the charge and density of clusters. For the crystal GM5 the calculated thermal activation energy of (0.06 ± 0.01) eV for $N^{1/3}$ $(N = n_0 + n_{t0} + p_{D0} \approx 2\, n_{t0} \sim \exp{[-(E_D - E_t)/2\, kT]})$ is in good agreement with the slope of 0.07 eV of a plot $\ln{(\mu\ T^{1/2})} = f(T^{-1})$ which fits the experimental mobility data (see Fig. 3). While for the crystal GM1 the temperature dependence and absolute values of mobility are in agreement with the scattering due to clusters of imperfections the quantitative analysis is impossible because of the lack of data on all discrete levels involved.

5. Conclusions

It has been demonstrated that for CdSe single crystals the steep current increase at the end of square law region can be caused by different effects in spite of the fact that SCLC is affected by the same discrete trapping level. Which of two phenomena — trap filling or field ionization of traps — will take place depends on the Fermi level location relative to the single trap level. If $E_f - E_t \approx 2$ to $3\ kT$, then trap filling occurs, and field ionization takes place if $E_f - E_t \approx 10\ kT$. The latter effect imposes restrictions on SCLC, and in order to extend the limits of the SCLC region smaller electrode spacings and lower measuring temperatures have to be preferred.

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References

[1] J. Viščakas, P. Mačkus, and A. Smilga, phys. stat. sol. **25**, 331 (1968).
[2] M. A. Lampert, Rep. Progr. Phys. **27**, 329 (1964).
[3] J. Viščakas, A. Smilga, and G. Juška, Fiz. Tekh. Poluprov. **1**, 1733 (1967).
[4] D. R. Boyd and V. T. Sihvonen, J. appl. Phys. **30**, 176 (1959).
[5] J. Viščakas, S. Karpinskas, S. Sakalauskas, and A. Smilga, Liet. Fiz. Rinkinys **8**, 151 (1968).
[6] R. Baubinas, A. Sakalas, A. Smilga, and J. Viščakas, phys. stat. sol. **24**, K91 (1967).
[7] M. V. Kurik, Phys. Letters (Netherlands) **24A**, 742 (1967).
[8] J. Ginter, phys. stat. sol. **8**, K141, (1965).
[9] E. Kendall, Phys. Letters (Netherlands) **24A**, 254 (1967).
[10] R. Geick, C. H. Peny, and S. S. Mitra, J. appl. Phys. **37**, 1994 (1966).
[11] J. G. Simmons, Phys. Rev. **155**, 657 (1967).
[12] G. G. Roberts and F. W. Schmidlin, Phys. Rev. **180**, 785 (1969).
[13] G. F. Garlick and A. F. Gibson, Proc. Phys. Soc. **A60**, 574 (1948).
[14] R. H. Bube, G. A. Dussel, Ching-Tao Ho, and L. D. Miller, J. appl. Phys. **37**, 21 (1966).
[15] W. G. Trodden, Brit. J. appl. Phys. **18**, 401 (1967).
[16] E. Nebauer and E. Jahne, phys. stat. sol. **8**, 881 (1965).
[17] J. Vaitkus, J. Viščakas, S. Karpinskas, and A. Urbelis, Fiz. tverd. Tela **11**, 2111 (1969).
[18] E. Gray, Brit. J. appl. Phys. **14**, 374 (1963).
[19] J. S. Ryabinkin, Fiz. tverd. Tela **6**, 2989 (1964).
[20] E. Harnik, J. appl. Phys. **36**, 3850 (1965).
[21] B. R. Gossik, J. appl. Phys. **30**, 1214 (1959).
[22] L. R. Weisberg, J. appl. Phys. **33**, 1817 (1962).

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See Short Note by R. E. Hummel and W. A. Slippy Jr.

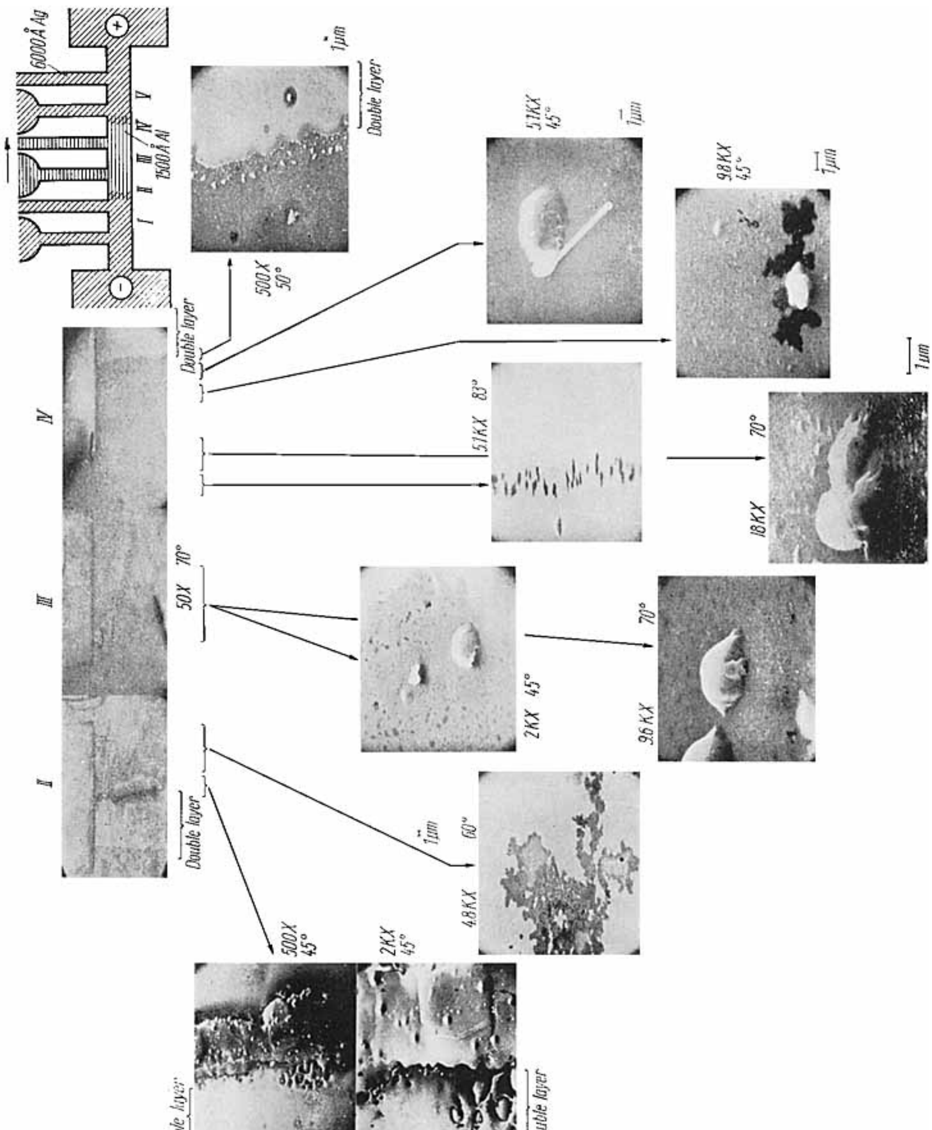
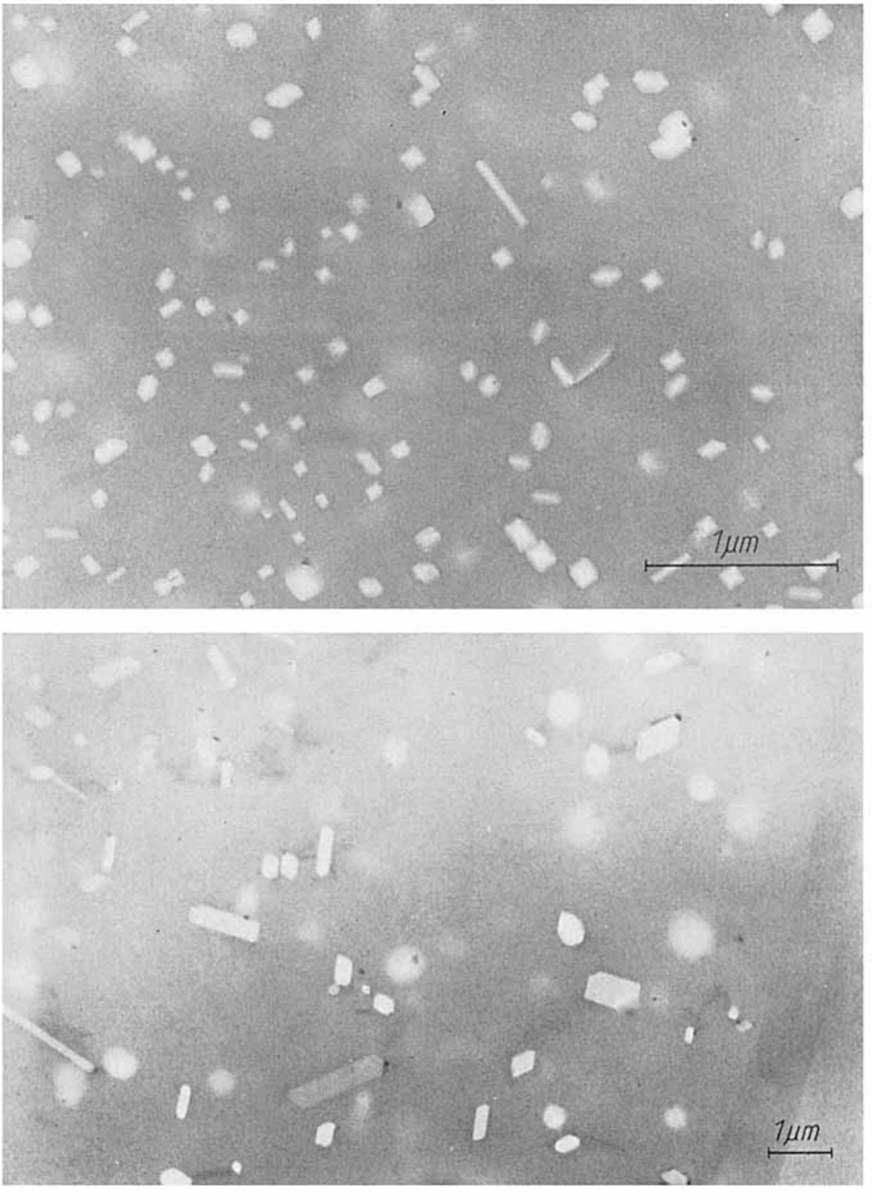


Fig. 3. Scanning electron micrographs of an aluminum sample which was subjected to a current density of 5×10^5 A/cm^2

See Short Note by K. Farrell and R. T. King



a

b

Fig. 1. Voids in high purity aluminum sheet irradiated to 4×10^{20} fast neutrons/cm² at a) 125 °C, b) 150 °C

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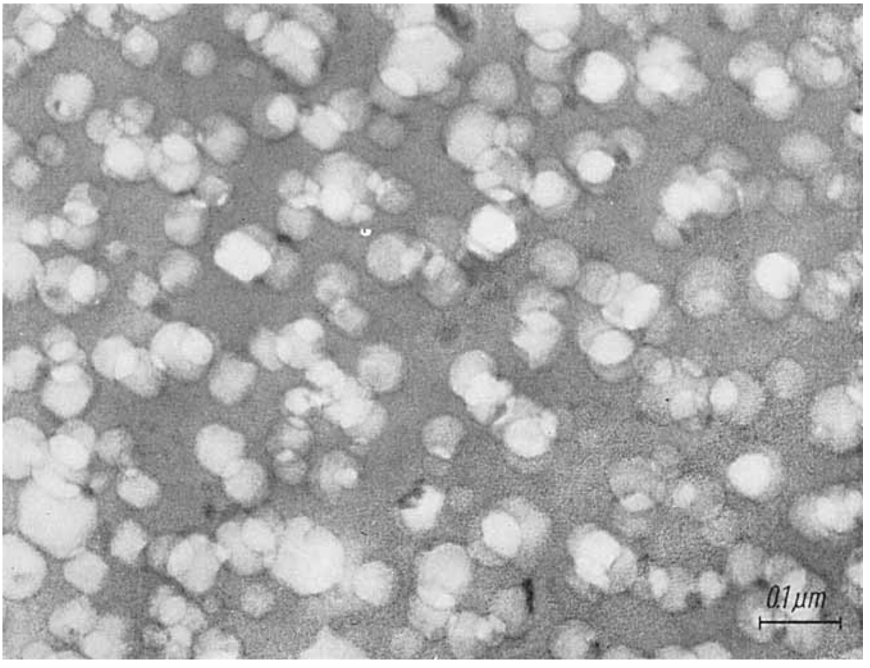

Fig. 2. Voids in high purity aluminum rod irradiated to 1×10^{22} fast neutrons/cm^2 at 60 °C