

MIXED CONDUCTION IN CUPROUS SELENIDE AT STRONG CURRENTS

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Abstract: Some approximate equations for the time dependence of voltage drop across the sample of non-stoichiometric cuprous selenide and its current-voltage characteristic are derived. These equations are an extension of Yokota's theory of mixed ionic and electronic conductivity to the range of strong currents, where the precipitation of the metallic component of a non-stoichiometric compound takes place. The calculated values are compared with the experimental results of the author and with the results of Miyatani, Suzuki and Kushida. Satisfactory agreement has been found.

1. Introduction

Cuprous selenide belongs to the group of compound semiconductors with a mixed conductivity. The transport of charge in a crystal of this compound takes place by means of single-charged copper ions and of holes present in the crystal due to stoichiometric deviations. According to Lorenz's and Wagner's investigations¹⁾, cuprous selenide is a compound with a wide range of homogeneity. The extreme compositions found at 400 °C are $\text{Cu}_{1.9975}\text{Se}$ and $\text{Cu}_{1.86}\text{Se}$. Owing to these onesided stoichiometric deviations, cuprous selenide behaves as a permanent p-type semiconductor.

The author has already reported on certain properties of the high-temperature phase of cuprous selenide²⁾. The measurements described in that paper were carried out with inert electronic contacts and potential probes under conditions of a weak current through the sample. The current density was so small that no precipitation of metallic copper occurred and only an internal rearrangement of copper ions took place. Some interesting phenomena have been observed in the case of strong currents passing through the sample. The precipitation of metallic copper greatly changed the time dependence

of voltage drop across the sample. The current-voltage characteristic of cuprous selenide also changed its shape. As far as is known there is no satisfactory explanation for these phenomena.

2. Basic equations

We shall now briefly discuss Yokota's equations³ for mixed conductivity in non-stoichiometric crystals. If a constant current of a density j is passing through a sample of length L with movable metallic ions and electrons, the concentration of excess metallic atoms N depends on time t and co-ordinate x as

$$N = N_0 \left\{ 1 + \frac{ejL}{N_0 \sigma_0} \frac{1}{(d\mu/dN)_0} \left[\frac{x}{L} - \frac{1}{2} + F \left(\frac{x}{L}, \frac{t}{\tau} \right) \right] \right\}, \quad (1)$$

provided that inert electronic contacts are used. This equation applies to the time interval from the moment when the current is switched on ($t = 0$), to the moment when the stationary distribution of atoms is formed ($t = \infty$). In the time range when this stationary distribution decays, the concentration of excess metallic atoms is governed by the equation

$$N = N_0 \left[1 - \frac{ejL}{N_0 \sigma_0} \frac{1}{(d\mu/dN)_0} F \left(\frac{x}{L}, \frac{t}{\tau} \right) \right]. \quad (2)$$

In both equations and in other formulas of the present paper the following notation was used:

- N_0 — equilibrium concentration of excess atoms in an unpolarized sample,
- σ_0 — electronic conductivity,
- σ_i — ionic conductivity,
- σ — total conductivity ($\sigma = \sigma_0 + \sigma_i$),
- μ — chemical potential of neutral metallic atoms,
- T — absolute temperature in Kelvins,
- e — electronic charge, and
- k — Boltzmann's constant.

The index zero denotes that the respective quantity does not depend on the coordinate.

The function $F(x/L, t/\tau)$ in equations (1) and (2) replaces the Fourier series

$$F \left(\frac{x}{L}, \frac{t}{\tau} \right) = \frac{4}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \left[- (2m+1)^2 \frac{t}{\tau} \right] \cos \left[(2m+1) \pi \frac{x}{L} \right] \quad (3)$$

in which τ denotes the time of diffusion, defined as

$$\tau = \frac{L^2}{\pi^2} \frac{\sigma_o e^2}{\sigma_{io} \sigma_{eo}} \left(\frac{dN}{d\mu} \right)_o. \quad (4)$$

Yokota has also derived an equation for potential distribution along the sample. If the potential zero is taken at the midpoint $x = L/2$, one can write

$$V_x = -j \int_{L/2}^x \frac{dx}{\sigma_o + (d\sigma/dN)_o (N - N_o)} - \frac{\sigma_{io}}{e (d\sigma/d\mu)_o} \cdot \ln \left[1 + \left(\frac{d \ln \sigma}{d\mu} \right)_o \left(\frac{d\mu}{dN} \right)_o (N - N_o) \right], \quad (5)$$

where V_x is the potential measured at the co-ordinate x . Details about derivation of these equations can be found in Yokota's original paper.

3. Application to cuprous selenide

The theory of mixed conductivity, whose equations are presented in the preceding paragraph, can also be applied to cuprous selenide. However, some modifications are necessary. First, for cuprous selenide N denotes the concentration of deficit copper atoms. At the same time, N is the concentration of holes, because it is reasonable to assume that all copper atoms in a crystal exist in the form of Cu^+ ions while charge neutrality is established (see the description of an analogous situation found for $\text{Cr}_{1-x}\text{S}^9$). Secondly, cuprous selenide is an average crystal⁵. Thus, the chemical potential of copper ions is practically independent of the composition, while the chemical potential of neutral copper atoms μ can be identified with the Fermi level E_F of electrons as far as the variation of N is concerned⁶. Finally, the ionic conductivity of cuprous selenide is only a small fraction of the total conductivity^{2,7}. This fact enables us to equalize the hole conductivity σ_{ho} with the total conductivity σ_o with only slight errors. Supposing that holes in cuprous selenide obey classical statistics, one can write $(d\mu/dN)_o = kT/N_o$, $(d\sigma/d\mu)_o = \sigma_{eo}/kT$ and $(d \log \sigma/d\mu)_o = 1/kT$, so that equation (1) transforms to

$$N = N_o \left\{ 1 - \frac{ejL}{\sigma_{ho} kT} \left[\frac{x}{L} - \frac{1}{2} + F \left(\frac{x}{L}, \frac{t}{\tau} \right) \right] \right\}. \quad (6)$$

Similarly equation (2) becomes

$$N = N_o \left[1 + \frac{ejL}{\sigma_{ho} kT} F \left(\frac{x}{L}, \frac{t}{\tau} \right) \right]. \quad (7)$$

The time of diffusion defined by (3) also transforms into its approximative form

$$\tau = \frac{L^2}{\pi^2} \frac{e^2 N_0}{\sigma_{ho} kT}. \quad (8)$$

Finally, equation (5) for potential distribution along the sample is subject to transformation. Instead of V , we shall rather express the equation for potential difference between two electronic probes. If they are placed on the sample at coordinates x_1 and x_2 , equation (5) will give

$$V = \frac{j}{\sigma_{ho}} \int_{x_1}^{x_2} \frac{N_0}{N} dx + \frac{kT}{e} \frac{\sigma_{ho}}{\sigma_{ho}} \ln \frac{N(x_1)}{N(x_2)}. \quad (9)$$

In certain cases this equation is reduced to a few simpler forms. For our purpose it is sufficient to discuss the stationary state only, which was reached after the formation process of polarization had finished. For $t = \infty$, equation (1) gives the stationary concentration gradient

$$N = N_0 \left[1 - \frac{ejL}{2\sigma_{ho} kT} \left(\frac{2x}{L} - 1 \right) \right]. \quad (10)$$

Inserting this result into (9), one obtains the stationary potential difference. By simple calculations and denoting $x_2 - x_1 = d$ we obtain⁹⁾

$$V = \frac{kT}{e} \ln \frac{1 + \frac{ejL}{2\sigma_{ho} kT} \frac{d}{L}}{1 - \frac{ejL}{2\sigma_{ho} kT} \frac{d}{L}}. \quad (11)$$

This equation represents the stationary current-voltage characteristic of the sample. The characteristic is evidently non-ohmic.

4. Strong currents

It is very easy to show that the presented theory is limited to low currents through the sample. Namely the concentration of deficit copper atoms in the stationary state and at $x = L$ according to equation (10) is given by

$$N = N_0 \left(1 - \frac{ejL}{2\sigma_{ho} kT} \right). \quad (12)$$

Since the concentration cannot be negative, the applicability of the theory is limited by the simple condition⁸⁾

$$a = \frac{ejL}{2\sigma_{\infty}kT} = \frac{jL}{2v_h N_0 kT} \leq 1, \quad (13)$$

where v_h is the mobility of the holes and the equation $\sigma_{\infty} = ev_h N_0$ is assumed. The case $a = 1$ gives the limiting current density

$$j_L = \frac{2v_h N_0 kT}{L} = \frac{2\sigma_{\infty} kT}{eL}. \quad (14)$$

If such a current is passed through the sample, the stationary concentration of deficit copper atoms at the negative contact is zero, i.e. the sample at $x = L$ has just the stoichiometric composition. Currents of greater densities cause the precipitation of metallic copper at the cathode.* Therefore, the range of current densities $j > j_L$ have been indicated as a strong current range.

Now, imagine that we start our experiment with a sample of an equilibrium concentration of copper deficit N_0 . If we apply the current $j = j_L$ the concentration at $x = L$ is $N(L) = 0$, and at $x = 0$ it is $N(0) = 2N_0$, after the stationary state has been reached. Precipitation still does not occur. The application of currents $j > j_L$ leads to a new stationary state. A certain amount of copper is precipitated at the cathode, but we have again $N(L) = 0$. However, at $x = 0$ it is now $N(0) > 2N_0$. Let it be $N(0) = 2N_*$. We cannot distinguish this stationary state from the state reached with a similar sample with equilibrium concentration N_* without precipitation. For the latter sample the current density j is just the limiting density and we have

$$\frac{jL}{2v_h' N_* kT} = 1, \quad (15)$$

or

$$j = \frac{2v_h' N_* kT}{L}. \quad (16)$$

Assuming that the mobility of holes does not depend on the concentration ($v_h' = v_h$), equations (14) and (16) give

$$N_* = N_0 \frac{j}{j_L}. \quad (17)$$

* As mentioned in the Introduction, the one extreme composition is $\text{Cu}_{0.975}\text{Se}$ and not Cu_2Se . This means that the precipitation of copper starts before the limiting case $a = 1$ is reached. For the sake of simplicity we apply the same condition (13) for cuprous selenide.

For $j = j_L$ we obtain $N_s = N_0$ as one would expect, because the limiting current does not cause precipitation.

In the following we wish to discuss Yokota's equation (6). It has a real meaning only as long as

$$\frac{ejL}{\sigma_{no} kT} \left[\frac{x}{L} - \frac{1}{2} + F \left(\frac{x}{L}, \frac{t}{\tau} \right) \right] \leq 1. \quad (18)$$

Since the Fourier series for $x = L$ becomes

$$f \left(\frac{t}{\tau} \right) = -\frac{4}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \left[- (2m+1)^2 \frac{t}{\tau} \right], \quad (19)$$

one can write the condition (18) in the form

$$\frac{ejL}{\sigma_{no} kT} \left[\frac{1}{2} - f \left(\frac{t}{\tau} \right) \right] \leq 1. \quad (20)$$

This condition enables us to conclude that all equations, being correct for weak currents through the sample, can also be applied for strong currents but only to a limited time t_1 defined by the equation

$$2f \left(\frac{t_1}{\tau} \right) = 1 - \frac{2 \sigma_{no} kT}{ejL} = 1 - \frac{j_L}{j}. \quad (21)$$

If we set $j = j_L$, the calculations give $t_1 = \infty$. This is a very plausible result, because the limiting current is still a weak current and the theory is valid without limitations. The limiting time t_1 is shorter if the current density is greater.

After the time t_1 the precipitation of metallic copper begins, and the total number of deficit copper atoms in the sample increases. In order to describe distribution of these atoms after t_1 , we introduce a time and current dependent equilibrium concentration $n_s = n_s(t, j)$ with the following properties:

$$\begin{array}{ll} 0 \leq t < t_1 & n_s = \text{const.} = N_0 \\ t_1 < t < \infty & n_s \text{ increases} \\ t = \infty & n_s = \text{const.} = N_s \end{array} \quad (22)$$

Moreover, for $j \leq j_L$ this concentration must be equal to N_0 at any moment. It is easy to show that for $t \geq t_1$ these conditions satisfy the function

$$n_s = N_0 \left[\frac{j}{j_L} - 2 \left(\frac{j}{j_L} - 1 \right) f \left(\frac{t - t_1}{\tau} \right) \right]. \quad (23)$$

Having such a function, one can find the stationary distribution of deficient copper atoms. At the limiting time $t = t_1$ equation (6) gives the expression

$$N = N_0 \left\{ 1 - \frac{ejL}{\sigma_{\infty} kT} \left[\frac{x}{L} - \frac{1}{2} + F \left(\frac{x}{L}, \frac{t_1}{\tau} \right) \right] \right\}, \quad (24)$$

which can be approximated by the linear function

$$N = 2N_0 \left(1 - \frac{x}{L} \right). \quad (25)$$

These two functions have three common points: $x = 0$, $x = L/2$ and $x = L$, and differ only slightly from each other. Accepting this approximation, one can describe the formation of the stationary distribution of deficit copper atoms by equation (25), provided the constant concentration N_0 is replaced by the time dependent concentration n_0 , defined by (23). This means that after the time t_1 the straight line (25) changes its slope only, having the fixed point $N(L) = 0$.

One can recapitulate: the stationary distribution of deficit copper atoms occurs in two separate time intervals:

$$1) \quad 0 \leq t \leq t_1 \quad N = N_0 \left\{ 1 - 2 \frac{j}{j_L} \left[\frac{x}{L} - \frac{1}{2} + F \left(\frac{x}{L}, \frac{t}{\tau} \right) \right] \right\}, \quad (26)$$

$$2) \quad t_1 \leq t \leq \infty \quad N = 2N_0 \left[\frac{j}{j_L} - 2 \left(\frac{j}{j_L} - 1 \right) f \left(\frac{t-t_1}{\tau} \right) \right] \left(1 - \frac{x}{L} \right). \quad (27)$$

After the current is turned off, the metal atoms deposited on the negative contact start to diffuse back into the sample. It is evident that the concentration of deficient copper atoms at $x = L$ is zero as long as metal is present at the contact. During the back-diffusion the equilibrium concentration n_0 decreases from the value N_0 at the time $t = 0$ (when the current is turned off) to the value N_0 which is reached at the moment when the diffusion of the precipitated copper is finished. From this moment the equilibrium concentration is constant. One can again introduce the concept of a limited time t_2 which divides the events after the current is turned off into two separate intervals. This time can be obtained from equation (7). For $x = L$ it is reduced to

$$N = N_0 \left[1 - 2 \frac{j}{j_L} f \left(\frac{t}{\tau} \right) \right]. \quad (28)$$

Positive values for N are obtainable only if

$$2 \frac{j}{j_L} f \left(\frac{t}{\tau} \right) \leq 1. \quad (29)$$

The limiting time t_2 is then defined by the equation

$$2 f \left(\frac{t_2}{\tau} \right) = \frac{j_L}{j}. \quad (30)$$

For $j = j_L$ it gives $t_2 = 0$, which means that the theory for weak currents applies already from $t = 0$. Similarly, we repeat that the decay of polarization takes place in two intervals:

$$1) 0 \leq t \leq t_2 \quad N = 2n'_0 \left(1 - \frac{x}{L} \right), \quad (31)$$

$$2) t_2 \leq t \leq \infty \quad N = N_0 \left[1 - \frac{2j}{j_L} F \left(\frac{x}{L}, \frac{t - t_2}{\tau} \right) \right]. \quad (32)$$

In the first equation n'_0 is a current- and time-dependent equilibrium concentration. For further calculations one needs not know its exact form, but it must be similar to n_0 with a retrograde action. As we see from (32), after the limiting time t_2 the decay of polarization is the same as for weak currents.

So far we have not mentioned any limitation in the current density j . However, it exists, because real crystals of cuprous selenide have only a limited range of composition. The concentration of deficit copper atoms can nowhere be greater than it is in selenide with the composition $\text{Cu}_{1.36}\text{Se}$ at 400°C . This means that it is the greatest current density that in the stationary state at $x = 0$ causes the largest possible concentration of deficit copper atoms. The highest current density can be easily calculated from equation (17) and the formula $N = N_0 (1 - x/L)$. Any exceeding of the value which is thus calculated will cause the appearance of two-phase system near the positive contact and abruptly change the contact conditions.

5. Potential difference and current-voltage characteristic

A potential difference between two inert probes placed on the sample is a definite function of deficit copper concentration, as seen from equation (9). Consequently, in the formation of the stationary potential gradient, or

in its decay, we also distinguish several definite intervals. At the moment when the current is switched on we have, according to (6), $N = N_0$ and the potential difference is

$$V = \frac{j d}{\sigma_{ho}} = V_i . \tag{33}$$

This voltage is called the initial voltage. It is of the same form as for weak currents. During the interval $0 < t \leq t_1$, the time-dependent concentration is governed by the equation (26). Inserting it in (9) we obtain

$$V = \frac{j}{\sigma_{ho}} \int_{x_1}^{x_2} \frac{dx}{1 - 2 \frac{j}{j_L} \left[\frac{x}{L} - \frac{1}{2} + F \left(\frac{x}{L}, \frac{t}{\tau} \right) \right]} + \frac{kT}{e} \frac{\sigma_{io}}{\sigma_{ho}} \ln \frac{1 - 2 \frac{j}{j_L} \left[\frac{x_1}{L} - \frac{1}{2} + F \left(\frac{x_1}{L}, \frac{t}{\tau} \right) \right]}{1 - 2 \frac{j}{j_L} \left[\frac{x_2}{L} - \frac{1}{2} + F \left(\frac{x_2}{L}, \frac{t}{\tau} \right) \right]} . \tag{34}$$

After the limiting time t_1 , i.e. in the range $t_1 \leq t \leq \infty$ the variation of deficit copper concentration is described by (27). In order to obtain a potential difference in the same range, equation (27) must be inserted into (9) and equation (23) into expressions for both conductivities. Instead of σ_{ho} and σ_{io} one now has $\sigma_h = nev_h$ and $\sigma_i = nev_d$, where v_d is the mobility of deficit copper atoms. By means of a short calculation we obtain

$$V = \left(\frac{j}{\frac{j}{j_L} - 2 \left(\frac{j}{j_L} - 1 \right) f \left(\frac{t-t_1}{\tau} \right)} + j_L \frac{\sigma_{io}}{\sigma_{ho}} \right) \frac{L}{2 \sigma_{ho}} \ln \frac{L+d}{L-d} . \tag{35}$$

At the time $t = t_1$ the voltage is

$$V = \left(j + j_L \frac{\sigma_{io}}{\sigma_{ho}} \right) \frac{L}{2 \sigma_{ho}} \ln \frac{L+d}{L-d} = V_L , \tag{36}$$

and may be called the limiting voltage. It should be noted that this voltage has not the same value as that calculated from equation (34) at $t = t_1$. This small discrepancy appears to be due to the approximation of equation (24) by (25). The limiting voltage is higher as the current density increases. But, in the stationary state, $t = \infty$, we obtain from (35) the stationary voltage

$$V = \frac{j_L L}{2\sigma_{bo}} \ln \frac{L+d}{L-d} = \frac{kT}{e} \ln \frac{L+d}{L-d} = V_0, \quad (37)$$

which does not depend on current density. This is a very interesting result. Due to polarization, the voltage should increase, but at the same time the precipitation of copper increases the conductivity of the sample and the total voltage drop remains constant.

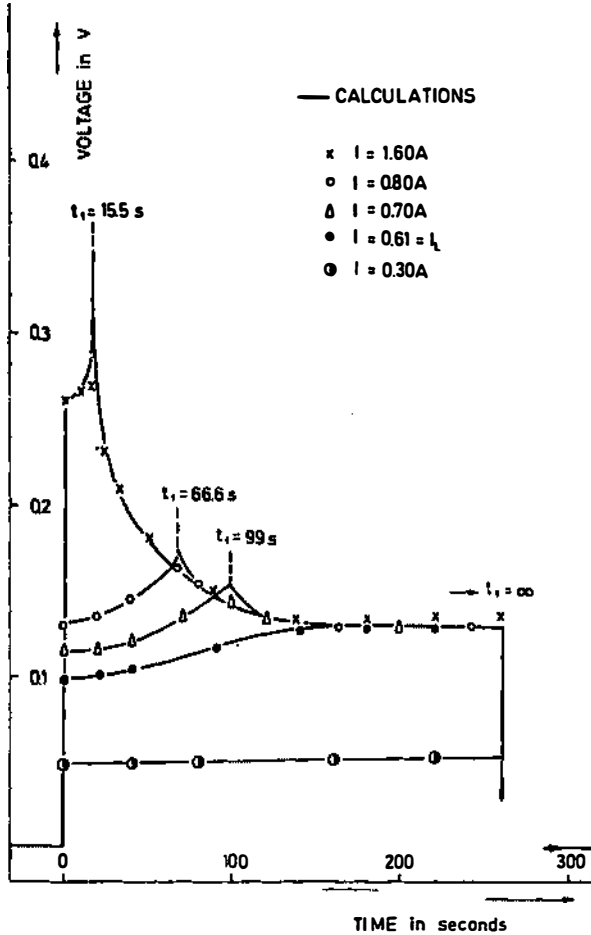


Fig. 1. Potential difference during the formation of the stationary state.

The time dependence of the voltage drop after the current is turned off ($t = 0$) can also be obtained from equation (9). Since $j = 0$, we have only the second part of it. In the range $0 \leq t \leq t_2$ the concentration (31) must be inserted for N at both coordinates. Thus we obtain the residual voltage

$$V = \frac{kT}{e} \frac{\sigma_{i0}}{\sigma_{bo}} \ln \frac{L+d}{L-d} = V_R \quad (38)$$

Similarly, if $t_2 \leq t \leq \infty$, equations (9) and (32) give

$$V = \frac{kT}{e} \frac{\sigma_{i_0}}{\sigma_{h_0}} \ln \frac{1 + 2 \frac{j}{j_L} F\left(\frac{x_1}{L}, \frac{t-t_2}{\tau}\right)}{1 + 2 \frac{j}{j_L} F\left(\frac{x_2}{L}, \frac{t-t_2}{\tau}\right)}. \quad (39)$$

The residual voltage does not contain the current density j . This means that V_R is constant up to the limiting time t_2 for each value of j . After t_2 it decreases according to (39) and $t = \infty$ becomes equal to zero.

As mentioned in Chapter 2, the stationary current-voltage characteristic is of a non-ohmic nature and can be represented by equation (11). Evidently, this equation is valid only for weak currents, i.e. as long as $j \leq j_L$. For strong currents it loses meaning and equation (37) becomes valid. Since it does not contain the current density j , it represents a straight line parallel to the j -axis. The current-voltage characteristic has a knee at the point $j = j_L$.

6. Comparison with experiments

In the following we wish to compare the graphical representation of the equations derived above with the results of the experimental measurements. We performed measurements at 510 °C on a cylindrical sample with a length of 2 cm and a cross-section of 0.145 cm². It had $\sigma_{h_0} = 61.5 \Omega^{-1} \text{ cm}^{-1}$, $\sigma_{i_0} = 1.8 \Omega^{-1} \text{ cm}^{-1}$ and $\tau = 55$ s. Consequently, the limiting current density calculated from equation (14) is $j_L = 4.18 \text{ A/cm}^2$. Let us consider the formation of the stationary potential difference. The first step is to calculate the limiting time t_1 . It can be established for various current densities by means of graphical

Table 1.

j (A/cm ²)	t_1 (s)	V_t (mV)	V_L (mV)	V_0 (mV)
11.03	15.5	261	343	132
5.52	66.6	131	174	132
4.82	99.0	114	152	132
4.18	∞	99	—	132
2.06	—	49	—	53

solutions of equation (21). The time t_1 is presented in Table 1 for 5 values of j , together with the values of initial, limiting and stationary voltages calculated from equations (33), (36), and (37). The last value of the stationary voltage is calculated by means of equation (11).

The time-dependent part of the curves is calculated using equations (34) and (35). In the first of them, numerical integration by the trapezoidal formula was used. Thus calculated, the values are represented in Fig. 1 with full curves, while the dots indicate the values read directly on the voltage-time recorder. A general agreement is evident, except in the very strong current region where both the observed and the calculated values slightly disagree. This fact can be understood assuming the existence of two additional effects — the Peltier effect and the thermo-electric voltage, which are due to the non-symmetrical heating of contact with unequal areas. Both effects may cause an increased stationary voltage if they have the same direction of action. For smaller current densities additional effects practically disappear.

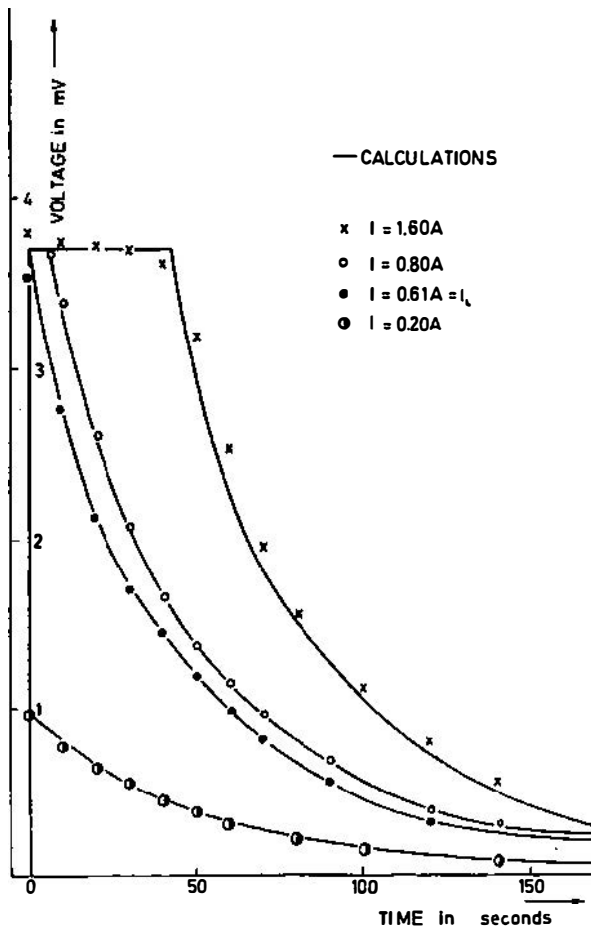


Fig. 2. Potential difference during the decay of polarization.

Below we shall compare the calculated residual voltage and its decay according to equations (38) and (39) with the experimental points. The resi-

dual voltages and the limiting times t_2 for 4 various current densities are indicated in Table 2.

Table 2.

j (A/cm ²)	t_2 (s)	V_R (mV)
11.03	42	3.70
5.52	6.8	3.70
4.18	0	3.70
1.38	—	0.96

These values together with the time-dependent parts are shown in Fig. 2 as full curves. The dots represent the measurements. A satisfactory agreement can repeatedly be observed for small current densities only, while for $j = 11.03$ A/cm² ($I = 1.60$ A) deviations appear. However, this disagreement could also be explained by the decay of thermo-electric voltage due to the Peltier effect and the non-symmetrical heating of contacts.

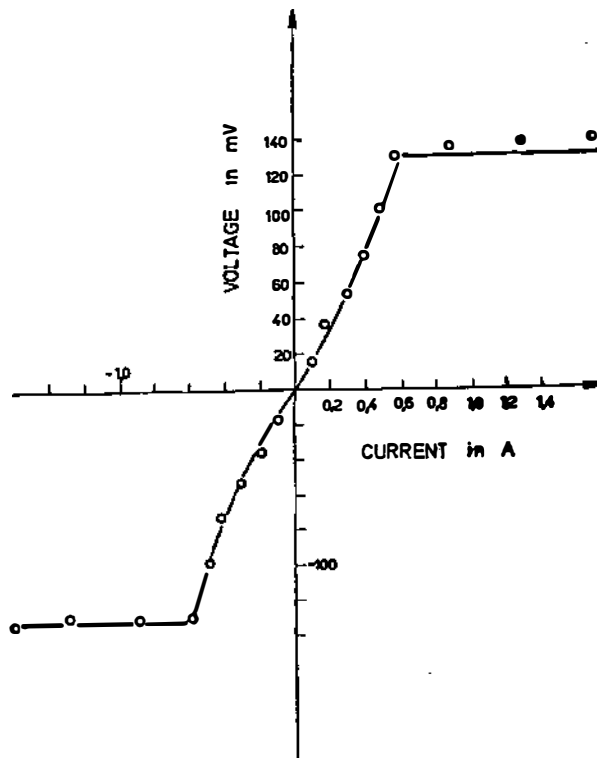


Fig. 3. Stationary current-voltage characteristic of cuprous selenide

We have also compared the theoretical and the observed current-voltage characteristics. Both are shown in Fig. 3. For current densities lower than $j = j_c = 4.18$ A/cm² ($I = 0.61$ A) the points of the characteristics are calculated from formula (11). Above this value voltage remains constant as predicted by

equation (37). We see a satisfactory agreement at small current densities and some deviations at higher values. It is interesting to mention that agreement is better for the negative direction of current. It seems that the Peltier voltage, which depends on the direction of the current cancels the thermo-electric voltage which is independent of current direction.

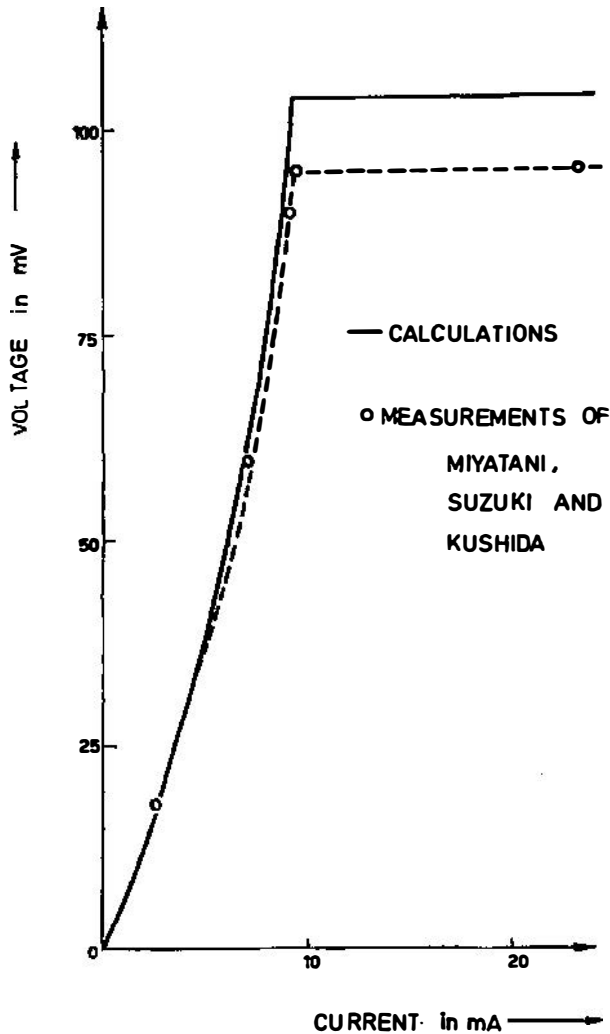


Fig. 4. Stationary current-voltage characteristic of cuprous sulfide

In conclusion we should like to compare results of our calculations with those of the measurements of Miyatani, Suzuki⁹ and Kushida¹⁰. These authors have established the current-voltage characteristic of cuprous sulfide indicated by dots in Fig. 4. Cuprous sulfide is also a p-type semiconductor with mixed ionic and electronic conduction. It has been found that copper vacancies serve as acceptors and that one can equalize the concentration of

vacancies with the concentration of holes. All conditions thus being fulfilled, we can use our equations to describe events in cuprous sulfide without limitations. Thus, in one experiment the sample of cuprous sulfide has the length $L = 2.65$ cm and the cross-section 0.092 cm². At temperature $T = 456$ °K the hole conductivity was $\sigma_{ho} = 3.45$ Ω^{-1} cm⁻¹ and the concentration of deficit copper atoms or holes $N_o = 4.5 \cdot 10^{19}$ cm³. As the probe separation was $d = 0.9 L$, all data in equations (11) and (37) are known and the current-voltage characteristic can be calculated. In Fig. 4 it is shown as a full curve. In spite of the fact that absolute values do not agree (probably due to insufficiently known d/L), a general agreement is evident.

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MIJEŠANA VODLJIVOST BAKAR SELENIDA KOD JAKIH STRUJA

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S a d r ŝ a j

Transport naboja u nestehiometrijskim poluvodičkim spojevima opće formule $A^{I+}B^{VI}$ vrši se s jednostruko nabijenim metalnim ionima i elektronima, odnosno šupljinama, koje su prisutne u kristalu zbog trajnih stehiometrijskih devijacija. Zbog relativno širokog područja homogenosti tih spojeva, prolaz

struje izaziva uvijek i pojavu koncentracionih gradijenata ili tzv. polarizaciju uzoraka. Ona uzrokuje odstupanje od normalne strujno-naponske karakteristike i daje padu napona duž uzorka naročitu vremensku zavisnost.

U radu su izvedene aproksimativne relacije koje opisuju te pojave, a predstavljaju proširenje postojeće teorije miješane električne vodljivosti na područje jakih struja, gdje se zbiva precipitacija metalne komponente nestehiometrijskog spoja. Rezultati su uspoređeni s vlastitim mjerenjima na bakar selenidu i s mjerenjima drugih autora na bakar sulfidu, te je utvrđeno odgovarajuće podudaranje.