

CURRENT-VOLTAGE CHARACTERISTIC OF SUPERIONIC Ag_2S IN TWO COEXISTING PHASES*

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Received 25 July 1983

UDC 538.93

Original scientific paper

Current-voltage characteristic of the two phase sample of silver sulphide placed between indium contacts is measured and described within the frame of Wagner's theory of mixed (ionic and electronic) conduction. Electrical field applied in the forward direction causes the formation of weak concentration gradients of moving particles, which at lower voltages leads to a linear characteristic. In the reverse biased cell the events are more complicated, including probably a partial decomposition of the sample and the formation of a highly resistive layer of indium sulphide. Characteristic in this case is exponential and similar to the characteristic of an electrolytic rectifier.

1. Introduction

Silver sulphide, Ag_2S , belongs to the group of compounds with two distinct properties: a variable stoichiometry and a mixed, ionic and electronic, conductivity. The high-temperature or α -phase of Ag_2S (stable above 177 °C) is a typical superionic conductor with Ag^+ ions serving as charge carriers, but at the same it is an electronic conductor as well, with almost metallic properties. Below transition temperature, in β -phase, Ag_2S behaves as a semiconductor characterized by an energy gap equal to 0.7 eV. The conductivity of this phase, however, is not purely

*Part of this work has been reported at the 8th Yugoslav Conference on the Physics of Condensed Matter, Poreč, 21—24 Sept. 1982.

electronic. As in the α -phase, a part of the charge transport occurs via Ag^+ ions. In this work we shall not concentrate on either phase, but rather on such conditions in which both phases coexist. As noticed by P. Junod¹⁾ such a two-phase sample has an unusual, asymmetric, current-voltage characteristic, which he identified as a characteristic of a contact between a metal and an n -type semiconductor. In this work we show that the characteristic is of a more complicated nature. Ionic properties of Ag_2S play an important role in its formation.

2. Experiment

A cylindrical sample of stoichiometric Ag_2S , having a cross-section area $S = 1.26 \cdot 10^{-5} \text{ m}^2$ and length 0.015 m, was provided by two indium contacts (as in Junod's experiment) and placed in a vertical furnace in which the temperature had been stabilized at about 178 °C. Since this temperature is a little above the transition point, the whole sample was initially in the high-temperature phase. However, the upper current lead was a thick copper wire (Fig. 1), which assured

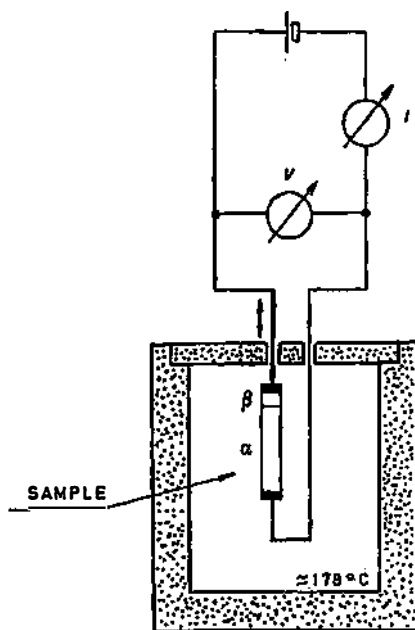


Fig. 1. Apparatus for the measurement of the characteristic.

the asymmetrical cooling of the sample. In the resulting temperature gradient, a part of the sample was transformed to the low-temperature phase, i. e. a two-phase sample had been formed. Its current-voltage characteristic was measured very slowly by standard dc technique (time interval between the two points was around five minutes). The results are shown in Fig. 2. While the forward biased

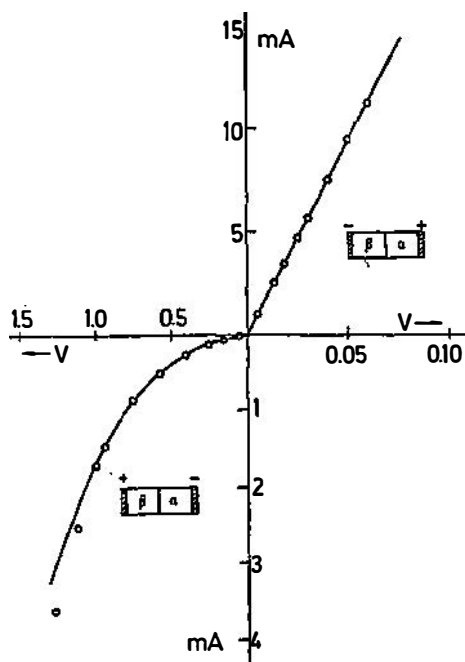


Fig. 2. Current-voltage characteristic. Inserts show how the forward and the reverse directions are defined.

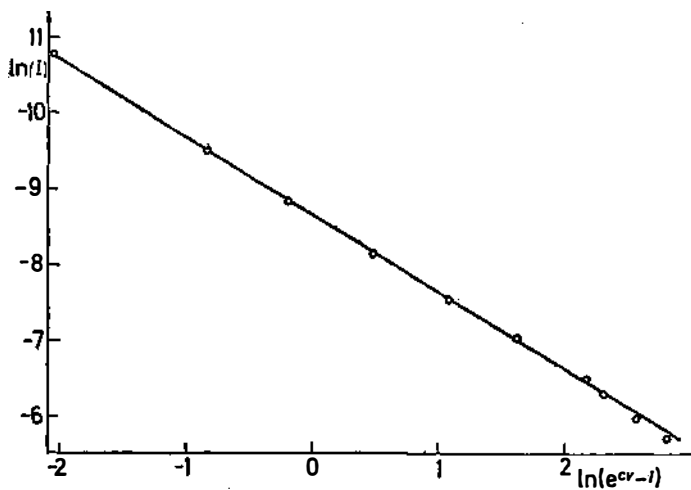


Fig. 3. Characteristic of the reverse biased cell in the logarithmic plot.

contact (β -phase negative) has a very steep linear characteristic, reverse bias (β -phase positive) leads to an exponential dependence of current upon voltage. This dependence does not show any saturation. The two parts of the curve are easily fitted by two equations:

$$I = AV \quad (1)$$

for the forward direction, and

$$I = B(e^{cV} - 1) \quad (2)$$

for the reverse direction (see Fig. 3). The three constants appearing in these equations have the following values: $A = 0.19 \Omega^{-1}$, $B = 1.72 \cdot 10^{-4} \text{ A}$ and $C = 2.4 \text{ V}^{-1}$. The measurements were reproducible, but the characteristic was stable only when the temperature difference between the ends of the sample had been small.

3. Charge transport through the cell

As noticed in *Introduction*, both phases of Ag_2S exhibit a mixed, ionic and electronic, conductivity. One consequence of relatively large ionic mobility is that the space charge cannot be formed anywhere in the sample. In spite of the fact that β -phase is a semiconductor, the formation of the usual metal-semiconductor potential barrier (e. g. at the contact between β -phase and In electrode) is improbable, meaning that an explanation of the curve in Fig. 2 cannot be based on such a barrier. The sample in our experiment should be treated more generally — as a complex electrochemical cell shown in Fig. 4.

Starting with the description of charge transport through such a cell, let us consider a simpler case (Fig. 4c) in which only β -phase is placed between two metallic contacts, one of which is silver. Let this contact be negative. The current densities of ions, j_i , and electrons, j_e , are then given by

$$j_i = \frac{\sigma_i}{e} \frac{d\eta_i}{dx}, \quad j_e = \frac{\sigma_e}{e} \frac{d\eta_e}{dx} \quad (3)$$

where σ_i and σ_e are ionic and electronic conductivities, respectively, and e is the charge of electron. For the electrochemical potentials η_i and η_e of the respective particles the following equations are valid:

$$\eta_i = \mu_i + e\varphi, \quad \eta_e = \mu_e - e\varphi \quad (4)$$

in which μ_i and μ_e are chemical potentials of ions and electrons, and φ is electrostatic potential. It is evident that the sum

$$\eta_i + \eta_e = \mu_i + \mu_e = \mu \quad (5)$$

represent the chemical potential μ of neutral silver atoms.

Current densities (3) are time dependent. Since the indium contact on the left cannot supply Ag atoms to the sample, ionic current should disappear in the

equilibrium: $j_t = 0$ and $d\mu_t/dx = 0$. Only the electronic current $j_e = \sigma_e (d\eta_e/dx)/e$ persists. Since equation (5) for this case gives $d\eta_e/dx = d\mu/dx$, we have finally

$$j_e = \frac{\sigma_e d\mu}{e dx} = \sigma_e \frac{dV}{dx}. \quad (6)$$

The derivative dV/dx represents the externally applied electrical field. Current density j_e obviously has two components. Besides electrons, the charge in $\beta\text{-Ag}_2\text{S}$ is also carried by the holes. If this material can be treated as a nondegenerate system, the concentrations of carriers (n of electrons and p of holes) are governed by the equation

$$d\mu_e = kT d \ln n = -d\mu_h = -kT d \ln p \quad (7)$$

in which μ_h is chemical potential of holes. Therefore, at an arbitrary coordinate x of the sample the concentrations of electrons and holes are:

$$n_x = n_o e^{\frac{\mu_x - \mu_o}{kT}}, \quad p_x = p_o e^{-\frac{\mu_x - \mu_o}{kT}}. \quad (8)$$

Or, using the voltage at the point x ,

$$n_x = n_o e^{-\frac{eV_x}{kT}}, \quad p_x = p_o e^{\frac{eV_x}{kT}}. \quad (9)$$

The concentrations of charge carriers are obviously strongly voltage dependent. The same is true for the partial conductivities so that total electronic conductivity σ may be written as

$$\sigma = \sigma_{eo} e^{-\frac{eV_x}{kT}} + \sigma_{ho} e^{\frac{eV_x}{kT}}. \quad (10)$$

The current density j_e and the total current I through the sample may then be obtained by the integration of equation (6) from $x = 0$ to $x = L$ (or from 0 to V):

$$I = \frac{kT S}{eL} [\sigma_{eo} (1 - e^{-\frac{eV}{kT}}) + \sigma_{ho} (e^{\frac{eV}{kT}} - 1)]. \quad (11)$$

Equation of this type was first derived by Wagner²¹. Let us repeat, it is obtained having in mind the simple cell shown in Fig. 4c. Thus, at coordinate $x = 0$, where the sample of $\beta\text{-Ag}_2\text{S}$ is in contact with silver, chemical potential μ is fixed at the value μ_o . All quantities with the subscript zero are therefore constant and independent of V .

4. Application to the complex cell

Equation (11) may be employed in the description of charge transport through a more complex cell (Fig. 4a and Fig. 4b), in which both phases of Ag_2S coexist, only under certain suppositions. They are, fortunately, simple and plausible.

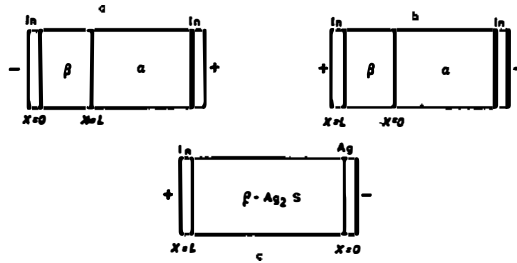


Fig. 4. Schemes defining the coordination system in the cell: forward biased cell (a), reverse biased cell (b), simple cell (c).

First of all, due to the fact that the conductivity of α -phase is more than two orders of magnitude higher than the conductivity of β -phase, almost the entire potential difference is concentrated on the β -phase layer. Even though this seemingly converts the complex cell into a simple one, the situations are not equivalent: the chemical potential μ at $x = 0$ and at $x = L$ in the complex cell is not fixed; it is floating. Strictly speaking, the integration (6) cannot be done since σ_{e0} and σ_{h0} are unknown functions of the applied voltage. However, let us show in the following that these quantities may nevertheless be taken as constants.

4.1. Forward biased cell

After the forward bias is switched on, the current in β -phase flows from the contact with α -phase to the In contact on the left. Initially all types of carriers migrate but if no silver is supplied from α -phase a depletion of Ag ions occurs near the contact of phases. Depletion in turn causes counter-oriented diffusion current, which in equilibrium just balances the drift current, and a stable concentration gradient of ions arises. Due to the electrical neutrality condition this gradient must be accompanied by an equivalent concentration gradient of electrons. In this situation the ionic current is completely suppressed while the electronic current continues to flow. Since our sample originally has a nearly stoichiometric composition, Ag_2S , the content of silver at $x = L$ should be somewhat smaller, i. e. $\text{Ag}_{2-\delta}\text{S}$, δ being³⁾ maximally $3.5 \cdot 10^{-5}$. Such a deficiency of silver, however, is not probable. Certain quantity of Ag, large enough to compensate for depletion, is always supplied from α -phase (which is a relatively large reservoir of silver) so that electron and hole conductivities at $x = L$ may surely be taken as not far from the conductivities of an undisturbed stoichiometric sample. According to Junod^{1,4)} these are $\sigma_{e0} = 54.8 \Omega^{-1} \text{m}^{-1}$ and $\sigma_{h0} = 16.3 \Omega^{-1} \text{m}^{-1}$ at 450 K. Using these constants and making the necessary transformation of (10) we obtain

$$\sigma = \sigma_{e0} e^{\frac{e(V-V_2)}{kT}} + \sigma_{h0} e^{-\frac{e(V-V_2)}{kT}} \quad (12)$$

so that the integration (6) gives

$$I = \frac{k T S}{eL} [\sigma_{eo} (e^{\frac{eV}{kT}} - 1) + \sigma_{ho} (1 - e^{\frac{eV}{kT}})]. \quad (13)$$

For very low voltages this equation reduces to a much simpler form,

$$I = \frac{S(\sigma_{eo} + \sigma_{ho})}{L} V \quad (14)$$

which may be compared with experimentally found dependence $I = AV$:

$$A = \frac{S(\sigma_{eo} + \sigma_{ho})}{L}. \quad (15)$$

If our approach is correct, this comparison should give a reasonable value for L — the thickness of the β -phase layer. Using $S = 1.26 \cdot 10^{-5} \text{ m}^2$, $(\sigma_{eo} + \sigma_{ho}) = 71.1 \Omega^{-1} \text{ m}^{-1}$ and $A = 0.19 \Omega^{-1}$ we obtain $L = 4.7 \text{ mm}$ (30% of the total length of the sample). This may be considered a reasonable value.

4.2. Reverse biased cell

After the reverse bias is switched on (Fig. 4b), similar events take place as in the forward biased cell. Depletion of silver now occurs near the In contact on the left and, since additional silver cannot be supplied from this side, stays uncompensated. Moreover, if one allows that a certain quantity of Ag is transported to α -phase, this depletion probably approaches its maximal value (i. e. $\delta = 2.5 \cdot 10^{-5}$). On the other side, at the contact with α -phase, the concentration of Ag may be considered practically unchanged, compared with an unbiased cell. Thus the current through the cell is given by equation (11) which, using (15), transforms into

$$I = \frac{k T A}{e(\sigma_{eo} + \sigma_{ho})} [\sigma_{eo} (1 - e^{-\frac{eV}{kT}}) + \sigma_{ho} (e^{\frac{eV}{kT}} - 1)]. \quad (16)$$

Mention should be made that equations (11), (13) and (16) are valid only within a limited range of voltages. They describe the current through a mixed conductor for the voltage lower than the so-called decomposition voltage of the respective compound. According to Hebb⁵⁾ the decomposition voltage of $\beta\text{-Ag}_2\text{S}$ (placed between two inert, Pt, contacts) is near to 0.2 V. At this voltage the depletion of silver, and therefore the excess of sulphur, becomes so large that the existence limit of Ag_2S is surpassed; sulphur is deposited at the negative electrode, i. e. electrolysis of the compound takes place. Total voltage E of the source is then divided: 0.2 V falls off at the Ag_2S layer, the rest at the S layer. Current-voltage

characteristic should therefore reflect the two regimes: first ($E < 0.2$ V), for which equation (16) is valid and second ($E > 0.2$ V), suited by a more complicated equation.

No signs of the two regimes were observed in our experiment. The measured current increases monotonously with voltage, apparently from $V = 0$. Besides, in the entire voltage range the currents are much smaller than those predicted by (16). This suggests that the decomposition was present in our experiment also. Free sulphur, however, can hardly play a role since it readily evaporates at 450 K. Another reaction seems more probable: sulphide, which is maximally depleted in silver with the reversely applied voltage, starts to react with indium contact. In other words, the reaction $2 \text{In} + 3 \text{Ag}_{2-\delta} \text{S} \rightarrow 3(2-\delta) \text{Ag} + \text{In}_2 \text{S}_3$ takes place, leading to a layer of highly resistive $\text{In}_2 \text{S}_3$ (energy gap > 2 eV)⁶. As in many other similar cases ($\text{Al}_2 \text{O}_3$, obtained by electrolytic oxidation is a typical example), the layer behaves as a barrier which passes current if In contact is negative (its resistance then is a contribution to the constant A) and blocks it if In contact is positive. In fact, by the reaction mentioned above an electrolytic rectifier is formed. A number of authors (for the references see Kroeger⁷) found that the following equation is then valid:

$$I = D \left(e^{\frac{FV}{d}} - 1 \right) \quad (17)$$

i. e. the current in the reverse direction is an exponential function of the applied field $V/d(V)$ (d is the layer thickness). Two constants, D and F , are related to the structure of the growing layer. If $\text{In}_2 \text{S}_3$ may be treated as an electronic conductor (no ionic conductivity), $d(V)$ is practically independent of voltage making equation (17) similar to experimentally proved equation (2).

5. Summary

Summarising the results of this work we can state that the unusual current-voltage characteristic of the two-phase sample of silver sulphide does not follow from the semiconducting properties of $\beta\text{-Ag}_2\text{S}$. A previous attempt in this direction failed due to the ignorance of the ionic properties of Ag_2S . Our approach — based mainly on the experimental observation that the equilibrium at each point of the characteristic is reached only after a relatively long time, which is a sign that mobile ions are involved in the process — gives at least a qualitative description of the characteristic. Quantitative interpretation of events in the reverse biased cell, however, is evidently hindered by the incomplete knowledge of the $\text{In-Ag}_2\text{S}$ tarnishing reaction (the constants D and F are unknown).

Acknowledgments

The authors are grateful for the helpful discussion of the subject to their colleagues Z. Vučić, V. Horvatić, O. Milat, M. Horvatić and M. Ilić.

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STRUJNO-NAPONSKA KARAKTERISTIKA SUPERIONSKOG Ag_2S U
UVJETIMA KOEGZISTIRAJUĆIH FAZA

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Originalni znanstveni rad

Izmjerena je strujno-naponska karakteristika dvofaznih uzoraka srebro sulfida s indijevim kontaktom, a rezultati su objašnjeni pomoću Wagnerove teorije miješane, ionsko-elektronske vodljivosti. Električno polje propusnog smjera uzrokuje stvaranje blagih koncentracijskih gradijenata iona i elektrona u uzorku, što kod niskih napona vodi na linearnu i strmju karakteristiku. U zaprečno polariziranoj ćeliji, međutim, zbivanja su znatno kompliciranija. Dolazi vjerojatno do parcijalne dekompozicije uzorka i do formiranja visokootpornog sloja indij sulfida. Karakteristika je tada eksponencijalna, ali se ne može pripisati samo jednom jedinom procesu.