ELECTRICAL PROPERTIES OF CdO AT HIGH TEMPERATURES

By Z. M. Jarzębski, B. Muszyńska and J. Obłąkowski

Institute of Material Engineering, Academy of Mining and Metallurgy, Cracow*

(Received November 12, 1971; Revised paper received March 11, 1972)

The electrical conductivity σ of CdO has been measured in the temperature range 970 K — 1270 K in conditions of thermodynamic equilibrium between the investigated samples and ambient oxygen in the air under atmospheric pressure. The linear dependence of $\log \sigma$ *vs* $1/T$ has been observed. From these data and Hall effect measurements at room temperature, the high temperature Hall mobility has been obtained. A good agreement has been found between the values of mobility obtained by this method and the conventional one. An analysis of experimental data of electrical properties of ceramic CdO and single crystals of this oxide was also given.

1. Introduction

Cadmium oxide has a cubic structure of NaCl type. The lattice parameter of this oxide amounts to 4.69 Å. In principle it is a ionic compound showing however about 20% of covalent bonding [1]. The energy gap of this oxide is found to be about 2.3 eV [2, 3]. Nevertheless CdO shows high, almost metallic, electronic conductivity at low and intermediate temperatures. It is generally assumed that this property is due to deviation from the stoichiometric composition — native atomic defects, which are donors.

Several works on non-stoichiometry in CdO have been published. They are reviewed in paper [4]. However it is not known till now what is the nature of predominating defects: Cd interstitials or oxygen vacancies. Haul and Just [5] deduced from oxygen tracer diffusion measurements that oxygen vacancies are present in CdO. On the other hand Cimino and Marezio [6] concluded from lattice parameter measurements on pure and doped cadmium oxide that interstitial Cd atoms or ions predominate in this compound. The same conclusion has been drawn recently by Koffyberg [7] on the base of defect diffusion measurements in the oxide considered here. The concentrations of the defects, obtained by different authors mentioned above, are almost the same (an order of magnitude of 10^{19} cm^{-3}) despite of completely different suggestions of defect structure. Similar concentrations of excess cadmium atoms in CdO have been obtained by Faivre [8] on the basis of chemical analysis, and by Engell [9] from electrochemical analysis.

The Hall effect measurements at room temperature, carried out in CdO samples

* Address: Instytut Inżynierii Materiałowej, Akademia Górniczo-Hutnicza, Kraków, Al. Mickiewicza 30, Poland.

rapidly cooled from various temperatures of heat treatment, have shown that the conduction electron concentration n in this oxide may change from 3.3×10^{18} to about 10^{20} cm^{-3} [10–13]. In the case of cadmium oxide the values of charge carrier concentrations obtained from Hall effect measurements agree thus approximately with the values of defect concentrations gained by different methods. It has been found also that n is a function of oxygen pressure [13] and temperature of heat treatment [10–13].

From the Mott criterion [14, 15] Benedict and Look [12] have shown that the donor wave functions in CdO are localized for $n < 2 \times 10^{18}$ cm^{-3}. Cadmium oxide with such concentrations of conduction electrons can be classified as a typical semiconductor. However it is difficult to obtained this oxide with the charge carrier concentrations lower than about 3.3×10^{18} cm^{-3} [10–12]. For $2 \times 10^{18} < n < 10^{19}$ cm^{-3} the donor wave functions form the impurity band and the quasi-free electrons can move in this band. CdO with above given region of n may be considered as a quasi-metal [12]. Finally, for $n > 10^{19}$ cm^{-3}, the Fermi level is in the host-lattice conduction band. Cadmium oxide with such high concentrations of n can be classified as a metal [12, 16]. Koffyberg [17, 18] states that the conduction band in CdO deviates significantly from a parabolic shape because of large defect concentration.

Electrical transport phenomena in this oxide were investigated by many authors since about 1900. The earlier investigations have been reviewed in the work [19]. At first it was assumed that at low and intermediate temperatures charge carriers in CdO were scattered mainly by longitudinal optical phonons [20–22] and on attempt was made to explain the mechanism of conduction in this oxide with the theory of Howarth and Sondheimer [23]. However subsequent works have shown that at room temperature the conduction electrons in CdO are scattered mainly by ionized donors [11, 13, 24]. Koffyberg [18] has recently measured the Hall effect and conductivity in CdO single crystals in a wide region of temperatures 81–1100 K. The results obtained by this author at low temperatures have supported the conclusion mentioned above, whereas at temperatures higher than about 700 K the mobility appears to be limited by optical phonon scattering.

Thus for satisfactory elucidation of scattering mechanism of conduction electrons in CdO it is necessary to carry out further investigations of temperature dependence of mobility in this compound, especially at high temperatures. However, Hall effect experiments at these temperatures are very difficult for technical reasons. Furthermore in the case of materials with high concentrations of charge carriers (as CdO) these difficulties are increased because of very small Hall voltages. Therefore the purpose of this work was to show a simpler method of estimation of high temperature Hall mobility in CdO on the basis of measurements of electrical conductivity at these temperatures and Hall effect at room temperature.

2. The method of estimation of high temperature Hall mobility

Investigations of electrical properties of CdO [12, 13, 18, 19, 25] show that for $n > 10^{19}$ cm^{-3}, all donors (native atomic defects and foreign impurities) in this oxide are fully ionized even at low temperatures (*cf.* introduction). This fact enables an estimation

of Hall mobility to be given in CdO at high temperatures from measurements of electrical conductivity σ at these temperatures and data of Hall effect obtained at low temperatures *e.g.* at room temperature). This is possible provided that concentrations of atomic defects (donors) in investigated samples are the same at high and low temperatures. The above mentioned condition may be fulfilled only when the applied cooling rate of the samples from high to low temperatures, is rapid enough to freeze approximately all native atomic defects in crystal lattice.

It is conveniently to measure the electrical conductivity in the state of thermodynamic equilibrium between the oxide and ambient oxygen, and determine the Hall coefficient in the samples which have been rapidly cooled from this state. In such a case the defect concentration is fully determined by the temperature of heat treatment and partial oxygen pressure, and does not depend on the so-called history of the material [26]. Therefore in this way one can measure also the conductivity in one series of samples and Hall effect in the other.

One can expect also that it should be possible to estimate the Hall mobility by the proposed method when conductivity is measured in the state of non-equilibrium between oxide and ambient oxygen. However in this case the samples should be cooled from high temperature, immediately after measuring their electrical conductivity. Furthermore the conductivity should be measured during a very short time and the Hall effect must be determined in the same samples in which values of σ have been obtained. In the present paper the first manner of determining mobility is used.

3. Experimental procedure and results

Sintered CdO samples were prepared in the manner described in papers [24] and [27]. Electrical conductivity was measured with direct current by the conventional method of two potential probes and two current electrodes. A stabilized transistor power supply was used as the current source and the voltage was measured with a high precision electrometer. The electrodes and potential probes, made of 0.2 mm platinum wires, were wrapped around the sample, similarly as described in paper [28]. Small notches were made on sample to improved the electrical contacts. The mentioned-above four platinum wires were insulated with alundum tubes. The sample, suspended on these wires, was placed in an larger alundum tube in a vertical, cylindrical furnace. The furnace temperature was regulated by a thermoregulator with an accuracy of ± 5 deg. by means of a Pt-PtRh thermocouple placed close to the sample. The electrical conductivity was measured within the temperature range 970–1270 K in ambient air under atmospheric pressure (partial oxygen pressure was approximately 0.2 atm).

The samples of CdO were heated at several constant temperatures and isothermal electrical conductivity at a given temperature was measured as a function of time of heat treatment until changes of σ during several hours, were smaller than measuring error. The last data of σ have been accepted as the values of electrical conductivity of CdO being in thermodynamic equilibrium with ambient oxygen in the air. The overall time of heating CdO at a given temperature was approximately the same (about 12 hours) as in paper

[24], in which the Hall coefficient data were published. A good proof of the establishment of equilibrium between the investigated samples and the surrounding gaseous atmosphere, within the temperature range applied, was obtained by taking measurements at decreasing and increasing temperature of heat treatment. In both cases the same values of conductivity were obtained at the same temperature of heat treatment.

The logarithm of CdO conductivity *versus* reciprocal temperature is given in Fig. 1. As can be seen from this Figure the equilibrium conductivity at partial oxygen pressure

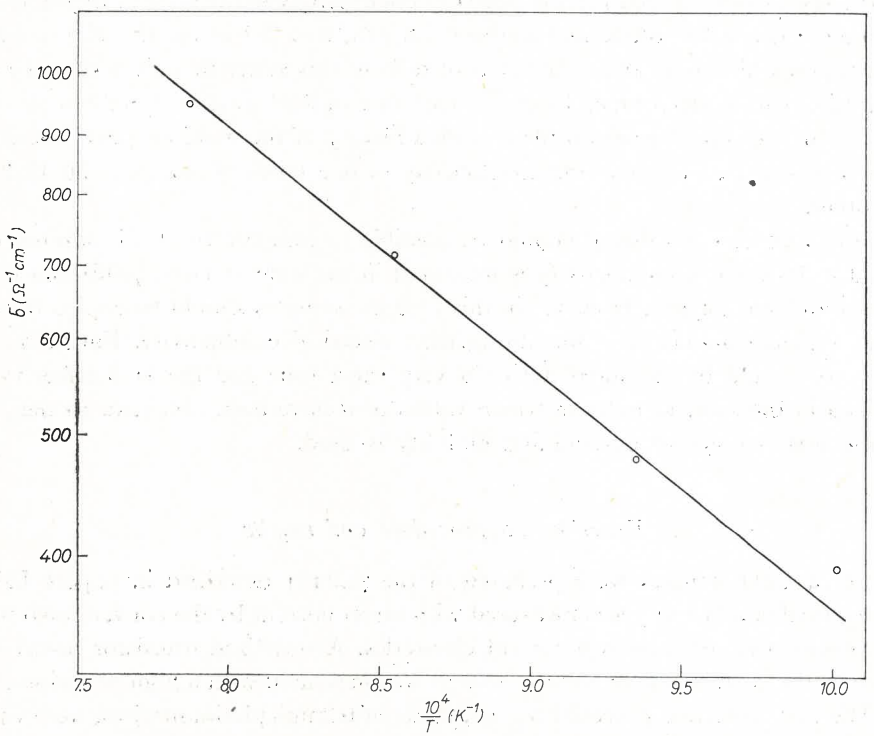

Fig. 1. Logarithm of the electrical conductivity of CdO as a function of reciprocal temperature of heat treatment in the state of thermodynamic equilibrium between the samples and ambient oxygen in the air under atmospheric pressure P_{O_2} (= 0.2 atm)

in the air, varies from the value of 390 ohm^{-1} cm^{-1} at temperature 970 K to 945 K ohm^{-1} cm^{-1} at 1270 K and approximately fulfils the linear dependence of $\log \sigma$ *versus* $1/T$.

The investigations of the Hall effect in degenerate CdO at room temperature as a function of temperature of heat treatment in which the samples were at equilibrium, were published in three papers [11, 13, 24]. The samples were rapidly cooled from high to room temperature. The compiled data of charge carrier concentrations are shown in Fig. 2. Curves *1* and *2* concern the ceramic samples which were at equilibrium with oxygen in the air under atmospheric pressure. Curves *3* and *4* concern single crystals of the oxide considered here. The first one shows the temperature dependence of n in the samples which were at equilibrium with oxygen under pressure of 0.135 atm, the second — under

oxygen pressure of 1 atm. The authors of the cited works believed that the obtained values of n at room temperature are approximately the same as those at high temperatures.

For the estimation of high temperature Hall mobility in CdO the values of n given in paper [24] were taken (curve *1*), because the present measurements of electrical con-

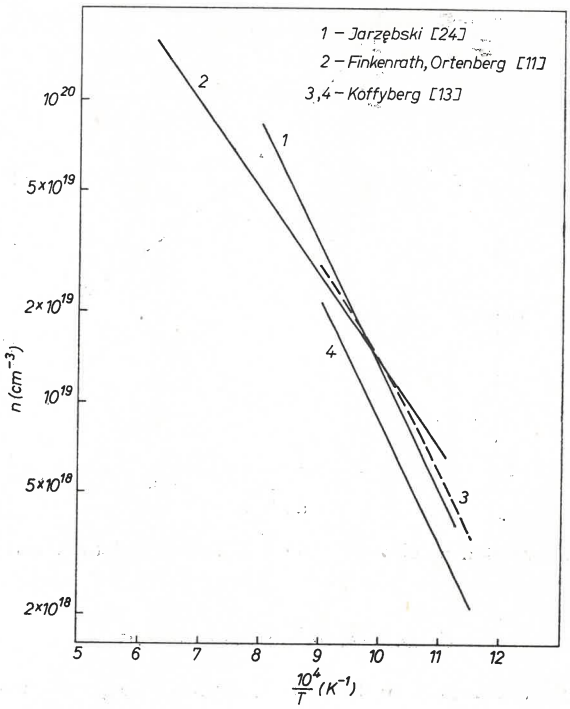

Fig. 2. Logarithm of the concentration of conduction electrons in CdO at room temperature as a function of inverse temperature of heat treatment according to different authors: *1*, *2* — ceramic samples which were at equilibrium with air ($P_{O_2} = 0.2$ atm), *3* — single crystal which was at equilibrium with oxygen under the pressure of 0.135 atm, *4* — single crystal which was at equilibrium with oxygen under the pressure of 1 atm

ductivity were carried out in ceramic samples of CdO, being at equilibrium in the same conditions as those in previous measurements of the Hall effect. Furthermore the above mentioned measurements of the Hall effect and conductivity have been carried out also on the same samples.

The Hall mobility u in CdO, calculated in the way described above, changes from 190 cm^2/Vs at temperature 970 K to 59 cm^2/Vs at 1270 K.

The obtained values of mobility are plotted in Fig. 3 in the same coordinate system as that in the work of Koffyberg [18]. This coordinate system was chosen in order to facilitate the comparison of the results of the above author and ours. It should be noted that the value of mobility at 1270 K is found from an extrapolated value of n as the measurements of Hall effect were carried out only to heat treatment temperature of 1200 K.

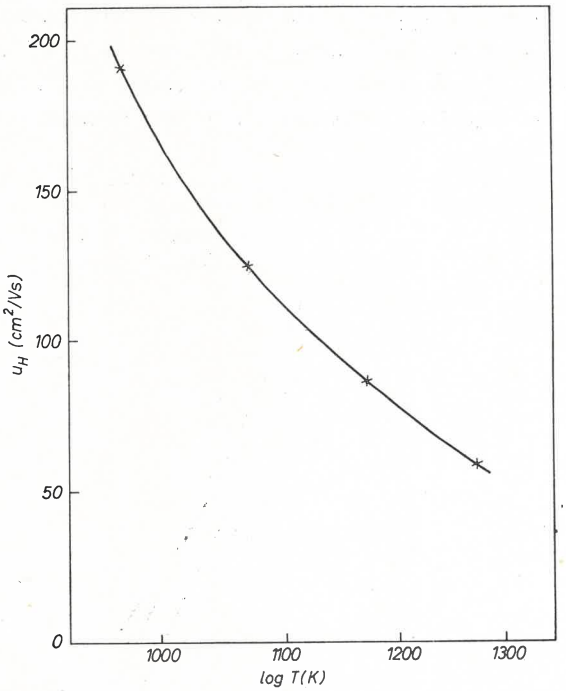

Fig. 3. High temperature Hall mobility in CdO as a function of the logarithm of temperature

4. Discussion and conclusions

As the present calculations of mobility in CdO have been based on the measurements of conductivity and Hall effect in ceramic samples, it should be pointed out that the above-mentioned properties have not been influenced considerably by potential barriers on grain-boundaries.

It was shown in paper [27] that after heating the pressed CdO specimens for 12 hours at temperatures higher than about 1000 K, the samples are completely sintered. These samples look almost like metal. As can be seen in Fig. 2 an activation energy E of conduction electrons in such ceramic samples of cadmium oxide (curve *1*) — calculated according to formula: $n \sim \exp(-E/kT)$ — is almost the same as in single crystals of this compound (curve *4*): 0.75 eV *versus* 0.79 eV. The slight displacement of these curves may be due to different partial oxygen pressures at which the samples were at equilibrium: about 0.2 atm in the case of ceramic CdO *versus* 1 atm for single crystals. Furthermore the values of n given by curve *1* are nearly the same as the values given by curve *3* corresponding to single crystals being at equilibrium under partial oxygen pressure of 0.135 atm.

As can be seen in Fig. 4 the dependence of mobility in CdO on charge carrier concentration at room temperature obtained both in single crystals and ceramic samples (curves *2* and *3*) are also very similar. Thus it seems that in the case of ceramic samples of CdO, sintered for 12 hours at temperatures higher than about 1000 K, both Hall effect

and Hall mobility are not influenced visibly by potential barriers on grain-boundaries. It should be noted that our samples of CdO were sintered at temperatures much higher than 1000 K.

As it was mentioned already, our calculations of mobility are valid only when the concentration of atomic defects in investigated samples at high temperatures (in which the thermodynamic equilibrium is obtained) is at least approximately equal to the one

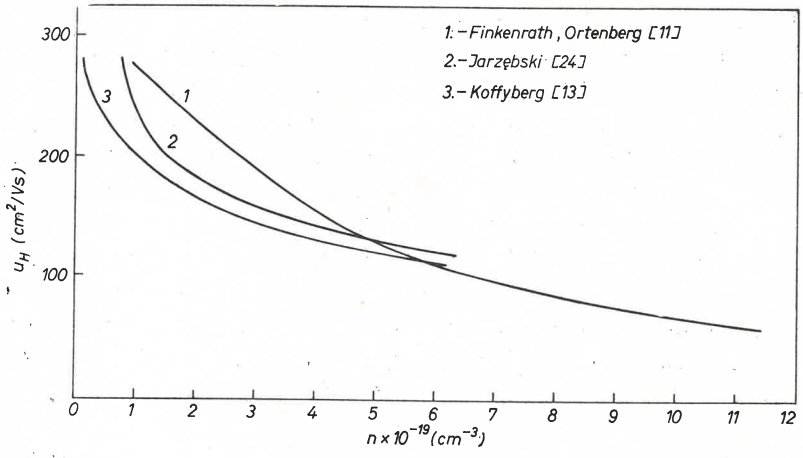

Fig. 4. Hall mobility in CdO at room temperature as a function of carrier concentration according to different authors: *1*, *2* — ceramic samples, *3* — single crystals

at room temperature. Unfortunately, the measurements of the Hall effect in CdO have not been carried out till now in equilibrium conditions. Therefore there is only one way of verifying of the above-mentioned assumption, namely by confrontation of our results with those obtained by Koffyberg [18] (see his Fig. 2).

Koffyberg has shown that at temperatures higher than about 700 K the conduction electrons in CdO are scattered mainly by optical phonons. However it can be seen in his Fig. 2 that at these temperatures the Hall mobility in cadmium oxide decreases not only with increase of temperature but also with increase of concentration of conduction electrons. Generally u_H, as found by the cited author, changes from about 125 cm²/Vs at 970 K to about 85 cm²/Vs at 1100 K. In the same time the carrier concentration varies from 0.65×10^{19} to 6.3×10^{19} cm^{-3}.

As can be seen in Fig. 3 the Hall mobility of CdO, calculated in this work, changes from 190 cm²/Vs at 970 K to about 110 cm²/Vs at 1100 K and 59 cm²/Vs at 1270 K. In the same time the carrier concentration changes from 1.3×10^{19} cm^{-3} at 970 K to $3.2 \times$ $\times 10^{19}$ cm^{-3} at 1100 K and about 10^{20} cm^{-3} at 1270 K.

The above-given data indicate that the function $u_H(T)$ in CdO, obtained in the present work, decreases more rapidly with increasing temperature than that found by Koffyberg. This difference may be explained by the fact that our values of Hall mobility have been calculated for CdO samples, in which the carrier concentration increased with temperature of heat treatment, while the cited author measured u_H at constant concentrations of con-

duction electrons. In particular, for 1100 K our value of u_H is 110 cm^2/Vs for $n = 3.2 \times 10^{19}$ cm^{-3}, and Koffyberg's value is $u_H = 90$ cm^2/Vs for $n = 2.7 \times 10^{19}$ cm^{-3}.

Thus the values of high temperature Hall mobility of CdO presented in this paper are in good agreement with those found by Koffyberg. This fact gives evidence for the validity of the proposed method of calculation of Hall mobility in CdO at high temperatures.

It is difficult however to give an exact theoretical description of our results because of the complexity of the problem. Koffyberg [18] has shown that the high temperature Hall mobility in CdO can be explained by the theory of Howarth and Sondheimer [23], but only in the case of less defective samples (n equals 0.37×10^{19} and 0.65×10^{19} cm^{-3}). If other types of scattering do not take place in the oxide considered here, then the theoretical description of $u_H(T)$, assuming optical phonon scattering in CdO with higher concentration of conduction electrons, could be obtained probably by including the corrections for the screening of the effective ionic charges by charge carriers [29].

On the base of considerations presented in this work one can draw the following conclusions:

1. The high temperature Hall mobility in CdO can be obtained by a simple method based on measurements of conductivity at high tempeatures and Hall effect at low temperatures. One can expect also that this method may be applied to other degenerated materials.

2. The conduction electrons in CdO at high temperatures are probably scattered mainly by optical phonons, but the conduction mechanism in this oxide is very complex.

3. The electrical properties of ceramic CdO sintered for 12 hours at temperatures higher than about 1000 K are very similar to those of single crystals of this compound.

REFERENCES

[1] J. C. Philips, J. A. Van Vechten, *Phys. Rev. Letters*, **22**, 705 (1969).
[2] K. Maschke, U. Rössler, *Phys. Status Solidi*, **28**, 577 (1968).
[3] M. Altwein, *Phys. Status Solidi*, **29**, 203 (1968).
[4] Z. M. Jarzębski, *Wiad. Chem.*, **22**, 45 (1968), in Polish.
[5] R. Haul, D. Just, *J. Appl. Phys. Suppl.*, **33**, 487 (1962).
[6] A. Cimino, M. Marezio, *J. Phys. Chem. Solids*, **17**, 57 (1960).
[7] F. P. Koffyberg, *Solid State Commun.*, **9**, 2187 (1971).
[8] R. Faivre, *Ann. Chim.*, **19**, 58 (1944).
[9] H. J. Engell, *Z. Elektrochem.*, **60**, 905 (1956).
[10] Z. M. Jarzębski, *Acta Phys. Polon.*, **29**, 37 (1966).
[11] H. Finkenrath, M. von Ortenberg, *Z. Angew. Phys.*, **22**, 279 (1967).
[12] R. P. Benedict, D. C. Look, *Phys. Rev.*, B **2**, 4949 (1970).
[13] F. P. Koffyberg, *J. Solid State Chem.*, **2**, 176 (1970).
[14] N. F. Mott, W. D. Twose, *Advances in Phys.*, **10**, 107 (1961).
[15] N. F. Mott, *Advances in Phys.*, **16**, 59 (1967).
[16] D. C. Look, *Phys. Rev.*, **184**, 705 (1969).
[17] F. P. Koffyberg, *Phys. Letters*, A **30**, 37 (1969).
[18] F. P. Koffyberg, *Canad. J. Phys.*, **49**, 435 (1971).

[19] Z. M. Jarzębski, *Wiad. Chem.*, **21**, 581 (1967), in Polish.
[20] J. A. Bastin, R. W. Wright, *Proc. Phys. Soc.*, A **68**, 241 (1955).
[21] R. W. Wright, J. A. Bastin, *Proc. Phys. Soc.*, **71**, 109 (1958).
[22] I. M. Cidilkovskii, *Thesis*, Fiziko-tekhnicheskii institut AN SSSR, 1959, *Abstracts Intern. Conf. on Semiconductor Physics*, Prague 1960, p. 96.
[23] D. Howarth, E. Sondheimer, *Proc. Roy. Soc.*, A **219**, 53 (1953).
[24] Z. M. Jarzębski, *Bull. Acad. Polon. Sci., Sér. Sci. Chim.*, **17**, 221 (1969).
[25] C. Kǒnǎk, P. Höschl, J. Dillinger, V. Prosser, *Proceedings of an International Conference on Crystal Growth*, Boston 1966, p. 20, *Suppl.* to *J. Phys. Chem. Solids*, 1967.
[26] Z. M. Jarzębski, S. Mrowec, *Półprzewodniki tlenkowe*, WNT, Warszawa 1969, in Polish.
[27] Z. M. Jarzębski, *Bull. Acad. Polon. Sci., Sér. Sci. Chim.*, **17**, 215 (1969).
[28] M. L. Volpe, J. Reddy, *J. Chem. Phys.*, **53**, 1117 (1970).
[29] H. Ehrenreich, *J. Phys. Chem. Solids*, **8**, 130 (1959).