HALL COEFFICIENT AND CONDUCTIVITY MEASUREMENTS OF CADMIUM OXIDE IN TERMS OF SINTERING TEMPERATURE

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In order to explain the divergences in the results obtained by various authors, and to find out the dependence of concentration of atomic defects on the sintering temperature, the Hall coefficient and the conductivity compressed and sintered samples of CdO were measured in room temperature. The samples have been sintered in the air of various temperatures and then rapidly cooled up to room temperature. A marked dependence of electron concentration upon the sintering temperature above 550°K has been observed. This complex dependence has been attributed to processes of oxydation and reduction taking place on the crystallites surface and changing the concentration of atomic defects inside the crystallites.

1. Introduction

The basic semiconductive properties of CdO are little known, owing mainly to the fact that till now no well developped single crystals have been obtained. The researches which have been carried out till now, have made with sintered samples and thin films. They concerned mostly transport phenomena, especially electrical conductivity, Hall effect and thermoelectric power. Cadmium oxide has a cubic structure of NaCl type (Davey and Hoffman 1920, Scherrer 1922). From optical measurements it can be assumed that the energy gap amounts to 2.5 eV (International Tables of Constants and Numerical Data 1961). The high electrical conductivity of CdO is due to non-stoichiometric excesses of one of the components of the crystal latttice. It is generally supposed that the excess cadmium atoms, placed in interstitial positions or oxygen vacancies are the donors (Bastin and Wright 1958 b, Haul and Just 1962). The results of researches of Haul and Just (1962) concerning oxygen diffusion in CdO lattices indicate that the oxygen vacancies are rather donors. The Effective electron mass is of the order of 0.1 m_0 (Wright and Bastin 1958a).

The electrical properties of CdO samples depend mainly on the kind of their preparation. According to the temperature and time of sintering, to subsequent heat treatment, at the temperature measurement, *etc.*, a degenerated or non-degenerated material has been obtained.

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But the results of the investigations were often contradictory, *e.g.* von Baumbach and Wagner (1933) have confirmed that the electron concentration depends only on oxygen pressure, Blackmore (1951) has obtained non-degenerated samples in cases of light sintering, Hogarth (1951), instead, confirmed non- degeneracy in higher temperatures and degeneracy in lower temperatures. Bastin and Wright (Wright 1951, 1953 Bastin and Wright 1955, 1958a) have always obtained fully degenerated samples. Furthermore, they did not find any distinct relation between sintering temperature (in the range from 600°K to 1200°K) and sintering time (in intervals of 0.5 to 180 hours) and electron concentration in room temperature, although in their measurements this concentration changed for samples sintered in different conditions from 2×10^{18} cm^{-3} to 3.7×10^{19} cm^{-3} (1958b). Depending on purity and manner of preparation of the samples different investigators have obtained electron concentrations rating from 10^{18} cm^{-3} to 10^{21} cm^{-3} (Milosławskii and Ranyuk 1960; Lakshmanan 1963).

The purpose of the present work has been to explain the divergences obtained by different authors, and to find out the relation between rthe concentration of atomic defects and the sintering temperature. Hall coefficient measurements are most suitable for this purpose, because this coefficient is a good measure of carrier concentration inside the crystallites, at least for samples formed of crystallites with high electron concentration, separated by narrow spaces of low conductivity. (Volger 1950).

2. Preparation of the samples

The material in form of CdO powder containing at most 10^{-3}% Zn, 10^{-4} % Pb, and Na, Mg and Cu in still lesser quantities, ground in an agat grinder during 4 hours and then compressed under about 6000 atm into the shape of rectangular samples of 2.5 cm × 1 cm × × 0.15 cm. The samples have been sintered at fixed temperatures in the range of 515°K to 1100°K during 5 hours. In each temperature two series have been sintered, 5 samples in each series. The sintering was taking place in air, it ist under a constant oxygen pressure. After sintering the samples were cooled on a big metal block, immediately after being taken out of furnace. Owing to the fact that the heat conductivity of CdO is comparatively great, the samples were getting room temperature quickly enough.

3. The measurement method

The Hall voltage was measured by a compensation method, passing through the sample a direct current of 0.5 amp. Only with samples not sintered a lesser current intensity was used. The magnetic induction was 17.6×10^3 gauss. The electrical conductivity was measured by the aid of potential probes.

The influence of sintering temperature on electron concentration and the conductivity at room temperature was investigated; hence all the measurements were carried through at this temperature. Bastin and Wright (1958a) had stated that over wide ranges of temperature up to 550°K the electron concentration in CdO does not depend on the temperature. Their investigations confirm the satisfactory agreement of the Hall coefficient with the

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theoretical expression, derived by Lewis and Sondheimer (1955). The expression may by put in the formula

$$R = \frac{r_n}{ne},$$

where r_n is a very complicated function of temperature and degeneration. Lewis and Sondheimer have proved that, in case of degeneration of the electron gas in ionic crystals, r_n equals approximately 1, and the error does not exceed 15%. Therefore the values of electron concentration n are calculated from this simple relation, assuming $r_n = 1$.

4. Results of the investigation

The results of the measurements show a very distinct dependence of the electron concentration at room temperature on the sintering temperature above 550°K. This dependence is shown in the graphic.

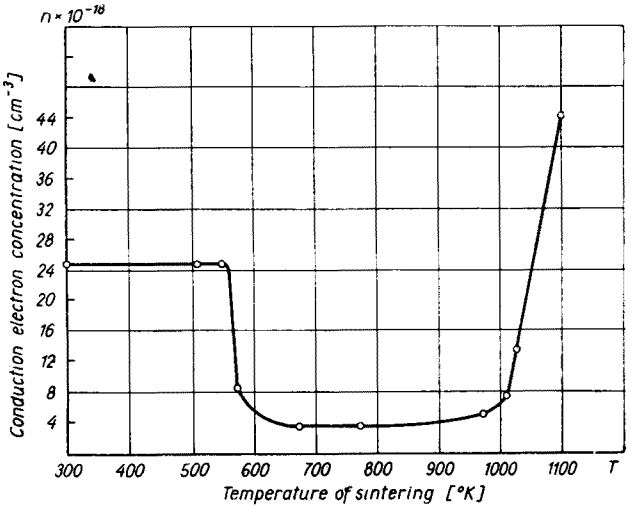

Fig. 1. Concentration of conductivity electrons *versus* sintering temperature

It is evident that in the range of 295°K to 550°K the electron concentration does no depend on the temperature of heating, and amounts to 2.5×10^{19} cm^{-3}. At the sintering temperature of about 550°K the concentration decreases rapidly down to about 4×10^{18} cm^{-3}. Bastin and Wright have observed (1958b) a certain instability of concentration at this temperature. In the range of sintering temperatures of about 550°K to 975°K the electron concentration is again nearly constant. The minimum concentration 3.5×10^{18} cm^{-3} corresponds to the sintering temperature of about 775°K. In the vicinity of the sintering temperature of 975°K a rapid rise of concentration takes place, connected with a colour change brown to black and a considerable increasing of conductivity, A similar increase of conductivity was observed also by Wright (1951) in the sintering temperature range of 975°K to 1075°K.

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The comparison of the results obtained from the measurement of the Hall coefficient and of conductivity points to the fact that in the range of sintering temperatures from 515°K to 975°K the increase of conductivity is connected mainly with the decrease of resistance of the contact surfaces between the crystallites, while above the sintering temperature of 975°K, it is due above all, to an increase in the electron concentration. A more accurate analysis of electrical conductivity dependence upon the sintering temperature seems to be risky, especially for samples sintered at lower temperatures, because of the great influence of the contact surfaces between the crystallites on the conductivity.

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5. *Conclusions*

If we assume that atomic defects (cadmium interstitials or oxygen vacancies) are completely ionized ,then the electron concentration in the conduction band will be proportional to concentration in the conduction band will be proportional to concentration of these defects. The invariability of carrier concentration in the range of the heating temperatures up till 550°K may be explained by the assumption that the mobility of the defects is very small in this temperature range. We may thus admit that these carriers are effectively frozen in the lattice. A similar view was put forward by Bastin and Wright (1958b). The electron concentration dependence upon the sintering temperature above 550°K may be explained by the following processes occuring on the surfaces of the crastallites:

$$\mathrm{Cd}_{\bigcirc}\cdot + \ominus + \frac{1}{2}\,\mathrm{O_2\,gas} \rightleftarrows \mathrm{CdO}$$

$$\mathrm{Cd}_{\bigcirc}\cdot\cdot + 2\ominus + \frac{1}{2}\,\mathrm{O_2\,gas} \rightleftarrows \mathrm{CdO} \qquad (1)$$

when the lattice is defective cationally, or

$$\mathrm{O}_{\bigcirc}\cdot + \ominus + \frac{1}{2}\,\mathrm{O_2\,gas} \rightleftarrows \mathrm{zero}$$

$$\mathrm{O}_{\square}\cdot\cdot + 2\ominus + \frac{1}{2}\,\mathrm{O_2\,gas} \rightleftarrows \mathrm{zero} \qquad (2)$$

if the lattice is defective anionally.

$\mathrm{Cd}_{\bigcirc}\cdot$, $\mathrm{Cd}_{\bigcirc}\cdot\cdot$ — means single and double ionized interstitial admium atoms,

$\mathrm{O}_{\square}\cdot$, $\mathrm{O}_{\square}\cdot\cdot$ — means single and double positive oxygen vacancies relative to the lattice

zero — non-defective lattice of CdO

$\ominus$ — electron passing into the conduction band.

One is allowed to suppose that in the range of sintering temperatures from 550°K to about 975°K the atomic defects diffuse to the surface of the crystallites, where the process to the right, presented by formulas (1) or (2), takes place the result being a fall in the defect concentration in the crystallites. Anove the sintering temperature of about 975°K the reverse process dominates. Then, on the surface of the crystalites a great amount of atomic defects

arises, which diffuse afterwards into the crystallites and cause an increase of the electron concentration.

The diversity of the results obtained by different investigator may be explained by complex dependence of the defect concentration and consequently of the electron concentration on the temperature, time of sintering, and oxygen pressure. The dependence of the electrical properties on oxygen pressure (von Baumbach and Wagner 1933, Lamb and Tompkins 1962) and the cooling speed near to 550°K (Bastin and Wright 1958 a, b) has been experimentally ascertained.

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