Discharge of ions and space charge formation in CdF_2 crystals with different kinds of electrodes

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Résumé. — Les échantillons de CdF_2 munis des différentes sortes d'électrodes et d'isolations sont examinés. On a généralement observé qu'à la suite d'une injection d'électrons, des particules métalliques se forment au-dessous de la surface. Celles-ci constituent une sorte « d'électrode réversible dendritique ». Là et/ou à la cathode externe les cations sont déchargés par ségrégation. Les deux maxima TSC de formation de charge spatiale connus sont mis en rapport respectivement au blocage des électrodes externes et à l'injection d'électrons. On montre que des indications d'une situation identique apparaissent dans les halogénures alcalins.

Abstract. — CdF_2 samples provided with different kinds of electrodes and insulations are investigated. It is found that, due to an electron injection which cannot be avoided, metal particles are formed below the surface which act as a kind of « reversible dendritic electrode »; that the cations are discharged by segregation there and/or at the external cathode; that the two known space-charge formation TSC-peaks are related to the blocking of the external electrode and to an electron injection resp. It is finally shown that there are indications of a similar situation in alkali halides.

1. Introduction. — CdF_2 is an electrolytic conductor [1] and by passing a current through it a surplus of Cd^{2+} and of F^- resp. is built up at the electrodes, forming there a space charge (cf. [2]). As a steady current can be sustained a discharge of these ions must take place. There exists a good deal of knowledge concerning the discharge at electrodes [3] as far as fundamental, i.e. simple *ideal* situations are concerned. This, however, does not help very much to understand the role different kinds of electrodes play. The crystal-electrode systems usually are not simple. They are complicated by the constitution of the electrode and crystal surfaces, their mutual distance, the presence of foreign material between them etc. The discharge could realize, according to circumstances in two different ways. By segregation of the ions at the electrodes or by a transfer of electrons to and from the crystal and a formation of neutral cadmium and/or fluor. Following, observations shall be described, which show how these processes contribute to the actual discharge. It is shown, too, that in other ionic compounds there occur similar processes. Finally, a correlation is between certain TSC-peaks ⁽¹⁾, the accumulation of defects at the surface and the electron injection. This opens new possibilities of investigation of electrode processes.

2. Evidence for a discharge by segregation at the electrodes. — Samples with sputtered Au-electrodes were exposed at 450 °C for various periods of time to a current (I). It was found that after a certain

exposure the cathode turned grey and its resistance within the plane increased. This is assumed to be an indication that an Au-Cd alloy has formed in consequence of a Cd-segregation. Further the current begun to diminish and eventually became zero and the anode-crystal interface became *black*. This in turn is assumed to be a consequence of the formation of a fluoride of gold which is gradually insulating the electrode.

3. Evidence for a discharge by electron injection. —

Different quantities of charge, $Q = \int I dt$, were passed through samples put without any coating between solid metal electrodes. If the current was strong enough, the surface layers took on a yellow to brown colour which grew stronger in due time and turned ultimately into grey. With weak currents only a slowly increasing extinction was observed as Q increased but in due time also these samples became grey at the cathode. Densitometric measurements showed an extinction varying from point to point, but the average optical density was proportional to Q (Table I). Under the microscope exposed samples showed a multitude of dense particles of about 0.1 μm in diameter under the surface, together with some few big clusters which eventually exceeded 10 μm (Fig. 1a). Focusing the microscope deeper below the surface the clusters were found to consist of a network of particles extending into the bulk (Fig. 1b). After a long exposure samples became eventually shorted, obviously by an extreme growth of some of the clusters : The

⁽¹⁾ TSC = Thermal Stimulated Current.

Table I. — Increase of the optical density (D) with the passage of a charge (Q) : i current density, S surface area.

i ($\mu\text{A}/\text{cm}^2$)	$10^3 \times Q/S$ (cm^{-2})	ΔD	$S \cdot \Delta D / Q$
19.8	3.46	0.305	88.1
11.0	6.20	0.61	98.4
7.2	8.40	0.825	98.2
28.0	11.40	1.47	129.0
32.0	18.7	1.825	97.6
20.0	22.7	1.71	75.3

a)

b)

Fig. 1. — Picture of a) the surface of a current exposed sample, of b) crystal layers below the surface. Magnification 500.

respective dark breakthrough channels could be observed by an unaided eye.

These observations lead to the conclusion that cadmium particles are formed below the surface. In the beginning they are considerably smaller than the wavelength of the visible light. Hence they scatter light and cause the coloration and extinction (cf. scattering by small nonabsorbing particles [4]). The formation of such particles shows that electrons are injected into the crystal where they reduce Cd-ions to atoms. The electrons are likely to be captured preferentially by Cd-particles so that, once formed, these are continuously charged and growing by

segregation of further cadmium. As the extinction due to scattering is increasing proportional to the square of the particle volume the assumed growth does not contradict the observations. As soon as the dimensions of the particles approach the wavelength they cause reflection and absorption and the coloration of the light vanishes (cf. scattering by colloids [4]). It may thus be inferred that the electron injection leads to a formation of a kind of « reversible dendritic » electrode system to which charge is transmitted by tunneling of electrons.

4. Initial decrease of the electrode resistance of bare samples. — The A - V characteristic at room temperature of an undoped sample provided alternatively with vacuum sputtered Au-electrodes and left with bare surfaces was measured. The voltage was increased in steps, between which the current was allowed to become steady. With the Au-electrodes the characteristic is reproducible and linear, except for a slight curvature near zero volts which is connected with the built up of a back voltage V' (1.45 V) [5]. With bare surfaces there is first a transient period (cf. Fig. 2), during which the resistance V/I of the system is continuously decreasing towards a reproducible saturation curve which is again linear at higher voltages ($V' = 16.7$ V). The successive formation of the dendritic electrode system with increasingly shorter tunneling distances and increasing surface area of the particles offers a satisfactory explanation for these findings.

Fig. 2. — Volt-Ampere characteristic of an undoped sample put bare between solid Ni-electrodes : 1) first run, 3) third, already reproducible run.

5. Electron injection into insulated samples. — Already a monolayer of foreign material or an insufficient contact of the (external) electrode will impede the segregation and an insulation layer will stop it completely. It cannot, however, prevent completely an electron injection. As the following data show, the steady current passing a sample is considerably diminished by a worsening contact and by an increasing thickness of an insulation, however, it still flows : Thus e.g. with graphite $i/V = 9 \times 10^{-8}$ A/cm² V, with $2 \times 6 \mu\text{m}$ of silicon oil 4×10^{-9} A/cm² V,

with $2 \times 4 \mu\text{m}$ insulation foil $2 \times 10^{-11} \text{ A/cm}^2 \text{ V}$ and with $40 + 4 \mu\text{m}$ Teflon $2 \times 10^{-15} \text{ A/cm}^2 \text{ V}$. This shows that a discharge by electron injection takes place in spite of the « insulation ».

6. Magnitude of the TSC space-charge peaks and electrode system constitution. — There exist two kinds of peaks in CdF_2 which are attributed to a space-charge formation. One first order kinetics peak with a maximum position between 140 [6] and 210 K [6,7] depending on the impurity concentration and an extremely broad peak which is observed depending on the polarization temperature between 250 and 300 K [8, 9]. In table II the specific magnitudes $Q/(S \cdot V_p)$ for $L = \text{constant}$ of these peaks are given

Table II. — *Specific magnitude $Q/(SV_p)$ of the space-charge TSD-peaks (*) for various arrangements of the electrodes (V_p polarization voltage, L sample thickness).*

Electrode system	$10^7 \times Q/(S \cdot V) \text{ (C/m}^2 \text{ V)}$	
	1st peak	2nd peak
Sputtered Au	0.002	560
Coloidal graphite layer	0.011	3.6
Detto, NaF doped	3.0	200
Bare, solid metal electrodes	0.035	1.3
$2 \times 4 \mu\text{m}$ insulating foil	1.6	2.8
$2 \times 6 \mu\text{m}$ silicon oil	3.7	2.2
$40 + 4 \mu\text{m}$ teflon	0.16	0.001

(*) TSD = Thermal Stimulated Depolarization.

for different arrangements of the electrodes. Both are found to change systematically with the *electrode resistance* R_i and the *distance* δ between the external electrodes and crystal surfaces. This shows, in the first place, that there exist simultaneously two kinds of space-charges and formation mechanisms. The first peak is increased by an increasing R_i , but decreased by an increasing δ . This is, as will be shown below, what is to be expected in principle of an interfacial polarization of the Maxwell-Wagner type [10] if the electrodes are only partially blocking. The second peak is steadily decreasing with an increasing R_i and δ . As pointed out before increasing δ and R_i means a decreasing electron injection. This shows that the peak is undoubtedly connected one way or other with the dendritic electrode system.

7. Interfacial polarization due to blocking electrodes. — Let us assume, that the discharge rate is basically given by the electron injection rate, which again is determined by R_i and δ . If this rate differs from the rate of transport of defects the latter will accumulate at the electrodes. The simplest model of such a situation is a Maxwell-Wagner interfacial polarization. It correctly predicts a negligible $Q/(SV_p)$ for low values of R_i and δ and a maximum value for $R_i \rightarrow \infty$ which is proportional to $1/\delta$. Thus for instance the theoretical value for the silicon oil insulated

sample is $1 \times 10^{-6} \text{ C/m}^2 \text{ V}$, the experimental $3.7 \times 10^{-7} \text{ C/m}^2 \text{ V}$, etc. The model further predicts correctly the first order kinetics of the polarization process with a relaxation time proportional to a Boltzmann factor with the activation energy of vacancy motion U . As can be seen from published data [6, 7, 8] there is a good agreement between U as obtained from conductivity data and from the first peak. Finally from the peak-maximum condition [11] the relaxation time was obtained. From its value it follows that there should occur above room temperature relaxation losses if an alternating voltage of 0.5 to 100 kHz is applied. Measurements confirm this expectation [12]. It is interesting to note that numerical calculations of the potential distribution in a totally blocked sample [13] lead to a thickness of the space-charge layer of less than a Debye length only. This suggests that the relaxation of a space charge follows approximately first order kinetics, as observed.

8. Polarization of the dendritic electrode system. —

It is reasonable to assume that there exists an exponential distribution of the particles forming the dendritic electrode system, because the probability of capture of electrons at a given point is proportional to the rate of their passage there. The Cd atoms which are formed constitute charge deficiencies like cation vacancies and the atom clusters are charged by captured electrons. Both will attract in consequence anion vacancies and cause thus a concentration gradient of defects and a space charge as it is deduced from experiment [8, 9]. It is to be noted that this will necessarily influence the field strength at the surface and the magnitude of the first peak. The two peaks are thus not independent one of the other. During depolarization, at the temperature of the first peak the vacancies bound to the dendritic electrode system become mobile but stay fixed, probably due to electrostatic attraction. There are reasons to believe that it is the segregation, which sets in only at higher temperatures, that removes finally this inhibition (cf. [12]).

9. Evidence for similar processes in alkali-halides. —

It is important to note that in the literature on conductivity evidence for more or less the same kind of effects in other polar crystals can be found. As far as the dendritic electrode system is concerned Sano and Tomiki [14] observed in dc-current exposed KCl under the microscope, too, dense particles below the crystal surface (which they believe to be material from the electrode). Then there exists a compelling evidence from potential distribution measurements for the existence of a space-charge which eventually reaches up to $100 \mu\text{m}$ into the bulk [15, 16]. It is to be noted further that in NaCl simultaneously with the deep reaching space-charge the kind of losses

connected with the first peak were observed [15] and in KCl they were observed in samples with and without particles [14]. A dependence of these losses on the

electrode resistance has also been observed [17]. Finally, in NaCl and KCl TSC-surface polarization peaks were found [18].

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