INFLUENCE OF CRUSHING TIME ON THE ELECTRIFICATION OF DUST PRODUCED FROM CdTe, HgTE and CdSe

By J. MALCHER

Department of Physics, Technical University, Wrocław*

(Received July 3, 1968, revised paper received October 19, 1968)

The electrification of dust produced from CdTe, HgTe, and CdSe increases with increasining crushing time of the material, becomes maximum, and then decreases when the crushing is continued. This time behaviour of dust electrification is explained in terms of two opposite mechanisms: production of electric charge on dust particles which is connected with the increase in surface during the crushing process and the neutralization occurring under the influence of multiple mutual contacts of particles. The production of electric charge becomes asymptotically saturated whereas neutralization leads to charge decrease on dust particles when time proceeds. According to these assumptions calculations are made and the function of the dependence of electrification on the crushing time is given.

1. Introduction

It was shown in previous investigations [1] that the electrification of dust is considerably influenced by the length of the crushing time. Apart of other factors the crushing process alone turns out to be essential for the amount of charge accumulated on dust particles. The present paper deals with the influence of the crushing time on electrification of dust produced from semiconducting materials. The production of dust from solid material was arranged in a way that the only changing parameter was the crushing time, all other parameters being fixed. The investigations were made on semiconductors of the $A^{\rm II}B^{\rm VI}$ type: CdTe, CdSe and HgTe with no admixtures. Cadmium telluride and selenide are typical semiconductors, whereas mercury telluride is regarded by some authors as a semi-metal. CdTe and HgTe crystallize in cubic (regular) system while CdSe in hexagonal system. It seems to be interesting to investigate compounds of the same type, having however different electric properties and crystal structure.

The investigated materials were obtained in the form of bulk samples and then crushed in a porcelain mortar with a porcelain pestle under a constant crushing force of 50-70 N. Since the mortar surface is coarse and becomes covered with the investigated material

^{*} Address: Katedra Fizyki Politechniki Wrocławskiej, Wrocław, Wybrzeże Wyspiańskiego 27, Polska.

already in an early stage of the crushing prosces, the influence of the contact of the dust with the mortar is negligible and can be neglected in further considerations [2].

Electric charge on dust particles is produced as the result of the break-up of the crystal lattice. This is connected with nonuniform distribution of electrons on the cleavage plane between the two surfaces. The amount of charge thus observed in dust particles depends on two factors:

- a) the amount of charge produced on dust particles,
- b) the ability to preserve this charge.

One may expect that intense crushing process will give as the result intense charge production on dust particles. For fixed crushing force in the mortar in which the material is crushed and broken-up, a mean particle-size is established after a certain crushing time. The number of large particles is then already rather small while medium-size particles are broken up already at a rather low rate. Besides, dust particles contact one another which can lead to a reduction of produced charge. The extension of crushing time must exert an influence on final electrification of the dust.

2. Result of measurements

Fig.1 shows the results of microscopic observations of dust samples taken from the mortar during the break-up of CdTe. These results have been obtained by counting the number of dust particles of different size in a view-field 50 $\mu \times 50~\mu$. Tenfold counting was performed for each dust sample taken during the crushing of the material.

Next, the contribution (in percent) of particles belonging to four different size groups was

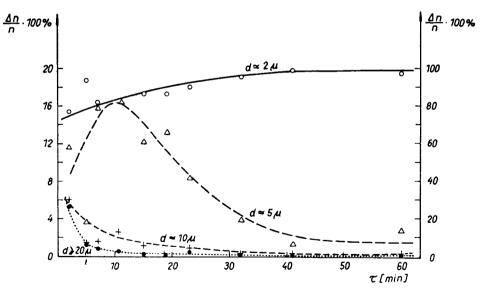


Fig. 1. Time dependence of the contribution (in per cent) of particles of various size during the process of crushing of cadmium telleride. The left-hand side scale concerns particles with diameters $\sim 5 \mu$, $\sim 10 \mu$ and $\gg 20 \mu$. The right-hand side scale concerns particles with diameters $\sim 2 \mu$. τ is the crushing time

calculated. These groups were: $d \approx 2\mu$, $d \approx 5\mu$, $d \approx 10\mu$, $d \geq 20\mu$. The results presented in the Figure illustrate the changes in the contribution of particles belonging to the particular size group, occurring during the crushing process. The intensity of the crushing process is defined by the increase of the contribution of particles belonging the first two groups $(2\mu$ and 5μ) and above all, by the decrease in the contribution of particles belonging to the third and fourth group $(10\mu$ and 20μ). In the initial stage the crushing intensity is considerable and then after about 8–12 minutes the crushing process is not so intense. Particles of the order of 2μ are still produced but only due to the break-up of 5μ -particles. The number of particles of larger size, which are the main source for obtaining small particles, changes only slightly.

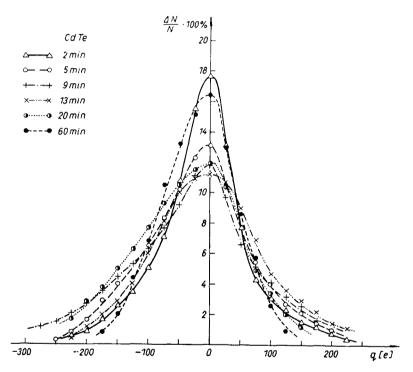


Fig. 2. Statistical distributions of charge in dust clouds produced from CdTe crushed for 2, 5, 9, 13, 20 and 60 minutes. $\frac{1}{q}$ is the mean charge of a dust particle in electron charge units. $\frac{\Delta N}{N}$ is the fraction of dust particles having charges contained in the interval $(q, q + \Delta q)$

It follows from the above-mentioned results that the intensity of the break-up process and thus of charge production connected with the former decreases with increasing crushing time. If only the charge production connected with the break-up of crystal lattice were taken into account, one should expect that the electrification of the dust should first increase with the crushing time and then after getting to a certain value, it should change only slightly. This simple mechanism however does not sufficiently explain the results of measumerent.



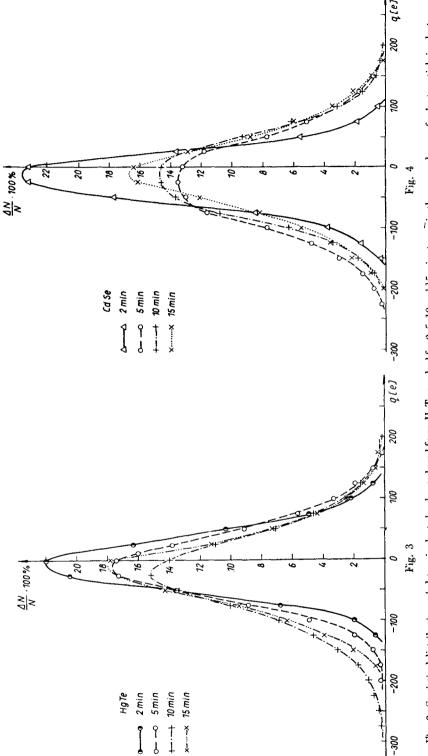


Fig. 3. Statistical distributions of charge in dust clouds produced from HgTe crushed for 2, 5, 10 and 15 minutes. \bar{q} is the mean charge of a dust particle in electron charge units. $\frac{AN}{N}$ is the fraction of dust particles having charges contained in the interval $(q,q+\Delta q)$

Fig. 4. Statistical distributions of charge in dust clouds produced from CdSc crushed for 2, 4, 10 and 15 minutes. q is the mean charge of a dust particle in electron charge units. $\frac{\Delta N}{N}$ is the fraction of dust particles having charges contained in the interval $(q,q+\Delta q)$

The electrification of dust produced from CdTe, HgTe and CdSe was measured by the author by means of the method given in Refs. [1, 2 and 3]. These references give also the method of evaluation of the results.

The influence of crushing time on the electrification of the dust is illustrated by the curves of the statistical distribution of charge (Fig. 2 for CdTe, Fig. 3 for HgTe and Fig. 4 for CdSe). The mean charge value \bar{q} and the standard deviation σ are listed in Tables I, II and III for dust obtained from Cd Te,HgTe and CdSe, respectively. The tables also give the number of degrees of freedom l, and the values χ^2 and χ^2_p which permit the statement that the statistical distributions can be regarded as normal distributions.

TABLE I
Cadmium telluride

Crushing time (minutes)	σ	\bar{q}	1	χ²	χ_p^2
	(electrons)				~p
2	43.75	-10.85	15	21.97	30.57
5	87.30	-18.85	15	9.21	30.57
9	99.13	-32.14	17	20.93	33.40
13	90.98	- 1.50	15	5.14	30.57
20	83.75	-36.70	14	16.78	29.14
60	61.12	-19.46	10	7.36	23.20

TABLE II

Mercurium telluride

Crushing time	σ	\overline{q}		χ ²	χ_p^2
(minutes)	(electrons)			~	
2	45.91	- 3.94	8	3.28	20.09
5	59.51	- 8.38	10	4.85	23.20
10	74.23	-29.21	12	13.50	26.21
15	62.09	18.80	11	11.37	24.72

TABLE III Cadmium selenide

Crushing time (minutes)	σ	\overline{q}	ı	χ²	χ_p
	(electrons)			^	
2	42.23	-19.36	8	12.81	20.09
5	70.85	-24.14	12	1.48	26.21
10	64.07	-13.36	11	1.21	24.72
15	65.53	-12.03	11	6.13	24.72

The dependences of the standard deviation on crushing time for dust produced from CdTe, HgTe and CdSe are given in Fig. 5. In the initial stage (2-10 min) the electrification of the dust increases. Prolonged crushing gives rise to a decrease in electrification.

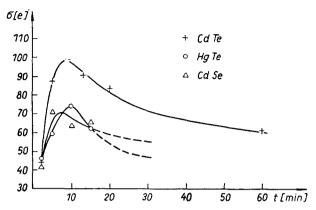


Fig. 5. Dependence of the standard deviation σ on crushing time t for CdTe, HgTe and CdSe

3. Discussion of the results

The behaviour of the dependence of electrification on crushing time in the initial stage, i.e., for short crushing times, can be explained by the production of charge connected with the break-up of crystal lattice. This mechanism however, does not explain the behaviour of electrification after prolonged crushing. One can conclude that after prolonged mutual contact of dust particles another process becomes dominant. This process is the neutralization of charge which must occur in the result of repeated mutual contact of dust particles with one another. These two opposite mechanisms, i.e., charge production and neutralization of charge in the crushing process can be evaluated only according to the resultant effect, i.e., final electrification of dust particles. On the basis of the above-mentioned considerations an attempt has been made of mathematical description of the electrification vs. crushing time dependence.

If at the instant t there are k positive and k negative charges in the given system (state B_k) then the following transitions can occur in the elementary time interval dt

$$B_k \xrightarrow{\lambda_k} B_{k+1}$$

$$B_k \xrightarrow{\beta_k} B_{k-1}$$

where: B_{k+1} — state corresponding to a unit charge increase

 B_{k-1} — state corresponding to a unit charge decrease

 λ_k — charge production rate

 β_k — neutralization rate

The possibility of simultaneous production or neutralization of two or more charges is here excluded (ordinary stochastic process [5]).

Production of charges

The production of charges is connected with the break-up of the material which results in an increase in the total surface of dust particles. Suppose that the surface area is given by the following formula

$$A(t) = a(1 - e^{-\gamma t}) \tag{1}$$

where γ — is a factor which defines the surface increases rate ($\gamma > 0$). According to this formula the surface increase is exponential and leads to the limiting value a. In the time interval dt the area of the surface is increased by dA

$$dA = a\gamma e^{-\gamma t}dt,$$

while the charge production rate is

$$\lambda_k = a\gamma \lambda e^{-\gamma t} = \lambda_0 e^{-\gamma t} \tag{2}$$

since it is proportional to dA/dt.

Neutralization of charges

During the mixing of dust particles opposite charges contact many times one another. The rate of contact of a fixed charge with opposite charges is proportional to their number k. The number of charges of the same sign is also k. Thus the total rate of contact is proportional to k^2 and can be denoted by bk^2 , where b is a coefficient depending on the way of mixing. The neutralization rate is however not identical with the contact rate of opposite charges since not every contact necessarily leads to neutralization. If we denote by β the probability of neutralization of the two opposite charge during their contact, where β is a constant depending on the material, then the charge decay rate becomes

$$\beta_k = bk^2\beta = \beta_0 k^2. \tag{3}$$

Derivation of equations

After making use of Eqs. 2 and 3 the diagram of transitions from initial state to states corresponding to an increase (or decrease) in charge by a unit can be written in the form

$$B_{k} \xrightarrow{\lambda_{0}e^{-\gamma t}} B_{k+1}$$

$$B_{k} \xrightarrow{\beta_{0}k^{2}} B_{k-1}$$

for $k \ge 1$.

This leads to the following equations for the probability $Pr_k(t)$ of the occurrence of the state B_k , i.e., of the occurrence of k postive and k negative charges:

$$\mathrm{d}\mathbf{r}_{k}(t+dt) \approx \mathrm{Pr}_{k-1}(t)\lambda_{0}e^{-\gamma t}dt + \mathrm{Pr}_{k}(t)[1-(\beta_{0}k^{2}+\lambda_{0}e^{-\gamma t})dt] + \mathrm{Pr}_{k+1}(t)\beta_{0}(k+1)^{2}dt$$

where the asymptotic equality symbol \approx means that higher order terms in dt are neglected. After bringing $\Pr_k(t)$ to the left-hand-side of the equation, dividing by dt and going over to the limit $dt \to 0$ we obtain for $k \ge 1$:

$$\Pr_{k}'(t) = \lambda_{0}e^{-\gamma t}\Pr_{k-1}(t) - (\beta_{0}k^{2} + \lambda_{0}e^{-\gamma t})\Pr_{k}(t) + \beta_{0}(k+1)^{2}\Pr_{k+1}(t)$$
(4)

For k = 0 the transition diagram looks different:

$$B_0 \xrightarrow{\lambda_0 e^{-\gamma t}} B_1$$

$$B_0 \xrightarrow{B_0}$$

The probability in this case is given by

$$\mathrm{Pr}_{\mathbf{0}}(t+dt) = \mathrm{Pr}_{\mathbf{0}}(t)(1-\pmb{\lambda_0}e^{-\gamma t}dt) + \mathrm{Pr}_{\mathbf{1}}(t)\pmb{\beta_0}dt$$

and hence

$$Pr_0'(t) = -\lambda_0 e^{-\gamma t} Pr_0(t) + \beta_0 Pr_1(t)$$
 (5)

Direct solution of the infinite set of equations (4) and (5) is rather difficult. We shall introduce an auxiliary function, the so-called generating function Φ [5]. This function permits the infinite set of equations (4) and (5) to be replaced by a single partial differential equation.

The generating function is given by the formula:

$$\Phi = \Phi(Z, t) = \sum_{k>0}^{\infty} Z^k \operatorname{Pr}_k(t)$$
 (6)

where Z is an auxiliary variable.

From Eqs. (4) and (5) we obtain:

$$\frac{\partial \Phi}{\partial t} = \sum_{k=0}^{\infty} Z^{k} [\lambda_{0} e^{-\gamma t} \operatorname{Pr}_{k-1}(t) - (k^{2}\beta_{0} + \lambda_{0} e^{-\gamma t}) \operatorname{Pr}_{k}(t) + (k+1)^{2}\beta_{0} \operatorname{Pr}_{k+1}(t)]$$

where $Pr_{-1}(t) \equiv 0$. After re-arrangement we obtain

$$\frac{\partial \Phi}{\partial t} = \lambda_0 e^{-\gamma t} \sum_{k=1}^{\infty} Z^k \operatorname{Pr}_{k-1}(t) - \lambda_0 e^{-\gamma t} \sum_{k=0}^{\infty} Z^k \operatorname{Pr}_{k}(t) - \beta_0 \sum_{k=0}^{\infty} k^2 Z^k \operatorname{Pr}_{k}(t) + \beta_0 \sum_{k=0}^{\infty} (k+1)^2 Z^k \operatorname{Pr}_{k+1}(t).$$

$$(7)$$

After writing the particular sums in suitable form, substitution into Eq. (7) and re-arrangement we obtain the equation for the generating function:

$$\frac{\partial \boldsymbol{\Phi}}{\partial t} = (Z - 1) \left(-\beta_0 Z \frac{\partial^2 \boldsymbol{\Phi}}{\partial Z^2} - \beta_0 \frac{\partial \boldsymbol{\Phi}}{\partial Z} + \lambda_0 e^{-\gamma t} \boldsymbol{\Phi} \right) \tag{8}$$

The generating function plays an auxiliary role. Its knowledge permits the determination of some quantities of interest, viz, the expected number of charges M(t) as a function of the time and the dependence of the standard deviation $\sigma(t)$ on t.

Thus from the definition of the expectation value and Eq. (6) we obtain:

$$M(t) = \sum_{k \ge 0} k \operatorname{Pr}_{k}(t) = \frac{\partial \Phi}{\partial Z} \Big|_{Z=1}$$
(9)

$$\left. \frac{\partial \boldsymbol{\Phi}}{\partial Z} \right|_{Z=1} = \sum_{k \ge 1} k Z^{k-1} \operatorname{Pr}_{k}(t) \right|_{Z=1} = \sum_{k \ge 1} k \operatorname{Pr}_{k}(t)$$
 (10)

Similarly we obtain the standard deviation which, according to the definition, is as follows:

$$\sigma^{2}(t) = \sum_{k \ge 1} k^{2} \Pr_{k}(t) - M^{2}(t)$$
 (11)

On the other hand we obtain from Eqs. (6) and (9)

$$\frac{\partial^{2} \Phi}{\partial Z^{2}} \bigg|_{Z=1} = \sum_{k \geq 1} k(k-1) Z^{k-2} \operatorname{Pr}_{k}(t) \bigg|_{Z=1} \sum_{k \geq 1} k^{2} Z^{k-2} \operatorname{Pr}_{k}(t) \bigg|_{Z=1} - \sum_{k \geq 1} k Z^{k-2} \operatorname{Pr}_{k}(t) \bigg|_{Z=1} = \sum_{k \geq 1} k^{2} \operatorname{Pr}_{k}(t) - M(t)$$

After substitution into Eq. (11) we obtain:

$$\sigma^{2}(t) = \left[\frac{\partial^{2} \Phi}{\partial Z^{2}} \Big|_{Z=1} + M(t) \right] - M^{2}(t)$$

which together with Eq. (9) yields:

$$\sigma^{2}(t) = \left[\frac{\partial^{2} \Phi}{\partial Z^{2}} + \frac{\partial \Phi}{\partial Z} - \left(\frac{\partial \Phi}{\partial Z} \right)^{2} \right]_{Z=1}. \tag{12}$$

The function $\sigma^2(t)$ defined by Eq. (12) gives the dependence of dust electrification on crushing time.

This function gives the solution of the problem under consideration although an explicit determination of the function Φ appearing in Eq. (12), and thus the determination of the function $\sigma^2(t)$ in analytical form which would be convenient in further calculations encounters considerable difficulties and requires the solution of the partial differential equation with suitable boundary conditions. The solution depends on the coefficients λ_0 , β_0 and γ appearing in Eq. (8) and thus on $a \cdot \gamma \lambda$ and $b\beta$ because of Eqs (2) and (3). The coefficient b which is defined by the way of mixing can be regarded as constant (crushing by means of a mill), however its numerical value is unknown. The surface increase rate coefficient γ is also unknown since the information on the time dependence of the crushing of the material is only qualitative (microscopic observations — Fig. 1). This coefficient may be dependent

on several physical properties of the material such as the crystal structure, hardness and cleavage. The coefficient β connected with neutralization is evidently dependent on surface conductivity. It should not be, however, identified with the latter. The coefficient λ which defines the rate of electric charge production and thus appears in Eq. (2) depends on the type of chemical bonds and on the degree of occurrence of lattice defects.

It follows from these considerations that dust electrification is the result of several complicated processes finally depending on factors, which cannot be described quantitavely, at least on the basis of investigations made so far.

The author is much obliged to Prof. S. Gładysz for performing the calculations.

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