

## PHOTOCONDUCTIVITY IN LEAD CHLORIDE AND LEAD BROMIDE

J. F. VERWEY\* and N. G. WESTERINK\*\*

*Afdeling voor chemie van de vaste stof, Universiteit van Utrecht,  
Rijnhuizen, Jutphaas, Nederland*

Received 6 September 1968

### Synopsis

Photoconductivity measurements on  $\text{PbCl}_2$  and  $\text{PbBr}_2$  at liquid nitrogen temperature are described. It was found that the holes are the dominant mobile charge carriers in these crystals. The range per unit field was estimated to be  $1.2 \times 10^{-4} \text{ cm}^2/\text{V}$  for  $\text{PbBr}_2$ . For  $\text{PbCl}_2$  the ranges are  $4 \times 10^{-4} \text{ cm}^2/\text{V}$  and  $0.3 \times 10^{-4} \text{ cm}^2/\text{V}$  for surface and bulk conductivity, respectively.

The wavelength dependence indicated that the first maximum at the long wavelength side of the fundamental absorption of  $\text{PbBr}_2$  and  $\text{PbCl}_2$  is an exciton peak.

*Introduction.* In the course of our investigations into the photochemical properties of lead halides<sup>1)</sup> it became necessary to study the behaviour of photogenerated charge carriers. The photochemical decomposition (photolysis) consists of an electrical and a mass transport part. To study the electrical part, photoconductivity and photovoltage measurements seem most feasible. Many measurements on  $\text{PbI}_2$  have been described in the literature. Kelder<sup>2)</sup> measured the photodiffusion voltage (Dember voltage) and he also carried out some photoconductivity measurements. Forty and coworkers<sup>3–6)</sup> investigated the photoconductivity of  $\text{PbI}_2$  crystals obtained from aqueous solutions as a function of temperature and as a function of the wavelength of the excitation light. Currie *et al.*<sup>7)</sup> reported on photovoltage and photoconductivity measurements of  $\text{PbI}_2$  grown from the melt. Henisch and co-workers<sup>8,9)</sup> measured the photoconductivity of gel-grown single crystals as a function of wavelength. Together with other measurements (optical absorption) they were able to construct an energy level diagram for their p-type crystals.

From the literature nothing is known about the photoconductive pro-

\* Present address: Natuurkundig Laboratorium der N.V. Philips' Gloeilampenfabrieken, Eindhoven, Nederland.

\*\* Present address: Hartog's Laboratorium, Oss, Nederland.

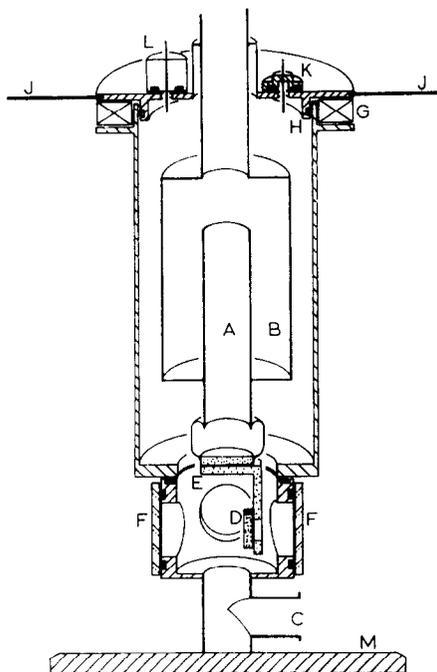


Fig. 1. Cryostat with crystal holder.

A = liquid nitrogen container (stainless steel).

B = outer part of liquid nitrogen container.

C = vacuum connection.

D = crystal.

E = crystal holder (copper).

F = quartz window (suprasil).

G = ball bearing.

H = O-ring seal.

I = handles to turn the liquid nitrogen container and with it the crystal holder and crystal.

K, L = lead throughs for the measurement of temperature (thermocouple Thermocoax) and photoconductivity, respectively. B can be filled with liquid nitrogen separately from A to establish at D temperatures above liquid nitrogen temperature.

properties of  $\text{PbBr}_2$  and  $\text{PbCl}_2$  crystals. As these substances are predominantly ionic conductors<sup>10,11</sup>) at room temperature, we measured the photoconductivity at liquid nitrogen temperature.

*Experimental.* The setup for the measurement of the photoconductivity has been published elsewhere<sup>12,13</sup>). It consisted of a high-pressure mercury lamp (HBO 200) and a quartz prism monochromator (Leiss). For the measurement of optical transmission the setup was furnished with a photomultiplier with a trialkali-cathode (EMI 9558 Q). The photoconductive response was measured by a vacuum tube electrometer (Keithley 610 B).

The preparation of the crystals of  $\text{PbBr}_2$  and  $\text{PbCl}_2$  has been extensively reported elsewhere<sup>12,14</sup>). Single crystals were grown from zone-refined material by the Bridgman method.

The crystals were placed inside a stainless steel dewar (see fig. 1). By filling this cryostat with liquid nitrogen the crystal could be cooled nearly to the boiling point of nitrogen.

*Experimental results.* It was not very easy to find suitable electrode materials. Several substances were tried but none gave an ohmic current-voltage characteristic. Therefore we used electrodes completely insulated from the crystal, because in this case the current-voltage curve can be analysed with Hecht's formula<sup>15</sup>). As a matter of fact, not current but displaced charge is measured in this way. Use was made of short light pulses of low intensity to avoid polarization of the crystal. Every measurement at a certain voltage was followed by a measurement at the same voltage but with reversed polarity, also to minimize this effect. A typical result is shown for a  $\text{PbBr}_2$  crystal in fig. 2. The response was greater if the insulated electrode at the illuminated side of the crystal was positive

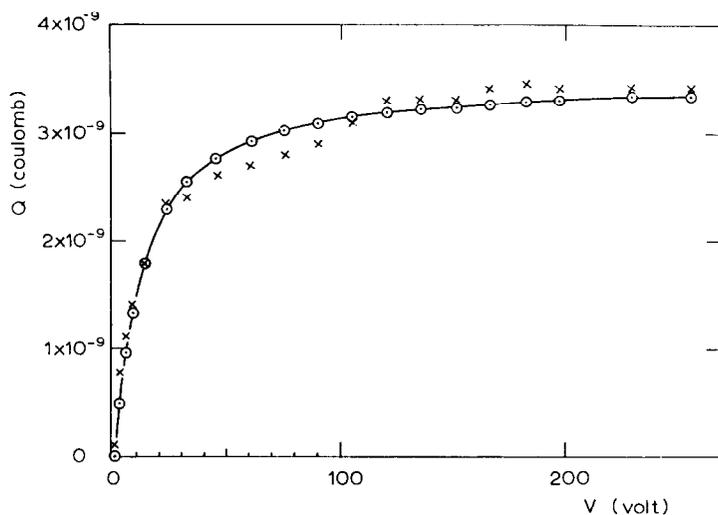


Fig. 2. Displaced charge  $Q$  in a lead bromide crystal at 100 K measured with electrodes insulated from the crystal. The thickness of the crystal was 0.05 cm. The electrode at the illuminated side was a punctured platinum foil. Crosses are measured points of  $Q$  as a function of the voltage between the electrodes, the illuminated electrode being positive with respect to the non-illuminated one. Circles are results of a machine calculation of the best fit curve of Hecht's formula to the measured points. This curve is

$$Q = 34 \times 10^{-10} \frac{V}{21.5} (1 - e^{-21.5/V}),$$

where  $V$  = voltage applied.

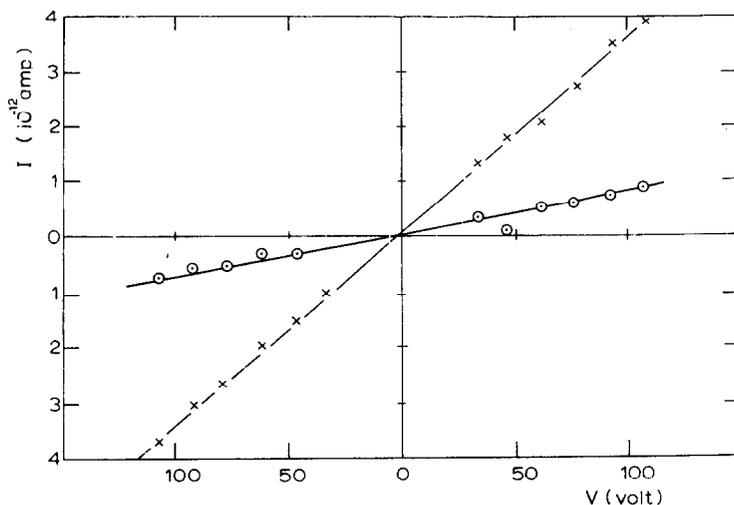


Fig. 3. Current-voltage curve of a  $\text{PbBr}_2$  crystal with indium amalgam electrodes.  
 crosses: photocurrent plus dark current.  
 points: dark current.  
 $\lambda = 345 \text{ nm}$ .

with respect to the electrode at the non-illuminated side. The displaced charge in this forward polarity condition was about 10 to 20 times the charge in the reversed condition both in  $\text{PbBr}_2$  and in  $\text{PbCl}_2$ .

Later we were able to use an electrode material which seems promising in giving ohmic contacts, namely, indium amalgam. We are indebted to Mr. F. Driedonks\* who supplied this substance ready for use. He also applied this electrode material to  $\text{PbI}_2$  crystals, where he found ohmic behaviour of the photocurrent up to voltages of  $10^3 \text{ V/cm}$ . In this case the crystals were illuminated with a tungsten lamp. Fig. 3 shows our results for a  $\text{PbBr}_2$  crystal. The indium-amalgam electrodes were applied at the same side of the crystal.

The wavelength dependence of the photoconductivity of lead bromide and lead chloride was measured with the above mentioned electrode configuration, *viz.*, indium amalgam applied at the same side of the crystal. The entrance and exit slits of the monochromator were 0.5 mm. The relative spectral response is shown in fig. 4 in arbitrary units. After these measurements the  $\text{PbBr}_2$  crystal was irradiated at room temperature for  $1\frac{1}{2}$  hours through the same monochromator (exit and entrance slit widths 1 mm) at the wavelength 365 nm. This is the wavelength of the optical absorption edge at room temperature (see below). After the irradiation the spectral response was measured again at liquid nitrogen temperature. The result is also shown in fig. 4 in the same arbitrary units.

\* Fysisch Laboratorium, Universiteit van Utrecht.

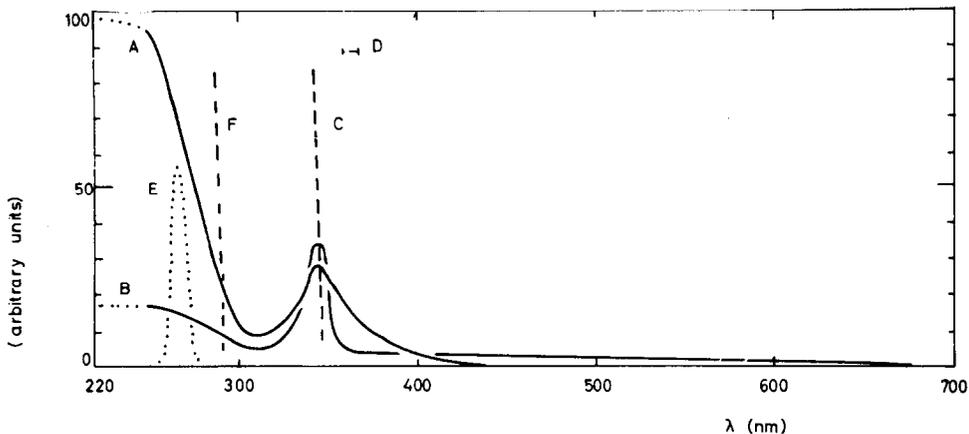


Fig. 4. Wavelength dependence of the photoconductivity in a  $\text{PbBr}_2$  and a  $\text{PbCl}_2$  crystal at liquid nitrogen temperature.

- A = relative spectral response of a  $\text{PbBr}_2$  crystal in arbitrary units.
- B = spectral response of the same crystal after irradiation at room temperature for  $1\frac{1}{2}$  hours.
- C = absorption edge  $\text{PbBr}_2$  at liquid nitrogen temperature.
- D = bandwidth monochromator.
- E = spectral response of a  $\text{PbCl}_2$  crystal in arbitrary units.
- F = absorption edge  $\text{PbCl}_2$ .

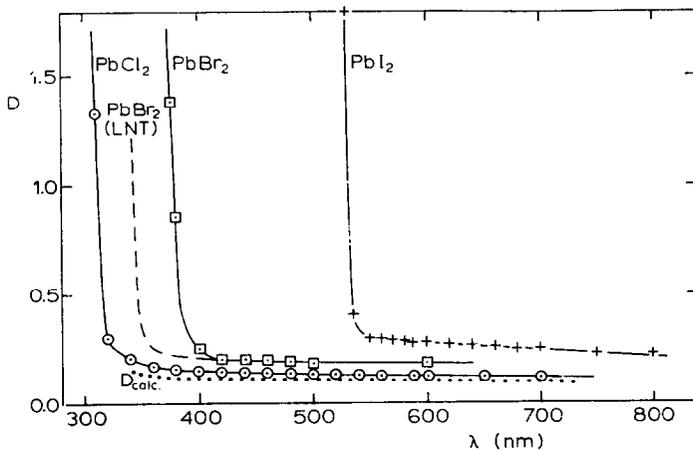


Fig. 5. Optical density of pure crystals  $\text{PbCl}_2$ ,  $\text{PbBr}_2$  and  $\text{PbI}_2$  measured at room temperature and for  $\text{PbBr}_2$  also at liquid nitrogen temperature (LNT) as a function of wavelength. The  $\text{PbCl}_2$  and  $\text{PbBr}_2$  crystals had a thickness of about 1 mm, the  $\text{PbI}_2$  crystal of about 0.5 mm.

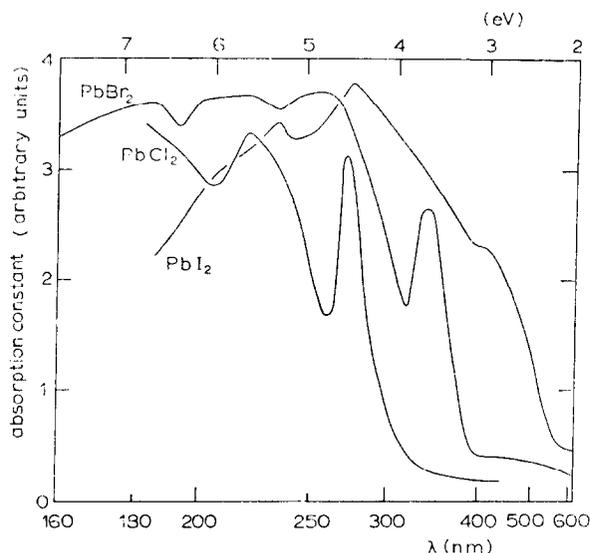


Fig. 6. Optical absorption (arbitrary units) at room temperature as a function of wavelength of thin layers of the lead halides  $\text{PbCl}_2$ ,  $\text{PbBr}_2$  and  $\text{PbI}_2$ . Taken from Fesefeldt's measurements<sup>16)</sup>.

For a discussion of the photoconductive properties of lead halides it is necessary to know the optical absorption. Fig. 5 shows the optical density of some crystals. For comparison the optical absorption of thin layers of the lead halides is given in fig. 6<sup>16)</sup>.

*Range of the charge carriers.* There are two reasons to assume that the holes in  $\text{PbBr}_2$  and  $\text{PbCl}_2$  are the dominant charge carriers. Upon illumination with strongly absorbed light the illuminated side of the crystal becomes negative with respect to the non-illuminated side. This can be detected with electrodes insulated from the crystals. Also the photoconductive response to strongly absorbed light is greatest if the electrode at the illuminated side is positive with respect to the other electrode at the non-illuminated side, which shows that holes drift more rapidly into the inside of the crystal. The response of a  $\text{PbBr}_2$  crystal is shown in fig. 2. The displaced charge  $Q$  as a function of voltage  $V$  is given by Hecht's formula

$$Q = Q_0 \frac{\omega}{l} (1 - e^{-l/\omega}) \quad (1)$$

where  $l$  = thickness of the crystal,  
 $\omega = \mu\tau V/l$  range of the holes (Schubweg),  
 $\mu$  = mobility of the holes,  
 $\tau$  = lifetime of the holes.

The quantity  $Q_0$  represents the charge of the holes created near the surface and, therefore, is linearly correlated to the number of photons absorbed and the quantum efficiency. For a discussion of this formula we refer to the literature<sup>17</sup>). From the best fit of Hecht's formula to the measured points in fig. 2 we calculate for the hole range per unit field  $\mu_h\tau_h$  in  $\text{PbBr}_2$ :  $\mu_h\tau_h = 1.2 \times 10^{-4} \text{ cm}^2/\text{V}$ . We measured  $\mu\tau$  in the same way for  $\text{PbCl}_2$ , in this case both for bulk and surface electrode geometries. Bulk and surface electrode geometries means electrodes at two opposite sides and at the same (illuminated) side of the crystal, respectively. The results are shown in table I, together with the results of others on related substances. All measurements were at liquid nitrogen temperature except for  $\text{PbI}_2$ . For this substance the room temperature value is shown, obtained by multiplying  $\mu_h$  and  $\tau_h$  as measured by Henisch *et al.*<sup>8</sup>).

TABLE I

Ranges per unit field ( $\mu\tau$ ) of dominant charge carriers			
Substance	charge carrier	range ( $\text{cm}^2/\text{V}$ )	ref.
KCl	e	$20.0 \times 10^{-8}$	18
KBr	e	$1.31 \times 10^{-8}$	18
RbI	e	$2.69 \times 10^{-8}$	18
AgCl	e	$1.05 \times 10^{-3}$ <sup>1)</sup>	
		$1.8 \times 10^{-6}$ <sup>2)</sup>	17
AgBr	e	$1.03 \times 10^{-4}$	19
$\text{PbI}_2$	h	$6 \times 10^{-4}$	8
$\text{PbBr}_2$	h	$1.2 \times 10^{-4}$	this work
$\text{PbCl}_2$	h	$4 \times 10^{-4}$ <sup>3)</sup>	this work
		$0.3 \times 10^{-4}$ <sup>4)</sup>	

1) air-grown; 2) vacuum-grown; 3) surface; 4) bulk

*Spectral response.* The relative spectral response of the photoconductivity of  $\text{PbCl}_2$  showed a peak at 248 nm (fig. 4). The shape and width of this peak could not be determined accurately because the lamp used has only a few lines of weak intensity in this spectral region. However, it is clear that a response at the absorption edge, which is present in  $\text{PbBr}_2$ , is absent in  $\text{PbCl}_2$ . Therefore, the first absorption band in  $\text{PbCl}_2$  (the first band from the right in fig. 6) is not due to an excitation of an electron into the conduction band. There are two other possibilities. Firstly, it can be a localized excitation of the  $\text{Pb}^{++}$  ion (*e.g.*  $6s^2 \ ^1S_0 \rightarrow 6s6p \ ^1P_1$  or  $\ ^3P_1$  in isolated ion notation). Secondly, it can be due to the creation of an exciton, this being consistent with the speculation made by Best<sup>20</sup>). An excited  $6s6p$  state like  $\ ^3P_1$  – provided it has a sufficient lifetime – might give an ESR signal. However, such a signal was not observed<sup>21</sup>). In both substances we ob-

served an intense luminescence if the crystals at liquid nitrogen temperature were irradiated with photons in the fundamental absorption. This luminescence was blue and orange for the  $\text{PbCl}_2$  and  $\text{PbBr}_2$  crystals, respectively. We tentatively postulate that both are of the same nature, *i.e.* due to the annihilation of an exciton.

The shift of the absorption edge\* as a function of pressure is the same for  $\text{PbCl}_2$  and  $\text{PbBr}_2$ <sup>22)</sup>, as was to be expected from the similar crystal structure. This behaviour of the pressure shift indicates a same band structure for both crystals.

In the light of these arguments it seems possible that the first absorption band in both substances must be caused by the creation of an exciton. Then, the photoconductivity response still present in this region in  $\text{PbBr}_2$  is caused by free hole production as the result of the decomposition of the created exciton at a lattice imperfection. The imperfection concentration is increased by the irradiation which causes an increase in the photoconductivity response at  $\lambda = 345$  nm. This response is caused by photons which penetrate relatively deeply into the crystal and, therefore, is less sensitive to changes at the surface. As the photodecomposition is concentrated at the surface, this decomposition has a considerable influence on the response in the region of 240 nm, because this response is caused by strongly absorbed photons. These photons possibly create free electrons and holes. We know that the latter have a longer range, and therefore conclude that the trapping of holes near the surface is enhanced by the changes caused by irradiation, or, more precisely, by the lead particles formed upon irradiation at room temperature.

Irradiation produced a remarkable decrease in the response at  $\lambda = 365$  nm. This decrease seems to be connected with the observation that the absorption near the absorption edge is diminished after very short irradiation times<sup>12)</sup>.

We have to compare these results with the optical absorption measurements by Kojima and Yanada<sup>23)</sup> on  $\text{PbCl}_2$ . Layers of  $\text{PbCl}_2$  evaporated in vacuum showed a gradual change of the fundamental absorption band upon exposure to moist air. The maximum of the first absorption band shifted to longer wavelength and the absorption at the long wavelength side increased. Adsorbed water apparently caused this phenomenon. In  $\text{PbBr}_2$  a decrease of the optical absorption at the long wavelength side of the absorption edge due to the removal of water from the surface presumably causes this change in photoconductivity response at this wavelength.

We observed (fig. 4) the onset of a weak photoconductivity at longer wavelengths (400–600 nm), after irradiating  $\text{PbBr}_2$  at room temperature.

\* There are indications that the absorption edge of  $\text{PbBr}_2$  is exponential<sup>24)</sup> as is the case in  $\text{PbI}_2$ <sup>9)</sup>. From this phenomenon, however, no detailed information can be gained concerning the fundamental process<sup>25)</sup>.

Possibly this is due to the release of electrons from colloidal lead formed, in agreement with the so-called photo-oxidation experiments. In photo-oxidation (ref. 12, p. 78) a bleaching of the colloid band occurred when a  $\text{PbCl}_2$  crystal irradiated in vacuum was given a further dose of 365 nm light in air. Supposedly, this light causes the excitation of electrons from the lead metal into the conduction band. In the photo-oxidation these electrons are trapped by the oxygen molecules adsorbed on the surface.

*Conclusions.* The lead halides show some interesting photoconductive properties. The results have contributed to a better understanding of the mechanism underlying the photochemical decomposition of these crystals. It was found that in  $\text{PbBr}_2$  and  $\text{PbCl}_2$  the holes are the dominant mobile charge carriers. The ranges of these holes are in the same order of magnitude as the range of the electrons in the silver halides (see table I). In the latter substances the photochemical process consists of the transport of electrons and interstitial silver ions<sup>26</sup>). In  $\text{PbBr}_2$  and  $\text{PbCl}_2$  anion vacancies are the mobile lattice defects<sup>10, 11</sup>). We are, therefore, led to the conclusion that the electrical and mass transport part of the photochemical decomposition in  $\text{PbBr}_2$  and  $\text{PbCl}_2$  consists of the transport of holes and anion vacancies, respectively.

From the wavelength dependence of the photoconductivity (fig. 4) we conclude that the first absorption band at the long wavelength side of the fundamental absorption is an exciton band.

*Acknowledgement.* We are indebted to Professor J. H. van Santen for encouraging this work and for many stimulating discussions.

#### REFERENCES

- 1) Verwey, J. F., J. Phys. Chem. Solids **27** (1966) 468.
- 2) Kelder, C., Thesis (Amsterdam, 1954).
- 3) Dawood, R. I. and Forty, A. J., Phil. Mag. **7** (1962) 1633.
- 4) Forty, A. J., Brit J. appl. Phys. **14** (1963) 3.
- 5) Tubbs, M. R., Proc. Roy. Soc. **A280** (1964) 566.
- 6) Dawood, R. I., Forty, A. J. and Tubbs, M. R., Proc. Roy. Soc. **A284** (1965) 272.
- 7) Currie, G. D., Mudar, J. and Risgin, O., Appl. Optics **6** (1967) 1137.
- 8) Henisch, H. K. and Srinivasagopalan, C., Solid-State Comm. **4** (1966) 415.
- 9) Dugan, A. F. and Henisch, H. K., J. Phys. Chem. Solids **28** (1967) 1885.
- 10) Verwey, J. F. and Schoonman, J., Physica **35** (1967) 386.
- 11) De Vries, K. J. and Van Santen, J. H., Physica **29** (1963) 482.
- 12) Verwey, J. F., Thesis (Utrecht, 1967).
- 13) Verwey, J. F., J. Phys. Chem. Solids, to be published.
- 14) De Vries, K. J., Thesis (Utrecht, 1965).
- 15) Hecht, K., Z. Phys. **77** (1932) 235, see also: Mott, N. F. and Gurney, R. W.,

Electronic Processes in Ionic Crystals, 2nd ed. (Dover Publications, Inc., New York, 1964) p. 122.

- 16) Fesefeldt, H., *Z. Phys.* **64** (1930) 741.
- 17) Van Heyningen, R. S. and Brown, F. C., *Phys. Rev.* **111** (1958) 462.
- 18) Huggett, G. R. and Teegarden, K., *Phys. Rev.* **141** (1960) 797.
- 19) Burnham, D. C., Brown, F. C. and Knox, R. S., *Phys. Rev.* **119** (1960) 1560.
- 20) Best, K. J., *Z. Phys.* **163** (1961) 309.
- 21) Arends, J. and Verwey, J. F., *Phys. Status Solidi* **23** (1967) 137.
- 22) Zahner, J. C. and Drickamer, H. G., *J. Phys. Chem. Solids* **11** (1959) 92.
- 23) Kojima, M. and Yanada, T., *Sci. Rep. Tohoku Univ. 1<sup>st</sup> Ser.* **45** (1961) 23.
- 24) Van Peski, A. C. H., Private communication.
- 25) Hopfield, J. J., *Comments on Solid State Physics* **1** (1968) 16.
- 26) Mees, C. E. K. and James, T. H., *The theory of the Photographic Process*, 3rd ed. (The Macmillan Company, New York, 1966).