

## ULTRAVIOLET ABSORPTIONS OF NON-STOICHIOMETRIC LEAD CHLORIDE $\text{PbCl}_2$

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### Synopsis

Tempering evaporated lead chloride films in a nitrogen atmosphere without or with excess lead or chlorine results in extra absorption bands between 268 and 360  $m\mu$  and at about 253  $m\mu$ , and in a change of the existing absorption at 265.5  $m\mu$  (measured at liquid nitrogen temperature). These absorptions are discussed in terms of transitions of electrons near single or clustered chloride ion vacancies.

*Introduction.* Ultraviolet absorption spectra of pure lead chloride, fig. 1, and lead chloride containing an excess of lead or chlorine have been reported by several authors, Hilsch and Pohl<sup>1)</sup>, Fesefeldt<sup>2)</sup>, Gudris<sup>3)</sup> and Kojima<sup>4)</sup>. We reinvestigated the influence of a possible "non-stoichiometry" on the optical properties of lead chloride for vacuum deposited thin films subjected to various treatments. We obtained extra absorptions which could be connected with electrons trapped near a chloride ion vacancy or at a lead ion.

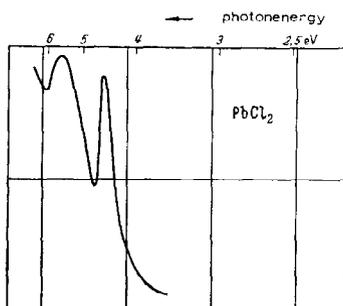


Fig. 1. Absorption constant as a function of photon energy, according to Hilsch and Pohl.

*Experimental technique.* In view of the high value of the absorption coefficient ( $\approx 10^5 \text{ cm}^{-1}$ ) in the wavelength region concerned, thin films with a thickness of 2000-4000  $\text{\AA}$  were used. The films were deposited by evapora-

tion of a lead chloride crystal from a tungsten crucible within a few seconds in a nitrogen atmosphere of about  $10^{-5}$  cm Hg. During evaporation of the film the substrate, an optically polished disc of fused quartz at about 50 mm distance from the crucible was held at an elevated temperature. It appeared from our measurements that the spectrum situated at the long wavelength side of the 270  $m\mu$  absorption of films deposited at or slight above room temperature, shows extra absorptions which alter with time. These aging effects, probably due to recrystallization, could be avoided by heating the substrate at 90°C. This temperature is well above the transition temperature (260°K) at which, according to Best<sup>5</sup>), "amorphous" layers are converted into crystalline ones.

The crystals used were grown by zone refining analytical grade J. T. Baker Chem. Co. lead chloride in a 6 cm Hg pressure chlorine atmosphere. After depositing the film, heating of the film was stopped and after a few minutes pure nitrogen was admitted via a liquid nitrogen trap to the evaporation chamber. The films thus prepared were transferred into the optical transmission cell, again under constant protection of purified nitrogen.

These films on which we have still to do the nonstoichiometry experiments, give quite the same spectra as Kojima<sup>4</sup>) observed for his fresh, dry air exposed, evaporated films. In contrast with Kojima the optical

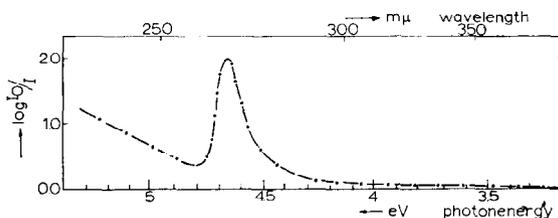


Fig. 2a. Extinction,  $\log I_0/I$ , as a function of photon energy.

absorptions of our films do not change with time, neither in vacuum nor in air. The deposited films give reproducible absorption spectra, fig. 2a. The optical absorptions were measured at 78°K with a Beckmann DK-2A spectrophotometer. We used a disc of polished fused quartz as reference.

*Experiments on lead chloride with excess lead.* By heating a deposited film of lead chloride during 15 minutes in a nitrogen atmosphere of  $10^{-2}$  cm Hg pressure over metallic lead at 330°C, we got after quenching to room temperature the absorptions of fig. 2b. Fig. 2b shows extra absorptions compared with fig. 2a. The extra absorptions in fig. 2b overlap each other considerably.

In other experiments a thin layer of lead was evaporated onto the lead chloride film. The thickness of the lead layer was about 1000 Å, it caused no appreciable extra absorption. By tempering these double layers at various

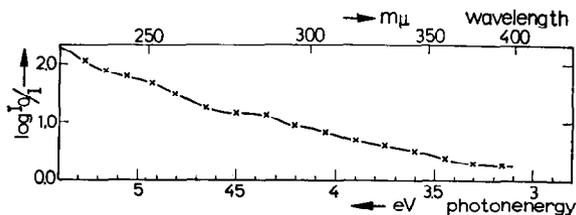


Fig. 2b. Absorption spectrum of a lead chloride film, heated during 15 minutes in a nitrogen atmosphere of  $10^{-2}$  cm Hg pressure over metallic lead at  $330^\circ\text{C}$ .

temperatures, between  $230$  and  $430^\circ\text{C}$  in a nitrogen atmosphere of  $10^{-2}$  cm Hg pressure we found the same absorptions as in fig. 2b, but now successively. We chose the double layer technique for investigating the extra absorptions. Stages in the development of the spectra at  $270^\circ\text{C}$  are given in fig. 3.

Immediately after depositing the lead film over the lead chloride film,

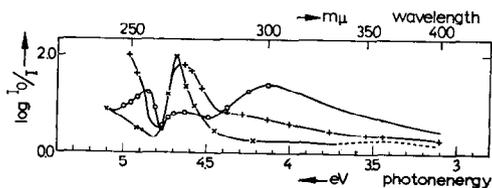


Fig. 3

- a.  $- \times - \times -$ , immediately after depositing the lead film over the lead chloride film.
- b.  $- + - + -$ , after tempering for 50 minutes at  $270^\circ\text{C}$  in a nitrogen atmosphere of  $10^{-2}$  cm Hg pressure.
- c.  $- \circ - \circ -$ , after tempering for 120 minutes at  $270^\circ\text{C}$  in a nitrogen atmosphere of  $10^{-2}$  cm Hg pressure.

we get fig. 3a, which is still identical with the result given in fig. 2a. Tempering for 30 minutes gives us absorptions (not given here) between  $320 \text{ m}\mu$  ( $3.9 \text{ eV}$ ) and  $360 \text{ m}\mu$  ( $3.4 \text{ eV}$ ) with approximately 0.30 extinction.

Tempering for 50 minutes (fig. 3b) shifts the  $4.66 \text{ eV}$  ( $265.5 \text{ m}\mu$ ) absorption slightly to  $4.63 \text{ eV}$  ( $268 \text{ m}\mu$ ). The  $270 \text{ m}\mu$  absorption measured at  $300^\circ\text{K}$  mentioned above, corresponds to the  $265.5 \text{ m}\mu$  absorption at  $78^\circ\text{K}$ . At the long wavelength side a tail develops covering the absorptions between  $3.9$  and  $3.4 \text{ eV}$ . At shorter wavelengths ( $4.9 \text{ eV}$ ) the absorption increases.

When we temper longer (120 minutes) fig. 3c is obtained. The absorption band at  $4.66 \text{ eV}$  is still present. In some experiments this  $4.66 \text{ eV}$  band was found to consist of several close lying sub-bands. There exists an absorption region with nearly  $0.6 \text{ eV}$  width at about  $4.13 \text{ eV}$  ( $300 \text{ m}\mu$ ). The position of this maximum can be influenced by the quenching rate. For high rates it lies near  $4.45 \text{ eV}$  ( $280 \text{ m}\mu$ ) and for low rates near  $4.10 \text{ eV}$  (about  $300 \text{ m}\mu$ ).

There is also a pronounced maximum at 4.88 eV (253  $m\mu$ ). We did not measure at energies higher than 5.45 eV (228  $m\mu$ ).

Longer tempering broadens and lowers the absorptions at 4.88 eV, 4.66 eV and 4.13 eV. The 4.13 eV absorption is shifted considerably to lower energies (about 3.4 eV).

During the tempering process the total extinction of the film decreases, presumably by evaporation of the film.

Irrespective of the temperature chosen for tempering, spectra of the type of fig. 3 are obtained. At 230°C reaching the stage of figure 3c takes about 10 hours; at 430°C, however, only 7 minutes are required.

*Tempering of lead chloride films.* Essentially the same absorptions are obtained when we temper films of only lead chloride in a nitrogen atmosphere of  $10^{-2}$  cm Hg pressure. However, we did not observe the absorptions between 320 and 360  $m\mu$ , which were found in the double layer systems in the first stage of tempering (cf. fig. 3). See fig. 4.

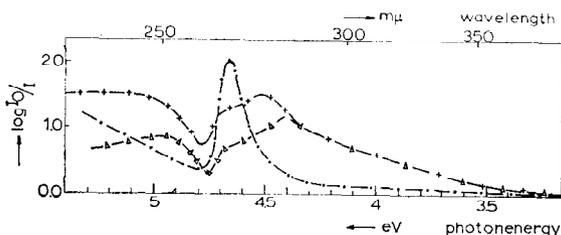


Fig. 4

- a. — ○ — ○ —, absorption spectrum of a lead chloride film immediately after depositing.  
 b. — + — + —, after tempering for 10 minutes at 330°C in a nitrogen atmosphere of  $10^{-2}$  cm Hg pressure.  
 c. — △ — △ —, after tempering for 19 minutes at 330°C in a nitrogen atmosphere of  $10^{-2}$  cm Hg pressure.

We examined the chemical composition of lead chloride films at different stages of tempering. For films showing absorptions at 4.88 eV, 4.66 eV and 3.4 eV, we detected at most 0.5 at% excess lead. For shorter tempering times no stoichiometry defect could be observed.

*Experiments on lead chloride and lead films exposed to chlorine.* Films of lead chloride were tempered at various temperatures between 230 and 430°C in a chlorine atmosphere of 0–1.2 atmospheres. The results are given in fig. 5. Again the absorptions are very similar to the ones shown in figs 3 and 4. Tempering lead films in chlorine atmospheres gives the same result (not given here). We do not agree with Gudris *e.a.*<sup>3)</sup>, that tempering lead chloride films in chlorine atmospheres causes characteristic, excess chlorine connected, absorptions.

The lead chloride films heated in chlorine show before vanishing by evaporation, the spectrum of fig. 5c. The only difference with earlier results is a shift of the 4.88 eV absorption to 4.83 eV. It is not sure, however, whether the shift is significant.

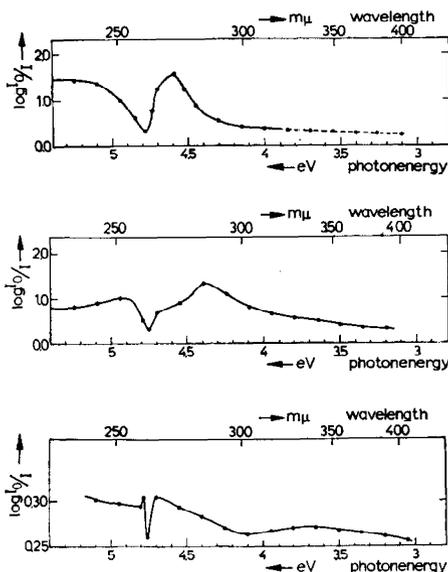


Fig. 5a. After tempering for 8 minutes at 330°C in a chlorine atmosphere of 45 cm Hg pressure.

Fig. 5b. After tempering for 15 minutes at 330°C in a chlorine atmosphere of 45 cm Hg pressure.

Fig. 5c. After tempering 40 minutes at 430°C in a chlorine atmosphere of 45 cm Hg pressure.

*Discussion.* Tempering the films, “shifts” the 4.66 eV absorption to 4.63 eV. This could indicate further crystallization. But in reality this shift is caused by a decrease of the 4.66 eV absorption and the formation of a new one at 4.63 eV. Moreover, there appear extra absorptions at 4.88 eV and at energies lower than 4.63 eV (cf. fig. 3b). Therefore we believe that we have to do with chemical reactions inside the film rather than with a crystallization process.

When comparing the absorption spectra of on the one hand pure lead chloride films and on the other lead chloride films covered with an evaporated lead film, it appears that before tempering virtually no difference can be detected. After short tempering times the samples with an extra lead film show relatively weak absorptions between 320 and 360  $m\mu$ , which are not shown by pure lead chloride films. On tempering further these extra absorptions are covered by the optical extinction of the tail of the “4.63” eV absorption and from now on the behaviour of all films is the same.

From X-ray investigations by Braekken<sup>6)</sup> and Sahl<sup>7)</sup>, it appears that the chloride ions in  $\text{PbCl}_2$  surrounding a given lead ion do not occupy positions at the same distance from this lead ion. The chloride ions at the largest distance are surrounded by four lead ions, whereas the closest chloride ions are surrounded by five lead ions. The optical absorption at about 4.66 eV shows a partly resolved structure which might be connected with this rather unsymmetrical arrangement. In analogy with alkali and silver halides Best<sup>5)</sup> has suggested the 4.66 eV absorption to be an exciton absorption, but on the other hand it might also be ascribed to a characteristic  $6s^2 \rightarrow 6s6p$  transition inside the lead ion.

The difference in bond length, the high concentration of lattice defects and the low value, (0.3 eV<sup>8)</sup>, of the energy for chloride ion vacancy migration, are the basis on which reactions involving optical absorptions in the lattice have to be discussed.

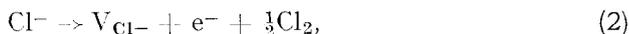
From chemical investigations with about 0.2% accuracy on films of pure lead chloride about ten times thicker than the ones we used for optical measurements, it appeared that when these films are tempered during 60 minutes at 330°C under the same conditions as used for optical purposes an excess of at most 0.5 at% lead is detectable. This stage, i.e. when practically no film is left, is characterized by the extra absorptions at 4.88 eV, 4.66 eV and 3.4 eV. Tempering shorter at the same temperature did not result in measurable amounts of excess lead or chlorine.

It appears that tempering gives rise to a stoichiometry defect of chlorine. On the other hand the extra absorptions are already appreciable at relatively short tempering times. We think therefore that the extra absorptions observed are connected with a deviation from stoichiometry that does not yet seriously affect the intrinsic optical properties of the lead chloride lattice. The stoichiometry defect gives rise, far before chemical detectability, to considerable changes in the optical absorption spectrum of  $\text{PbCl}_2$ .

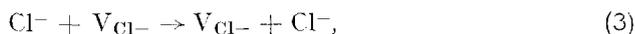
The decomposition of lead chloride can be described by the over-all reaction equation



It is reasonable to suppose that chlorine leaves the lattice near the surface, according to



(here  $V_{\text{Cl}^-}$  stands for a chloride ion vacancy), whereas, according to



chloride ions are subsequently supplied from the bulk. The vacancies formed by (2) migrate into the bulk of the material. The electrons can be

trapped in different ways. For instance at a chloride ion vacancy, which is effectively a single positive charge,



Such a trapped electron might be called a colour centre. Obviously there are different colour centres because the chloride ions occupy different crystallographic positions. Moreover, an electron can be localized, according to

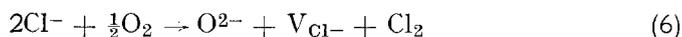


Assuming that a missing chloride ion affects the absorption connected with nearest and next-nearest neighbours, it is found that one missing chloride ion influences the absorption of at least 28 to 40 chloride ions. When the 4.66 eV absorption is connected with the specific surrounding of a lead ion by chloride ions, then it is clear that this absorption must be influenced greatly by processes (2) and (3).

It is evident from figs 3b, 3c, 4b and 4c that the 4.66 eV absorption is directly affected and has disappeared by about half its original value when absorptions at about 4.88 eV and at energies lower than 4.63 eV appear. In our experimental method the absorptions between 4.63 and 4.1 eV are always accompanied by an absorption at about 4.88 eV. By the heating process the place of the 4.88 eV absorption is not influenced, only its extinction. This is not the case with the absorptions at energies lower than 4.63 eV which shift to lower energy and widen.

Let us now try to explain the extra absorptions observed in terms of defects mentioned above. The absorption in the 4.66 eV region might be essentially the 4.66 eV absorption of pure PbCl<sub>2</sub>, slightly modified by the presence of chloride ion vacancies. The extra absorptions at 4.63–4.1 eV might be ascribed to colour centres of the  $V_{\text{Cl}^-} \cdot e^-$  type, whereas the absorptions at 3.7–3.5 eV are probably connected with higher associates of simpler defects. The extra absorptions at 4.88 eV might tentatively be ascribed to a band-band transition influenced by the presence of an anion vacancy.

The spectra Kojima<sup>4)</sup> obtained by exposing his deposited lead chloride films to moistened room air, look like ours. We believe that Kojima used an experimental technique different from ours. Tentatively it may be supposed that his films react with oxygen, according to



When the concentration of vacancies becomes greater, it may cause effects as we noted.

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