

## EPR AND LUMINESCENCE OF u.v. IRRADIATED $\text{PbCl}_2$ AND $\text{PbBr}_2$ CRYSTALS

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Results are presented of EPR-measurements on  $\text{PbCl}_2$  and  $\text{PbBr}_2$  single crystals at low temperatures.  $\text{Pb}^+$ ,  $\text{Pb}^+$ -pairs and colloidal lead particles are formed during u.v. irradiation. The concentration of the  $\text{Pb}^+$ -pairs increases after the irradiation is stopped. The red luminescence of both lead halides is associated with the  $\text{Pb}^+$  centres.

### 1. INTRODUCTION

IF LEAD CHLORIDE and lead bromide crystals are exposed to u.v. radiation at room temperature a photochemical change occurs, which has been ascribed<sup>1</sup> to the formation of colloidal lead particles and halogen. Verwey<sup>1</sup> proposed a mechanism for this change according to which halogen molecules are formed at and desorb from the crystal surface, leaving two anion vacancies diffusing into the crystal. Electrons are trapped by the anion vacancies. The  $F$ -centres created in this way are supposed to be instable, producing associates of the type  $(V_X \cdot \text{Pb}^+)^x$ . These associates then disproportionate giving lead colloids and  $\text{Pb}^{2+}$  ions. Room for the lead colloid is provided by annihilation of anion frequencies

Crystals irradiated at 100 K do not show a photochemical change in optical absorption. If the crystal is warmed up, an absorption band develops which is ascribed to the colloid. This band shifts to longer wavelengths and is bleached on further warming to room temperature.<sup>1</sup>

At temperatures below 200 K  $\text{PbCl}_2$  and  $\text{PbBr}_2$  crystals show photoluminescence. The present paper deals with the EPR investigation of the luminescence centres created by u.v. irradiation in the temperature region 10–200 K.

### 2. EXPERIMENTAL

In view of the hygroscopic character of  $\text{PbCl}_2$  and  $\text{PbBr}_2$ , the single crystals were prepared under circumstances in which adsorption and inclusion of water are avoided. Details of the preparation were published elsewhere.<sup>2</sup> Analyses by emission spectroscopy show that the impurity content is very small.<sup>3</sup> For our investigations platelets of 2–4 mm thickness were cleaved from large single crystals parallel to the (001)-plane. To prevent premature formation of photolysis products, the  $\text{PbBr}_2$  samples were cleaved and mounted in the dark ( $\text{PbBr}_2$  is more sensitive to daylight than  $\text{PbCl}_2$  because of a smaller bandgap).

The EPR measurements have been carried out with an X-band spectrometer built in this laboratory. Its sensitivity is about  $5 \cdot 10^{12}$  spins/G. The circular  $TE_{011}$  EPR-cavity is part of the cryostat and is provided with windows to allow u.v. irradiation of the sample. The sample is mounted in the centre of the evacuated cavity and can be rotated about an axis perpendicular to the static magnetic field  $\vec{H}$ . Details of the apparatus will be published elsewhere.<sup>4</sup> The microwave frequency is measured with an HP 5257 A transfer oscillator. An AEG NMR gauss-meter is employed to measure  $|\vec{H}|$ . Due to the different locations of NMR-probe and sample, the accuracy with which  $g$  values can be determined is limited to  $1:10^4$ .

### 3. THE EPR RESULTS

At room temperature no EPR signals are observed in our samples before, during, or after irradiation.

In  $\text{PbCl}_2$  at 77 K very weak signals are found during irradiation (wavelength 260 nm, intensity about  $10^{16}$  photons  $\text{cm}^{-2}\text{sec}^{-1}$ ). After the irradiation has been interrupted, the strength of this signal increases with time. The spectrum (spectrum 'A') is reproduced in Fig. 1. Repeated irradiation with

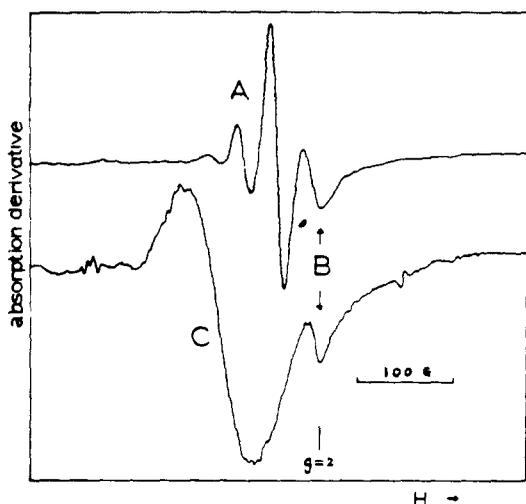


FIG. 1. Typical recorder-tracings of the A, B and C absorption derivative versus magnetic field strength in  $\text{PbCl}_2$  at 9.4 GHz and 77 K (upper trace) and 10 K (lower trace).

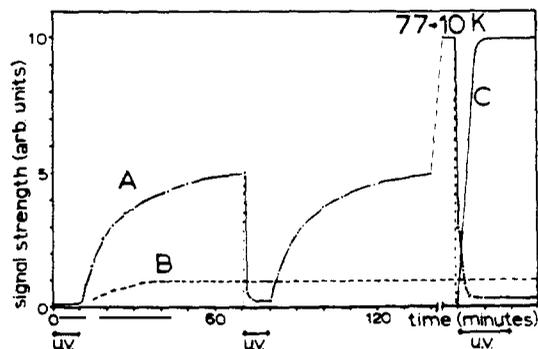


FIG. 2. Strength of the A, B and C EPR signals in  $\text{PbCl}_2$  as a function of time and irradiation history at 77 K and at 10 K.

the same intensity reduces the strength of the A signal by a factor of about 30. This is a reproducible process as indicated in Fig. 2. Repeated irradiation with an intensity of about  $10^{14}$  photons  $\text{cm}^{-2}\text{sec}^{-1}$  gives only a very slight decrease of the A signal strength.

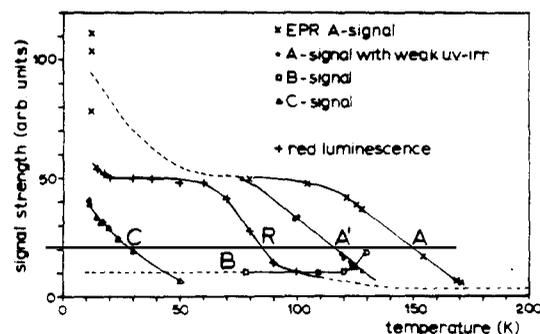


FIG. 3. Temperature dependences of the red luminescence (R), the EPR signal A without and during (A') weak u.v. irradiation ( $10^{14}$  photons  $\text{cm}^{-2}\text{sec}^{-1}$ ), and the EPR B and C signals in  $\text{PbCl}_2$ .

The signal A becomes somewhat stronger upon cooling down to 10 K, but now u.v. irradiation reduces its strength irreversibly (cf. Fig. 2). A new signal develops (signal 'C') which increases in strength up to a certain level in some minutes of irradiation. The A signal only reappears after warming up to 77 K and waiting for one hour. After warming up the sample to room temperature (bleaching) and subsequent cooling down again to 77 K, no EPR signals are found at 77 K. However, irradiation produces the same results as described in the preceding paragraph. When after bleaching the sample is cooled down directly to 10 K, subsequent irradiation produces the C and the B (see below) signals, and possibly a weak A signal. After subsequent warming up to 77 K the A signal returns without further irradiation. The entire process is completely reproducible and is observed in most of the  $\text{PbCl}_2$  samples.

Following the first irradiation usually a 'B' signal develops (cf. Figs. 1 and 2). Its strength does not change significantly as a function of time or irradiation intensity.

The temperature dependences of the three signals are given in Fig. 3.

The *A* and *B* signals have also been reported by Arends and Verwey.<sup>5</sup> Our interpretation, however, is different. The *C* signal and the kinetics of the *A*, *B* and *C* signals are reported here for the first time.

**Profile of the *A* signal:** The *A* signal consists of five equidistant Gaussian shaped lines. Their distance is 35 G which is independent of the microwave frequency and the angle between  $\vec{H}$  and the crystal axes. The ratios of the line-strengths vary slightly with time and irradiation history, but are on the average 0.03:0.24:1.00:0.22:(?). (Accuracy is  $\pm 0.01$ ; the last component is usually hidden in the *B* signal.) The peak to peak width of these lines is 15 G. The *g* value of the central line is anisotropic and its angular dependence is given by  $g = 2.0665 (1 - 0.0310 \cos^2 \theta)$  when  $\vec{H}$  is rotated in the (001)-plane.

The *B* signal is an isotropic line with a *g* value of 2.0024 and a peak to peak width of about 18 G. This signal usually has a pronounced asymmetric line shape, which resembles the line shapes calculated by Webb<sup>6</sup> for conduction electrons in spherical metal particles.

The *C* signal is a rather broad (72 G) Gaussian shaped line. The *g* value is slightly angular dependent:  $g = 2.064 (1 - 0.008 \cos^2 \theta)$  when  $\vec{H}$  is rotated in the (001)-plane.

The EPR signals of PbBr<sub>2</sub> appeared to be very weak, during as well as after u.v. irradiation. An *A*-type signal could be identified among a number of other lines which possibly could be ascribed to trapped holes. This *A* signal shows qualitatively the same behaviour as in PbCl<sub>2</sub>. The *g* value of the central line of the bromide *A* signal is about 2.053 while no angular dependence could be detected. Also the *B* signal shows up in several PbBr<sub>2</sub> samples.

#### 4. DISCUSSION

We ascribe the *A* signal to pairs of Pb<sup>+</sup> ions with isotropic exchange coupling. The Pb<sup>+</sup> ion has a ( $6s^2p^1$ ) ground state ( $S = \frac{1}{2}$ , while the orbital

momentum is quenched). The central line of the *A* signal originates from pairs with only the <sup>204</sup>Pb, <sup>206</sup>Pb and <sup>208</sup>Pb isotopes. These isotopes, together 78.6% abundant in our crystals\*, do not possess a nuclear spin. The satellites result from hyperfine interaction with the nuclei of the 21.4% abundant <sup>207</sup>Pb isotope ( $I = \frac{1}{2}$ ,  $\mu_N = 0.5837$ ). One expects two satellites on both sides of the central line, yielding an equally spaced five line spectrum with intensity ratios 0.018: 0.266: 1.000: 0.266: 0.018. This agrees well with our experimental findings. The small discrepancy between the theoretical intensity ratios of the Pb<sup>+</sup> pair spectrum and the measured ratios is due to the presence of single Pb<sup>+</sup> ions. A signal originating from single Pb<sup>+</sup> ions would result in a spectrum of three lines, coinciding with the central line and the two outermost satellites of the pair spectrum and with intensity ratios 0.136: 1.000: 0.136.

Symmetry considerations in conjunction with the angular dependence measurements suggest that the Pb<sup>+</sup> pairs are oriented parallel to the [100]-axis. Other types of pairs have various orientations in the crystal lattice. Their occurrence would result in a splitting of the *A* signal for most directions of  $\vec{H}$ , which has not been observed.

We propose that the pairs are created in the following way: The u.v. irradiation creates electron-hole pairs. The holes are rather mobile ( $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$  at 77 K).<sup>1</sup> The electrons will be trapped at various trapping sites, finally creating Pb<sup>+</sup> centres.

Those trapped electrons will hop randomly until they are stabilized in a Pb<sup>+</sup>-pair near hole centres (possibly accommodated in a Cl<sub>3</sub><sup>-</sup> - or Br<sub>3</sub><sup>-</sup>-complex). The hopping will occur preferentially in the [100]-direction, because in this direction the lead-to-lead distances are shortest.<sup>8</sup> There will be a distant distribution of the photoelectrons over the various traps and the conduction band as a function of irradiation intensity, leading to small Pb<sup>+</sup> signals during irradiation. After stopping the irradiation, the higher traps are

\* We thank Dr. E.H. Hebeda of the Z.W.O. Laboratory for Isotope Geology in Amsterdam for carrying out the analysis.

gradually emptied, leading to growth of the Pb<sup>+</sup>-pair signal.

In accordance with Arends and Verwey<sup>5</sup> the *B* signal is supposed to be due to conduction electrons in metallic lead particles. We suppose that Pb<sup>0</sup>-atoms are formed due to disproportionation of the Pb<sup>+</sup>-pairs at sites in the crystal where dislocations are present. (Dislocations are probably abundant under the surface due to cleaving<sup>9</sup> and it should be borne in mind that the u.v. irradiation penetrates only about 0.3 μ into the crystal.<sup>3</sup>) Clustering of lead atoms is supposed to occur by slip along dislocations.<sup>10</sup> The increase of the *B* signal at higher temperatures (see Fig. 3) can be understood with the mechanism mentioned by Verwey (cf. section 1).

About the *C* signal we remark that the positive shift ( $\Delta g = +0.058$ ) of the *g* value with respect to the free electron value indicates that the centre concerned could carry a hole.

## 5. COMPARISON WITH THE LUMINESCENCE RESULTS

In the temperature region 10–200 K, PbCl<sub>2</sub> as PbBr<sub>2</sub> single crystals show four emission bands under excitation with u.v. viz., one in the u.v. part of the spectrum, a second one in the blue, a third one in the yellow and a fourth one in the red. The u.v. emission has been attributed to the recombination of cation excitons.<sup>3,7</sup> The yellow emission of PbCl<sub>2</sub> exists at very low temperatures only and is quenched above 40 K. At 77 K in PbCl<sub>2</sub> as well as in PbBr<sub>2</sub> the yellow emission is observed only after prolonged irradiation (one or

two hours). On the ground of temperature dependence measurements the yellow luminescence is associated with the EPR signal *C*.

For PbCl<sub>2</sub> and PbBr<sub>2</sub> the temperature dependences of the blue emissions are quite different. The blue emission of PbBr<sub>2</sub> is quenched above 30 K whereas that of PbCl<sub>2</sub> is constant up to 110 K and decreases in the region 110 → 200 K. The EPR signal *A* was measured in both halides at 77 K, as well as at 10 K. Therefore, the blue luminescence is not likely to be due to excitation and decay of the centre associated with the *A* signal.

The red emissions of both lead halides are present in the temperature region 10–200 K. We measured the temperature dependence of the *A* signal in PbCl<sub>2</sub> without irradiation as well as during a low intensity irradiation (see Fig. 3, signal *A* and *A'*). The weak irradiation shifts the fall-off of the *A* signal to lower temperatures. The temperature dependences of the red luminescence of PbCl<sub>2</sub> and of the *A* signal agree rather well, taking into account that the luminescence measurements also require u.v. irradiation. This suggests that the red luminescences can be ascribed to excitation and decay of the centres that are responsible for the EPR signal *A*.

Further work on these phenomena is in progress.

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Es werden Ergebnisse mitgeteilt von EPR-Messungen an  $\text{PbCl}_2$ - und  $\text{PbBr}_2$ -Einkristallen bei niedrigen Temperaturen.  $\text{Pb}^+$ ,  $\text{Pb}^+$ -Paare und kolloidale Bleiteilchen werden formiert während u.v.-Bestrahlung. Die Konzentration der  $\text{Pb}^+$ -Paare wächst nach Beendigung der Bestrahlung. Die rote Lumineszenz von beiden Bleihalogeniden wird assoziiert mit den  $\text{Pb}^+$ -Zentren.