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# FLASH PHOTOLYSIS OF Q-PARTICLES OF $Cd_3P_2$ IN AQUEOUS SOLUTION

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Colloidal solutions of Q-$Cd_3P_2$ of different mean particle size were flashed and the changes in optical absorption recorded. An absorption band at long wavelengths in the visible and near-infrared is attributed to surface-trapped holes. A bleaching band close to the onset of absorption is attributed to excess electrons on the particles. Both bands shift to longer wavelengths with increasing particle size. These light-induced changes have lifetimes measured in seconds. Multiple flashing leads to the formation of small amounts of Cd metal on the colloidal particles.

## 1. Introduction

Cadmium phosphide, $Cd_3P_2$, is a black semiconductor with a band gap of 0.52 eV which has recently been prepared in the form of extremely small colloidal particles in aqueous solution [1]. These small particles show drastic size quantization effects in their optical properties due to the spatial confinement of the charge carriers which are generated following light absorption [2]. In the present communication, a flash photolysis study is described dealing with changes in optical absorption caused by the presence of charge carriers on the $Cd_3P_2$ particles.

## 2. Experimental

The cell used in flash experiments had an optical path length of 6 cm and a thickness of 0.7 mm. The xenon flash lamp and the cell were located at the two focuses of an elliptical cavity. The lamp was triggered by a spark-gap using a 4 μF/10 kV capacitance. A 100 W quartz halogen lamp was used to produce the analyzing light beam. The signals were detected with a photomultiplier EMI 9558 and recorded with a transient recorder DL905 (Data Lab., England). The flash had a half-time of 9 μs and the energy was approximately 100 J/pulse.

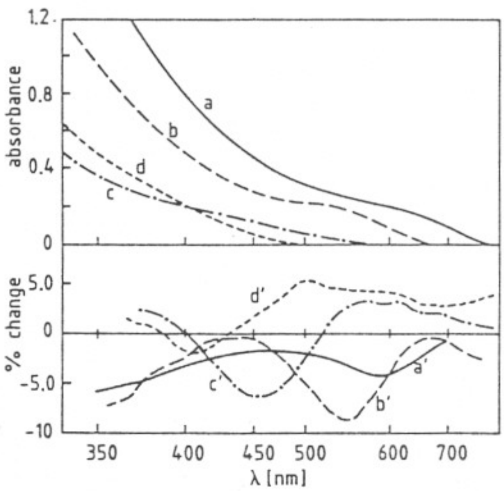


Fig. 1. Upper part: absorption spectrum of deaerated $Cd_3P_2$ solutions of different colour: (a) dark red, (b) red, (c) green, (d) yellow. Decreasing particle size in the order (a) → (d). Lower part: optical changes 5 ms after the light flash.

## 3. Results and discussion

The upper part of fig. 1 shows the absorption spectrum of deaerated $Cd_3P_2$ solutions containing particles of different size. As the mean size decreases from sample (a) to (d), the onset of light absorption is shifted to shorter wavelengths. The lower part of the figure shows the absorption changes which were observed 5 ms after the light flash. Depending on the wavelength either absorption or bleaching signals were observed. The minimum shifts to longer wavelengths in going from curve (d′) to (a′), i.e. with increasing particle size. Sample (d′) has a very broad absorption band at longer wavelengths. The band is red-shifted in the case of sample (c′) and it seems that the absorption band for samples (b′) and (a′) lies in the infrared.

Similar absorption changes were observed in a previous pulse radiolysis study where free radicals such as oxidizing OH radicals [3] or reducing hydrated electrons [4] were produced in the bulk solution and subsequently reacted with the colloidal particles. For $Cd_3P_2$ and CdS, OH radicals were found to "inject" a positive hole onto the particles, and this process was accompanied by the build-up of a broad absorption band in the visible which was red-shifted with increasing particle size. Hydrated electrons, on the other hand, were found to produce bleaching in their reaction with the colloidal particles, this bleaching being confined to a wavelength range of about 100 nm below the onset of the absorption of the particles. Because of these similarities the absorption changes in fig. 1 are attributed to positive holes and electrons which still reside on the colloidal particles after the light flash. Excess electrons on CdS particles which lived for several 100 μs after the flash have also been observed by Albery et al. [5].

These excess charge carriers on the $Cd_3P_2$ particles are rather long-lived. The 550 nm absorption signal of sample (d′), for example, still had 20% of its original strength after 10 s. It seems doubtful that the hole–electron pair produced in a particle could survive for so long without recombination taking place. One is therefore inclined to believe that some $Cd_3P_2$ particles possess a single electron or a single hole after illumination. It has recently been observed at the Hahn-Meitner-Institut in Berlin that electrons are emitted from $Cd_3P_2$ [6] as was earlier found in the flash photolysis of CdS [7]. The emitted electrons could be seen as hydrated electrons which in turn reacted with $Cd_3P_2$ particles. Electron emission could be a mechanism which leads to particles with one excess charge carrier. This mechanism is corroborated by the results of some experiments we carried out with solutions containing $N_2O$. It was found that the band at longer wavelengths was increased by almost 100% while the bleaching band was weaker

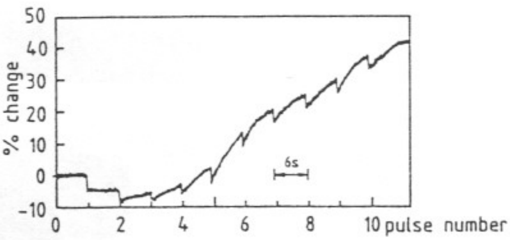


Fig. 2. Changes in optical absorption after illumination of colloid c with a train of flashes.

by 30%. Hydrated electrons are known to react with $N_2O$: $e_{aq}^- + N_2O + H_2O \rightarrow N_2 + OH^- + OH$, the OH radicals subsequently injecting positive holes onto the colloidal particles.

Experiments were also carried out with trains of light pulses, the interval between the flashes being about 10 s. Such experiments have recently been reported for the radiation-induced reaction of hydrated electrons with colloidal CdS particles [4]. Fig. 2 shows the changes that take place in the 450 nm absorption of sample (c). It is seen that the first flash produces bleaching. The second flash produces additional bleaching, but part of this bleaching recovers until flash No. 3 is applied. Each following flash produces bleaching, but the absorption increases between the flashes, the result being a net increase in absorption. The bleaching is attributed to the action of electrons produced in a flash and surviving in traps afterwards. When electrons are accumulated on a particle $Cd^{2+}$ is reduced to $Cd^0$. It is known that a cadmium metal layer on a colloid produces an increase in absorption at all wavelengths [8]. In fact, the absorption spectra of our solution showed this increase after ten pulses had been applied. The cadmium metal rapidly dissolved admission of air to the illuminated solution (as known from previous work [8]).

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