broad band at 3428 cm^{-1} which we think may be due to some OH groups in the synthetic sample, because if they were due to H$^-$ ions they should have been very weak. The bands compare in intensity with the bands obtained with sample A which is 3·3 cm thick.

The spectra were recorded on a Hilger U.V.Spec. photometer and a Hilger double beam H 800 spectrophotometer with Merton grating containing 7500 lines per inch and a selenium polarisor Lithium doped quartz was prepared by heating. quartz with lithium in an autoclave and was examined in the form of a thin disc prepared with KBr as base. All othes pieces were ground and polished except A which was used as such.

We thank Dr. Kats of Philips Research Laboratories for sending sample B and Dr. Dodd and Dr. Ballman of Bell Telephone Laboratories for sending us four synthetic quartz samples stated above.

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The photolysis of lead chloride and lead bromide

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1. Introduction

THE lead halides decompose upon irradiation with ultraviolet or even visible light.[1-4] We started the investigation of the darkening of lead chloride and lead bromide by measuring the optical absorption of monocrystals. Although there might be differences in the mechanism, the result of the photochemical decomposition of lead chloride seems to be identical with the 'print-out' effect in the silver halides.[5,6] An attempt was made to calculate the quantum efficiency for the photo product formation during the initial stage of photolysis.

2. Experimental

Lead chloride darkened after irradiation with light in the region of the fundamental absorption of the crystal. This brownish black coloration appeared in the absorption spectrum of the irradiated crystal as a very broad absorption region, however, without any structure. This can be seen in Fig. 1 which shows the optical density of a lead chloride monocrystal as a function of wavelength before and after irradiation. The crystal was irradiated at room temperature with a high pressure mercury lamp (Philips H.P.K. 125 W) during 2 hr. The number of photochemical active photons ($\lambda < 300$ *nm*) in the unfiltered radiation was calculated from the specifications of the manufacturer of the lamp. This photonflux F absorbed by the lead chloride is 5×10^{15} photons per cm^2 per sec. Viewing the irradiated crystal through a microscope ($\times 200$) revealed a homogeneous brown coloration only.

The photochemical product is located near the surface as is clear from curve 3 of Fig. 1.

Figure 2 shows in addition an absorption spectrum of a lead bromide monocrystal before and after irradiation.

Figure 3 shows for lead chloride the increase of the optical density at one fixed wavelength $\lambda = 340$ *nm* as a function of irradiation time.

3. Discussion

We assume that the increase of the absorption is due to colloidal lead. On this assumption we can calculate the quantum efficiency for the photochemical reaction. According to the theory of MIE[7] the extinction coefficient K of a dispersion of colloidal metal particles is given by

$$K = T(\lambda)[Me], \qquad (1)$$

where $[Me]$ = volume fraction of metal (cm^3 metal per cm^3)

$$= \frac{MN}{Ld},$$

M = at. wt. of the metal,
N = number of metal atoms per cm^2,
d = density g/cm^3 of the metal,
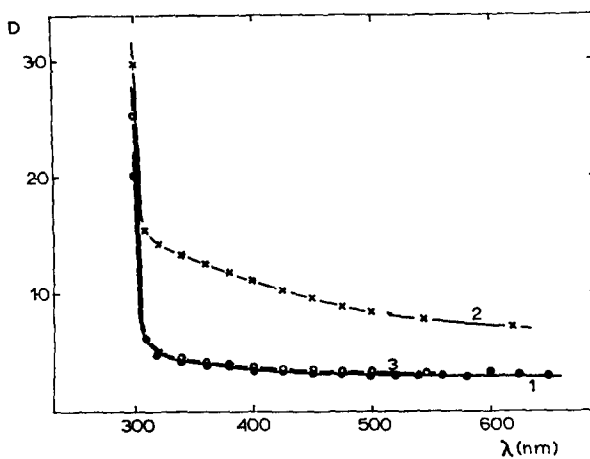L = Avogadro's number.

FIG. 1. Optical density D as a function of wavelength.
1—Polished lead chloride crystal. 2—Same crystal after
2 hr irradiation with a high pressure mercury lamp.
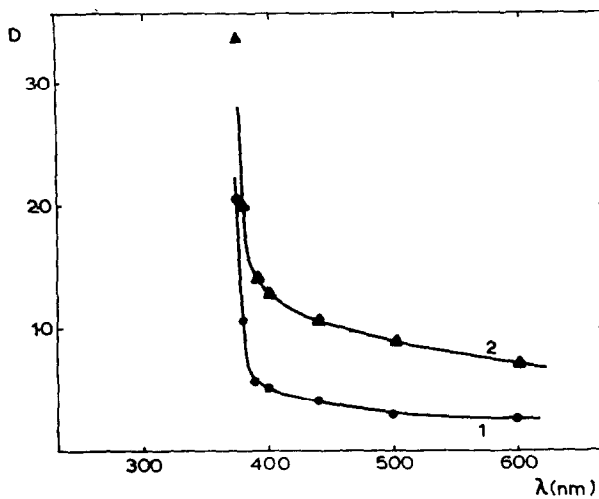3—Etched in concentrated ammonium acetate (0·033
mm removed).

FIG. 2. Optical density D as a function of wavelength.
1—Polished lead bromide crystal. 2—Same crystal after
20 min. irradiation.

For very small particles (diameter small compared with the wavelength of the light in the medium) $T(\lambda)$ is given by[8]

$$T(\lambda) = \frac{36\pi}{\lambda} \cdot \frac{nk/n_0}{[(n/n_0)^2+(k/n_0)^2]^2+[(n/n_0)^2-(k/n_0)^2+1]},$$

(2)

n = index of refraction of the metal,
k = absorption coefficient of the metal,
n_0 = index of refraction of the crystal.

Now we look at the increase of the extinction at one fixed wavelength λ_m as a function of irradiation time (Fig. 3). At the beginning of the photolysis
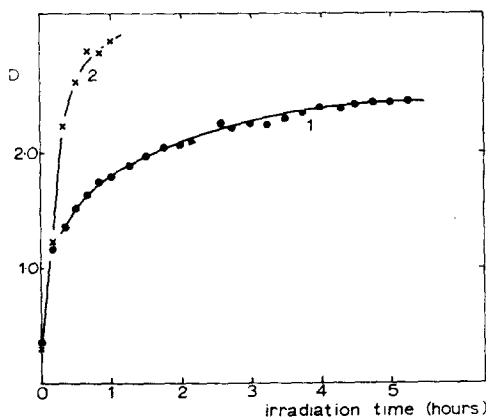

FIG. 3. Optical density D of lead chloride crystals at $\lambda = 340$ nm as a function of irradiation time. 1—Irradiated at a pressure of 10^{-2} mm Hg. 2—Irradiated in a saturated vapour of ethanol.

we have small colloidal particles, so we should be allowed to apply (2) to the first (linear) part of the curve. The slope is given by

$$\frac{dK}{dt} = \frac{T(\lambda)M}{Ld}\eta F,$$

(3)

where
F = number of photons absorbed per cm^2 per sec.,
η = quantum efficiency for the formation of lead.

The photolytic product is located near the surface and so the increase of the optical density D is independent of the thickness of the crystal. The expression for η then becomes

$$\eta = \frac{2\cdot3Ld}{FT(\lambda)M} \cdot \frac{dD}{dt}.$$

(4)

At $\lambda_m = 340$ nm : $n = 1\cdot04,$[9] $k = 2\cdot18,$[10] $n_0 = 2\cdot36.$[11] $F = 5\times10^{15}$ photons/cm^2/sec. For the photolysis of $PbCl_2$ either at a pressure of 10^{-2} mm Hg or in a saturated vapour of ethanol (Fig. 3) $dD/dt = 0\cdot16$ sec^{-1}. Substituting the numerical values in (4) gives $\eta = 0\cdot1$ lead atom per absorbed photon.

4. *Photolysis of silver halides: application of the Mie theory to the work of* SLIKER *et al.*[12,6]

SLIKER[12] gives an analysis of the measurements of MOSER *et al.*[6] concerning the rate of volume photolysis of copper-doped silver chloride. The photo-created electron and hole react with silver ions and copper(I) ions respectively to form silver atoms in aggregates and copper(II) ions on normal lattice sites.

The attenuation of the light ($\lambda_m = 600$ nm) in the crystal is given by[12]

$$-\frac{\partial I_m}{\partial x} = c_4 N_{Cu} I_m,$$

(5)

where
N_{Cu} = number of copper(II) ions per cm^3,
c_4 = parameter determined from the experiments.

As a matter of fact the attenuation comes both from the copper(II) ions and the colloidal silver So

$$c_4 N_{Cu} = AN_{Ag}+BN_{Cu} = (A+B)N_{Cu},$$

since the number of silver atoms N_{Ag} equals the number of copper(II) ions N_{Cu}.

The constant A can be calculated from the Mie theory.

$$A = \frac{T(\lambda)M}{Ld},$$

(6)

where all the symbols have the same meaning as in (3). For $\lambda_m = 600$ nm we calculate (with the necessary constants of silver from Ref. 10) $A = 0\cdot6\times10^{-17}$ cm^2 per Ag-atom.

The constant B can be estimated from the measurements of the optical density of un-irradiated silver chloride crystals doped with copper(II) chloride (Moser c.s., Figs. 5 and 6). This gives $B = 0.6 \times 10^{-17}$ cm^2 per Cu^{++} ion.

We substract this value of B from the experimental value $c_4 = 3.3 \times 10^{-17}$ cm^2 per centre (Ref. 6, Table 4 and Fig. 4). This gives $A_{exp} = 2.7 \times 10^{-17}$ cm^2 per silver atom. We see that the calculated value of A has the right order of magnitude. The difference might be explained by the occurrence of deviations from the idealized model of pure metal particles in a crystal.

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The transformation of γ- to α-arsenic and the susceptibility of polycrystalline arsenic

RECENTLY in this Journal, we reported, *inter alia*, the principal susceptibilities of arsenic and the susceptibilities of polycrystalline arsenic.[1] It was noted that arsenic annealed at 700–800°C for several days and then ground gave susceptibilities that were numerically lower than the polycrystalline susceptibilities calculated from single crystal data. It was inferred that on grinding, the crystallites are cleaved along the 0001 plane, and the resulting 'platelets' tend to lie horizontally in the susceptibility container, leading to low values for the susceptibility. Moreover, we considered the possibility of incomplete transformation of γ— to α—As, which again would result in numerically lower susceptibilities.

Since these explanations were offered, differential thermal analyses have been obtained on γ—As, ground to 200 mesh, in evacuated Vycor tubes with re-entrant thermocouple wells. The transformation to α—As (confirmed by X-ray diffraction) was found to be exothermic, irreversible, and very sharp. The transformation temperature was dependent on heating rate: $292° \pm 3°$C at 0·4 deg/min; $297° \pm 3°$C at 1·0 deg/min; $299° \pm 3°$C at 1·4 deg/min; and $308° \pm 3°$C at 1·9 deg/min. Extrapolation gives a transformation temperature of $288° \pm 3°$C at zero heating rate. Estimated from the area of the DTA signal, the enthalpy of the transformation at the transformation temperature is -25 ± 6 cal/g ($-1·8 \pm 0·4$ Kcal/g atom).

Obviously the suggestion that low susceptibility values for any polycrystalline sample might be due to the presence of γ—As is not tenable if the sample has been annealed above 288°C. The interpretation involving preferred orientation of the crystallites as a result of grinding is the only obvious alternative.

The arsenic remained as a loose powder during the transformation, indicating a random orientation of crystallites in the product. The susceptibility of a specimen of α—As prepared at a relatively low temperature from γ—As, and without grinding following the transformation, should be the true polycrystalline susceptibility. The agreement between the measured values for a sample of γ—As annealed at 370°C for 9 hr and that calculated from the principal susceptibilities is excellent, as shown in the Table 1.

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9