

Hole Conduction in Pure and Doped Lead Bromide Crystals

J. SCHOONMAN

Solid State Department, Physical Laboratory, University of Utrecht, Utrecht, The Netherlands

Received October 27, 1971

The conductivity of pure and doped lead bromide was measured in a bromine atmosphere in the temperature region 25–200°C. The defect chemistry of nonstoichiometric lead bromide is presented. The hole mobility was derived from the time dependent change in the conductivity after admission/removal of the bromine ambient. Preliminary evidence is presented for hole trapping at Fe^{2+} and Cu^+ centres in lead bromide.

Expressions for the hole concentration in undoped and thallium(I) bromide-doped lead bromide were calculated from hole conduction and the hole mobility in these crystals. A value for the enthalpy of hole formation in lead bromide is given.

The thermodynamic parameters of both ionic imperfections and electron holes were used to predict the equilibrium constant of lead bromide in contact with metallic lead.

1. Introduction

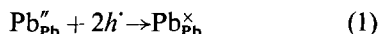
The reaction of nominally pure and doped lead bromide crystals with a bromine atmosphere causes a deviation from stoichiometry in these crystals. The excess bromine gives rise to electronic conduction, since the spatial migration of the electronic charge carriers is not directly related to the diffusion of the bromide ions (I).

If the ionic conductivity increases/decreases on changing the chemical nature of the crystal ambient no distinction can be made between the conductivity by electrons or by holes. On the basis of additional experiments the electronic conduction in lead bromide can be interpreted as a p -type semiconduction, as is the case in, for instance, silver bromide. The experimental results which lead to the conclusion that p -type semiconduction does occur will be mentioned briefly below.

Stasiw and Teltow (2) investigated the bromine-induced bleaching of colour centres in chalcogenide-doped silver bromide. Their results confirmed the formation of holes in AgBr in contact with bromine vapour.

Arends and Verwey (3) carried out ESR experiments on uv irradiated single crystals of lead bromide. These authors showed that ESR signals could be obtained from very small lead

particles. In some of the crystals they measured a resonance signal attributed to a photohole trapped at a vacant lead ion site. In crystals annealed in bromine vapour at 300°C before irradiation the resonance signal attributed to the $(V_{\text{Pb}} \cdot h)'$ centre became very intense, whereas the resonance signal due to the lead particles was almost absent. If lead bromide crystals were treated with bromine after uv irradiation bleaching occurred (4). Bleaching is markedly accelerated by increasing the temperature. In addition, X-ray fluorescence analysis (4) before and after the bromine treatment of uv irradiated crystals showed that after bleaching the bromine-to-lead ratio exceeded the value of this ratio measured in an unirradiated crystal. These results, and the ESR measurements of Arends and Verwey (3) can be understood if it is accepted that as a result of bromine incorporation holes are formed in the lead bromide crystals. The bromine-induced bleaching of photolytically formed lead can be represented by the reaction



(Here and throughout this paper the defect notation of Kröger is used (5).)

The incorporation of an excess of bromine into lead bromide (1) and silver bromide (6, 7) gives

rise to the formation of holes in a concentration proportional to the square root of the bromine pressure. In lead bromide the p -type semiconduction is increased by impurities which enhance the concentration of the bromide ion vacancies, the mobile species.

The aim of this paper is to present the defect chemistry of nonstoichiometric lead bromide, and further electronic conductivity data together with experimental results concerning the mobility of the holes.

2. Experimental

Measurements were carried out both on nominally pure crystals, and on crystals doped with TlBr, CuBr and FeBr₂.¹ The crystals were mounted in a stainless steel conductivity equipment as is schematically represented in Fig. 1. Ohmic contacts between the crystal and the platinum electrodes were established by means of colloidal graphite (Aquadag). The temperature in the conductivity cell was measured with a Pt-Pt/Rh thermocouple. The actual crystal temperature was determined by a method described previously (11). The bromine was obtained from J. T. Baker Chemicals, or E. Merck AG and was not purified or dried before use. Since lead bromide is sensitive to traces of water (8) we measured hole conductivities in the presence of water

¹ The author is indebted to Mr. J. H. W. de Wit, Inorganic Chemistry Department, University of Utrecht, who supplied anhydrous FeBr₂ ready for use.

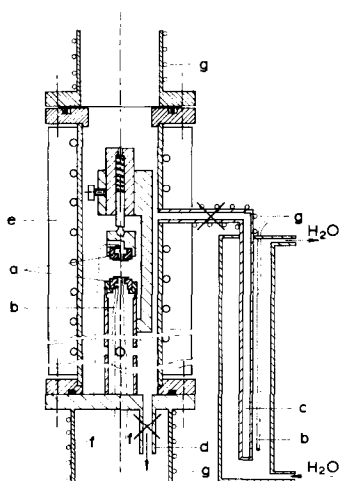


FIG. 1. Conductivity equipment. (a) ceramic supports with platinum electrodes cemented at the end, (b) thermocouples, (c) bromine container, (d) vacuum connection, (e) furnace, (f) outgoing platinum leads, (g) local heating.

vapour. It appeared that hole conduction is not affected by water vapour up to a pressure of 40 mm Hg.

The pressure of bromine gas in the conductivity cell could be varied by changing the temperature of the water circulating around the stainless steel bromine container (Fig. 1). The temperature inside the bromine container equalled the temperature of the circulating water within 15 min after starting circulation. Therefore the temperature of the circulating water, which was measured with a chromel-alumel thermocouple, was used to determine the bromine pressure (9).

Equilibrium conductivities of crystals in a bromine atmosphere were measured with an impedance bridge (General Radio 1608A) with external oscillator (General Radio 1210C) and an amplifier-null-detector (General Radio 1232A).

The apparent diffusion coefficient of the bromine-induced holes was calculated from the rate of attaining the equilibrium conductivity after admission/removal of the bromine vapour. This time dependence of the conductivity was measured with an automatic capacitance bridge assembly (General Radio 1680A), coupled to a data transfer unit (Solartron) and a paper tape punch (Facit 4070).

The annealing experiments were carried out as described previously (1).

3. Reactions and Equilibrium Relations

The reactions and equilibrium relations necessary to understand the interaction of lead bromide with a bromine atmosphere can be formulated as follows, assuming that the concentrations of the various imperfections remain low,

$$0 \rightleftharpoons e' + h', E_i \quad K_i = np \quad (2)$$

$$0 \rightleftharpoons V_{Pb}'' + 2V_{Br}' \quad \Delta H_f \quad K_{sch} = [V_{Pb}''] [V_{Br}']^2 \quad (3)$$

$$\frac{1}{2} Br_2(g) + V_{Br}' \rightleftharpoons Br_{Br}^{\times} + h', \Delta H_{Br_2} \quad (4)$$

$$K_{Br_2} = \frac{p}{[V_{Br}'] P_{Br_2}^{1/2}}$$

$$Br_2(g) \rightleftharpoons 2Br_{Br}^{\times} + V_{Pb}'' + 2h',$$

$$\Delta H_{Br_2 Pb}, K_{Br_2 Pb} = (p^2 [V_{Pb}''] / P_{Br_2}). \quad (5)$$

Square brackets denote concentrations.

It is not significant which of the mechanisms (4), or (5) is chosen, the different relations being coupled by the Schottky mechanism

$$K_{sch} (K_{Br_2})^2 = K_{Br_2 Pb}. \quad (6)$$

The overall electroneutrality condition can be represented by (10)

$$[V_{Br}'] + [Me_{Pb}'] + p = 2[V_{Pb}'''] + [A_{Br}'] + [Me_{Pb}'] + n. \quad (7)$$

Me_{Pb}' denotes a trivalent cation, and Me_{Pb}' a monovalent cation at a lead ion site. A_{Br}' is a divalent anion at a bromide ion site. An expression for the equilibrium constant K_{sch} is deduced from ionic conductivity measurements (11)

$$K_{sch} = (4.5 \pm 0.1) \times 10^3 \exp\left(\frac{-1.71 \pm 0.09 \text{ eV}}{kT}\right) (\text{mole fractions})^3. \quad (8)$$

According to simple semiconductor theory (5, 7)

$$K_i = g_c g_v A_e A_h \exp(-\beta/k) \exp(-E_i^0/kT); \quad (9)$$

g_c and g_v are the weight factors of the conduction and the valence band, respectively. The band model for lead bromide is unknown. The absorption edge of lead bromide shifts to lower energies with increasing temperature

$$E_i = E_i^0 + \beta T,$$

with

$$E_i^0 = 4.34 \text{ eV}, \quad \text{and} \quad \beta = -2 \times 10^{-3} \text{ eV/K} \quad (13).$$

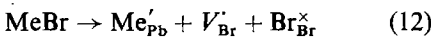
With $A_e = 4.84 \times 10^{15} (m_e^*/m)^{3/2} T^{3/2} (\text{cm}^{-3})$ and a similar expression for A_h , and $T^3 \cong 1.88 \times 10^9 \exp(-0.11 \text{ eV}/kT)$, an expression approximately valid between 25–300°C (7, 12), we obtain from the optical band gap data the expression

$$K_i = 5 \times 10^{50} g_c g_v (m_e^* m_h^*/m^2)^{3/2} \times \exp(-4.45 \text{ eV}/kT) (\text{cm}^{-3})^2; \quad (11)$$

m_e^* and m_h^* denote the effective mass of an electron and a hole, respectively

In order to obtain an experimental expression for the equilibrium constant K_{Br_2} , we have to find expressions for the concentration of bromine-induced holes, p , in nominally pure and MeBr-doped crystals, respectively.

Incorporation of monovalent cations at lead ion sites requires the following lattice reaction



The electroneutrality condition in accordance with Eq. (7) is given by

$$[V_{Br}'] + p = 2[V_{Pb}'''] + [Me_{Pb}']. \quad (13)$$

We have neglected the electron term in Eq. (7), since it can only become relevant for lead bromide in contact with metallic lead.

Substituting the equilibrium relations (3) and (4) into relation (13) gives

$$p^3 - \frac{[Me_{Pb}'] K_{Br_2} P_{Br_2}^{\frac{1}{2}}}{(K_{Br_2} P_{Br_2}^{\frac{1}{2}} + 1)} \times p^2 - \frac{2K_{sch} K_{Br_2}^3 P_{Br_2}^{3/2}}{(K_{Br_2} P_{Br_2}^{\frac{1}{2}} + 1)} = 0.$$

As a solution a rather cumbersome expression is obtained,

$$p = K_{Br_2} (P_{Br_2})^{\frac{1}{2}} (A + B + C), \quad (14)$$

with

$$A = [Me_{Pb}']/3\alpha, \quad \text{and} \quad \alpha = K_{Br_2} P_{Br_2}^{\frac{1}{2}} + 1$$

$$B(+), C(-) = \left\{ \left(\frac{[Me_{Pb}']}{3\alpha} \right)^3 + \frac{K_{sch}}{\alpha} \pm \alpha^{-1} \left[K_{sch}^2 + \frac{2K_{sch}}{\alpha^2} \left(\frac{[Me_{Pb}']}{3} \right)^3 \right]^{\frac{1}{2}} \right\}^{1/3}$$

From the experimental results (Section 4-1), showing $\sigma_p \ll \sigma_{V_{Br}'}$ and the general assumption $\mu_p \gg \mu_{V_{Br}'}$ we conclude $p \ll [V_{Br}']$ and with Eq. (4) $K_{Br_2} P_{Br_2}^{\frac{1}{2}} \ll 1$.

In the case $[Me_{Pb}'] = 0$ we obtain from Eq. (14) $A = C = 0$ and $B = (2K_{sch})^{1/3}$ and therefore,

$$p = K_{Br_2} (2K_{sch})^{1/3} P_{Br_2}^{\frac{1}{2}}. \quad (15)$$

Equation (15) holds for the intrinsic range of ionic conductivity of undoped crystals, and if $([Me_{Pb}']/3)^3 \ll K_{sch}$ for that of the doped crystals too.

In the case $([Me_{Pb}']/3)^3 \gg K_{sch}$, the extrinsic range of ionic conductivity, we obtain from Eq. (14) $A = B = C = \frac{1}{3}[Me_{Pb}']$, and therefore,

$$p = K_{Br_2} [Me_{Pb}'] P_{Br_2}^{\frac{1}{2}}. \quad (16)$$

In this case the lead ion vacancy concentration is practically zero, so Eq. (13) reduces to

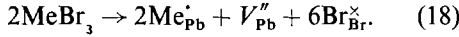
$$[V_{Br}'] + p = [Me_{Pb}']. \quad (17)$$

Equation (17) substituted into Eq. (4) gives with $p \ll [V_{Br}']$ directly Eq. (16). In relation (15) $(2K_{sch})^{1/3}$ can be replaced by the intrinsic bromide ion vacancy concentration, $[V_{Br}']_0$, and $[Me_{Pb}']$ in relation (16) can be replaced by the extrinsic bromide ion vacancy concentration. The bromination is governed by the bromide ion vacancy concentration in such a way that under isothermal and isobaric circumstances the hole concentration increases with the bromide ion vacancy concentration.

It was impossible with our conductivity equipment to measure hole conduction in crystals doped with trivalent cations, since in these cry-

stals $[V_{Br}^{\cdot}]$ is very low. For completeness we shall make some remarks on the reaction of bromine with these doped crystals.

Incorporation of trivalent cations at lead ion sites, Me_{Pb}^{\cdot} , requires the following lattice reaction



The electroneutrality condition is then given by

$$[V_{Br}^{\cdot}] + [Me_{Pb}^{\cdot}] + p = 2[V_{Pb}''] \quad (19)$$

In this case we obtain on introducing the relations (3) and (4) into this electroneutrality condition an equation similar to Eq. (14). As a solution Eq. (15) holds for the intrinsic ionic conductivity region too. In the extrinsic part of the ionic conductivity plot the bromide ion vacancy concentration cannot be ignored, since in these crystals anionic conduction still prevails (10, 11). On introducing into Eq. (3) $[V_{Pb}''] = \frac{1}{2}[Me_{Pb}^{\cdot}]$ as required by reaction (18), and into Eq. (4) the resulting bromide ion vacancy concentration we obtain

$$p = K_{Br_2} \left(\frac{2K_{sch}}{[Me_{Pb}^{\cdot}]} \right)^{\frac{1}{2}} P_{Br_2}^{\frac{1}{2}} \quad (20)$$

So far we have found expressions for the hole concentration in the intrinsic ionic conductivity region of nominally pure and doped crystals, and in the extrinsic conductivity region of crystals doped with monovalent and trivalent cations.

The extrinsic ionic conduction of nominally pure crystals is due to the remaining impurity content of these crystals. All monovalent and trivalent cationic, and divalent anionic impurities influence the ionic disorder ultimately leading to an effective bromide ion vacancy concentration ($[V_{Br}^{\cdot}] = [Me_{Pb}^{\cdot}] + 2[V_{Pb}'']$, c.f. Eqs. (12) and (18)), which accounts for the measured conductivity. It can be shown (Fig. 4 in ref. 11) that in the temperature region $T < 50^{\circ}C$ a reduced electroneutrality condition can be used: $[V_{Br}^{\cdot}] + p = [Me_{Pb}^{\cdot}]$, which means that Eq. (16) can be used, inserting $[Me_{Pb}^{\cdot}] = [Me_{Pb}^{\cdot}]$. $[Me_{Pb}^{\cdot}]$ denotes the bromide ion vacancy concentration as calculated from extrinsic conductivity data. Therefore $[Me_{Pb}^{\cdot}]$ is not representative for the total remaining impurity content.

The general expression describing the hole conduction in lead bromide equilibrated with a bromine atmosphere has been given in a previous paper (1).

$$\sigma_p \equiv \sigma_{Br_2} - \sigma_0 = pe(\mu_p - \mu_{V_{Br}^{\cdot}}) \quad (21)$$

where σ_{Br_2} denotes the equilibrium conductivity in bromine vapour, and σ_0 the conductivity in an

inert atmosphere. μ_p is the hole mobility, and $\mu_{V_{Br}^{\cdot}}$ the mobility of the bromide ion vacancies. It must be pointed out that $\sigma_0 = \sigma_{V_{Br}^{\cdot}}$, since lead bromide is an anionic conductor up to the melting point.

In view of Eq. (21) we can make a distinction between the following limiting cases:

- (i) $\mu_p = 0$, bromine-induced holes are trapped. The conductivity remains ionic. Since anion vacancies are occupied by excess bromide ions, and since only a shift of the Schottky equilibrium is measured the conductivity in a bromine atmosphere decreases.
- (ii) $\mu_p > \mu_{V_{Br}^{\cdot}}$, the total conductivity in bromine increases. In the case $\mu_{V_{Br}^{\cdot}}$ is negligibly small with respect to μ_p , the hole conductivity σ_p can be interpreted as the product (hole concentration \times hole mobility).

Since conductivity experiments yield such products only, it is necessary, for the evaluation of both entities, to obtain carrier mobilities from additional experiments. Here we derive the hole mobility from the time dependent change of the hole conductivity upon admission/removal of the bromine atmosphere.

4. Conductivity Results

4-1. Hole Conduction: Isothermal Experiments

In general, hole conduction is measured isothermally as a function of bromine pressure, or as a function of temperature under isobaric circumstances (1, 6). The hole conductivity is then calculated from the difference between the conductivities of the crystal in the presence and absence of bromine vapour (Eq. 21).

In a previous paper we reported hole conductivity activation energies as obtained from isobaric and from isothermal experiments; 0.21 ± 0.02 eV and 0.23 ± 0.02 eV, respectively (1). We investigated again nominally pure, and crystals doped with thallium(I) bromide. Some of the results are presented in Fig. 2. For the nominally pure crystal we calculated

$$\sigma_p = (7 \pm 2) \times 10^{-5} P_{Br_2}^{\frac{1}{2}} \times \exp\left(\frac{-0.25 \pm 0.03 \text{ eV}}{kT}\right) \Omega^{-1} \text{ cm}^{-1} \quad (22)$$

The hole conductivity in the thallium(I) bromide doped crystal can be represented by

$$\sigma_p = (2.7 \pm 0.3) \times 10^{-5} P_{Br_2}^{\frac{1}{2}} \times \exp\left(\frac{-0.17 \pm 0.01 \text{ eV}}{kT}\right) \Omega^{-1} \text{ cm}^{-1} \quad (23)$$

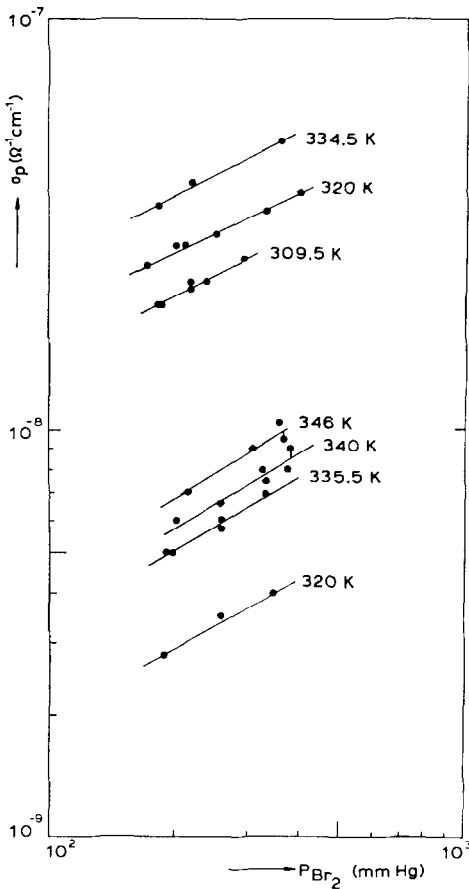


FIG. 2. The hole conductivity, σ_p , isothermally plotted as a function of the bromine pressure. 320–346K: undoped PbBr_2 ; 309.5–334.5K: $\text{PbBr}_2\text{-TlBr}$ (4.9×10^{-4} mole fraction).

The reference conductivity, measured under vacuum, can be represented for the undoped lead bromide crystal by

$$\sigma_0 = (2.0 \pm 0.5) \times 10^{-2} \times \exp\left(\frac{-0.31 \pm 0.03 \text{ eV}}{kT}\right) \Omega^{-1} \text{ cm}^{-1}, \quad (24)$$

and for the $\text{PbBr}_2\text{-TlBr}$ crystal by

$$\sigma_0 = (8 \pm 1) \times 10^{-2} \times \exp\left(\frac{-0.28 \pm 0.01 \text{ eV}}{kT}\right) \Omega^{-1} \text{ cm}^{-1}. \quad (25)$$

Expression (24) is valid in the temperature region involved (viz. Fig. 2), whereas expression (25) represents the extrinsic ionic conductivity of the thallium(I) bromide-doped crystal. As compared to Eq. (16) the experimental hole conductivities

indicate that in both crystals the hole mobility does not depend on bromine pressure.

The hole conductivity in the nominally pure crystal shows an activation energy comparable to the activation energies reported previously (1). For $\text{PbBr}_2\text{-TlBr}$ this parameter shows a lower value.

We can offer two possibilities to explain this difference. If in nominally pure crystals the reduced electroneutrality condition $p + [V_{\text{Br}}] = [Me_{\text{Pb}}]$ does not hold, we obtain for p a temperature coefficient in between the values ΔH_{Br_2} and $(\Delta H_{\text{Br}_2} + \frac{1}{2}\Delta H_f)$ in accordance with Eq. (16) and (15), respectively. In the thallium(I) bromide-doped crystals Eq. (16) is valid. If the hole mobility in undoped and in doped crystals has the same temperature coefficient the larger activation energy is due to the fact that in the undoped crystals $[V_{\text{Br}}]$ is not constant in the extrinsic ionic conductivity region (compare Eq. (2) and Fig. 1 in ref. 1).

In addition the lead ion vacancy concentration in the nominally pure crystals is larger than the corresponding concentration in $\text{PbBr}_2\text{-TlBr}$ crystals. Photochemical decomposition studies of lead bromide at room temperature showed that V_{Pb}'' can act as a shallow trap for holes (8, 14). If hole trapping occurs we must expect a somewhat larger temperature coefficient for the mobility of the holes (15).

If it is assumed that the ionic disorder does not influence the hole mobility the ratio of the hole conductivities in both crystals must equal the ratio of the reference conductivities in both crystals, since reaction (4) describes the bromination. The ratio of the hole conductivities is dependent on temperature: moreover, the errors in the pre-exponential factors are considerable. This excludes a careful analysis.

In order to obtain better information on the relation between the concentration of anion vacancies and the hole conductivity we measured isothermally, and under isobaric circumstances, σ_p , in crystals doped with different amounts of thallium(I) bromide. The concentration of the bromide ion vacancies in these crystals was calculated from the ionic conductivity as measured under vacuum and the known mobility of the anion vacancies (11). The isotherm presented in Fig. 3 indicates a slope of one in accordance with Eq. (16).

We are now able to predict the hole conductivity in the intrinsic ionic conductivity region from σ_p data, measured in the extrinsic region

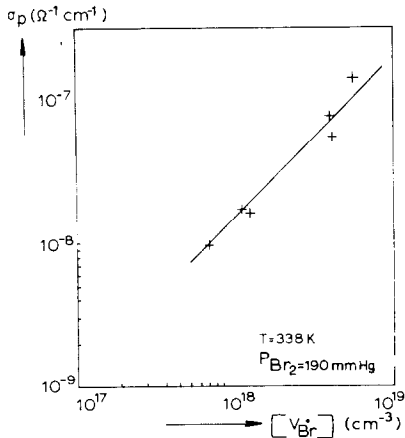


FIG. 3. The hole conductivity, σ_p , plotted as a function of the bromide ion vacancy concentration under isothermal and isobaric circumstances.

of ionic conductivity. From Eqs. (15), (16), and (21) we obtain

$$\sigma_p(\text{intr}) = ([V_{\text{Br}\cdot}]_0/[Me'_{\text{Pb}}]) \sigma_p(\text{extr}) \quad (26)$$

since the experimental equations (22) and (23) clearly indicate $\mu_p > \mu_{V_{\text{Br}\cdot}}$.

On introducing into Eq. (26) for $[V_{\text{Br}\cdot}]_0$ Eq. (27) (11)

$$[V_{\text{Br}\cdot}]_0 = (21 \pm 2) \times \exp(-0.57 \pm 0.03 \text{ eV}/kT) \text{ mole fraction} \quad (27)$$

together with $[Tl'_{\text{Pb}}] = 4.9 \times 10^{-4}$ mole fraction, as calculated from Eq. (25), we calculated for the one atmosphere isobar

$$\sigma_p(\text{intr}) = (1.2 \pm 0.2) \times \exp(-0.74 \pm 0.03 \text{ eV}/kT) \Omega^{-1} \text{ cm}^{-1} \quad (28)$$

4-2. The Mobility of the Holes

The apparent diffusion coefficient, D_p , can be derived from the time dependent change of the hole conductivity in undoped and Me^+ -doped crystals upon admission/removal of the bromine ambient.

Following Dünwald and Wagner (16), Jost (17) and Luckey (18) we can write for diffusion into the crystal

$$1 - [\sigma_p(t)/\sigma_p(\text{eq})] \cong 8/\pi^2 \exp(-t/\tau) \quad (29)$$

and for diffusion out of the crystal

$$[\sigma_p(t)/\sigma_p(t=0)] \cong 8/\pi^2 \exp(-t/\tau) \quad (30)$$

with $\tau = d^2/(\pi^2 D_p)$. $\sigma_p(t)$ denotes the time dependent hole conductivity. $\sigma_p(\text{eq})$ and $\sigma_p(t=0)$

denote hole conductivities, when the crystal is in equilibrium with a bromine atmosphere. d is the thickness of the crystal, which must be small compared to the electrode surface area.

From Eqs. (22) and (23) in comparison with Eqs. (24) and (25), respectively, we can see that the hole transport number, t_p , defined as $t_p = \sigma_p/(\sigma_p + \sigma_{V_{\text{Br}\cdot}})$ is very small. Together with the Einstein relation we obtain $D_p \times p \ll D_{V_{\text{Br}\cdot}} \times [V_{\text{Br}\cdot}]$, which means that in this case (ambipolar diffusion) D_p determines the diffusion (5).

The experimental increase, or decrease of the conductivity upon admission, or removal of the bromine ambient was fitted to Eqs. (29) and (30), respectively, by a least-squares computer analysis. A finite evaporation rate of bromine and a possible retardation effect in cell evacuation might be influential. The use of Eqs. (29) and (30) is, however, limited to values for which $t > 0.5\tau$. In the calculations this condition was taken into account. Mobilities were calculated from apparent diffusion coefficients, using the Einstein relation. The mobilities are plotted in Fig. 4. The temperature dependence of the hole mobility can be represented by

$$\mu_p = (4.5 \pm 1.5) \times 10^{-1} \times \exp(-0.07 \pm 0.01 \text{ eV}/kT) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}. \quad (31)$$

At constant temperature D_p was independent of bromine pressure in the region 0–350 mm Hg. The reference conductivity of the thallium(I) bromide-doped crystal exceeds the reference conductivity of the undoped crystal in the tem-

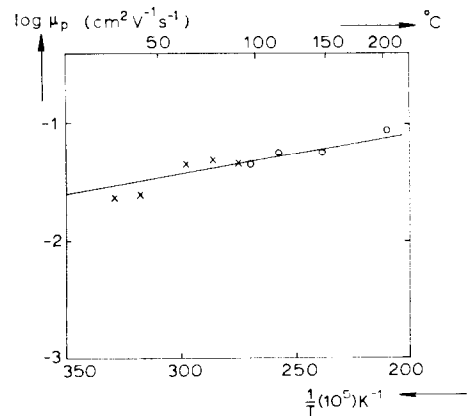


FIG. 4. Hole mobility calculated from apparent diffusion coefficients in PbBr_2 : \circ —undoped PbBr_2 ($d = 0.178$ cm), \times — PbBr_2 - TlBr ($d = 0.147$ cm). Experimental points represent averaged values of at least four diffusion runs into and four diffusion runs out of the crystal.

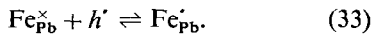
perature region 25–200°C, indicating that μ_p does not depend on the lead ion vacancy concentration.

In undoped and thallium(I) bromide-doped lead bromide the conductivity in a bromine atmosphere exceeds the reference conductivity measured under vacuum, i.e., $\mu_p > \mu_{V_{Br}}$. In Fig. 5 we have plotted the conductivity as $\log \sigma$ versus $1/T$ of a crystal doped with CuBr (curve 1). The crystal was annealed *in vacuo*: 43 h at 525K. A part of this crystal was annealed in bromine vapour: 120 h at 543K ($P_{Br_2} = 350$ mm Hg). Curve 2 represents the conductivity of the brominated crystal. The conductivity of a crystal doped with FeBr₂ is shown by curve 3. A part of this crystal was annealed in bromine vapour too: 120 h at 525K ($P_{Br_2} \approx 760$ mm Hg). The conductivity of this crystal is represented by curve 4. All conductivities were measured in a nitrogen atmosphere.

In view of Eq. (21) we can understand these results by accepting hole trapping at the Cu'_{Pb} and Fe'_{Pb} centres, i.e., $\sigma_p = -pe\mu_{V_{Br}}$. The bromination of both doped crystals can be represented by reaction (4), followed by



and



for the crystal doped with CuBr and FeBr₂, respectively. Since p is equal to the difference between the concentration of anion vacancies in the crystal before and after bromination, we have mainly measured the shift of the Schottky equilibrium.

5. Discussion

Data for Hall and drift mobilities of (photo)holes in lead bromide are still lacking in the literature. Therefore we cannot compare Hall mobilities, drift mobilities and our apparent diffusion coefficients.

The Einstein relation is not valid for the drift mobility and the apparent diffusion coefficient of holes in AgBr: the discrepancy exceeds even four powers of ten at room temperature (19). The temperature dependence of the apparent diffusion coefficient in AgBr shows an activation energy of about 0.70 eV (18), whereas drift and Hall mobilities decrease on increasing temperature in the same temperature region. The temperature dependence of the latter is much less

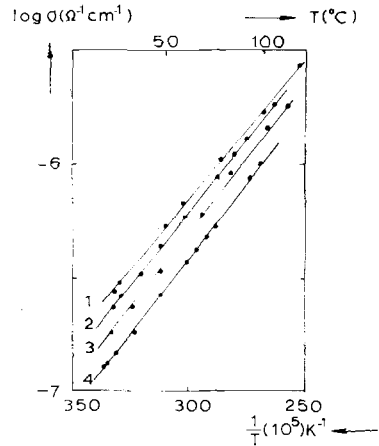


Fig. 5. The conductivity plotted as $\log \sigma$ versus $1/T$ for crystals doped with CuBr and FeBr₂ before and after annealing in bromine vapour (see text).

pronounced than that of the former (7). These discrepancies could be explained with a trapping scheme, in which it is assumed that deep hole traps are in thermal equilibrium with the valence band (19). The nature of these hole traps is still uncertain, although negatively charged silver ion vacancies seem an attractive choice.

In a recent review article (4) the photodecomposition of silver bromide was compared with the photochemical decomposition of lead bromide. During photodecomposition of silver bromide electrons drift to the surface, whereas photoholes are trapped. The photochemical decomposition of lead bromide shows a different mechanism: deep traps for electrons prevent their motion, whereas shallow hole traps enhance the formation of bromine at the surface (1, 4, 8, 20).

We are inclined to believe that a discrepancy between Hall mobility and apparent diffusion coefficient of holes, if present at all, will be much less pronounced in lead bromide than in silver bromide. In fact V''_{Pb} is a shallow trap for holes at room temperature as was mentioned before. Furthermore the hole mobilities calculated from the experimental apparent diffusion coefficients using the Einstein relation, indicate that μ_p does not depend on $[V''_{Pb}]$ at temperatures above room temperature.

The mobilities of holes in silver chloride, calculated by Müller et al. (15) from their experimental apparent diffusion coefficients show a large increase in the temperature region 25–65°C. This behaviour was attributed to hole trapping. In the temperature region 65–250°C μ_p was almost

independent of temperature: $\mu_p \approx 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a situation closely similar to our experimental results. It is therefore most likely that the difference in activation energy for hole conduction in undoped and TlBr-doped lead bromide (I, Section 4-1) originates from a slight temperature dependence of $[V_{\text{Br}}^{\cdot}]$ in the extrinsic region of the undoped crystals.

From Eqs. (22), (23) and (31) we calculated the following expressions

$$p = (9 \pm 1) \times 10^{-8} P_{\text{Br}_2}^{\frac{1}{2}} \times \exp(-0.18 \pm 0.03 \text{ eV}/kT) \text{ mole fraction} \quad (34)$$

and

$$p = (3.6 \pm 0.1) \times 10^{-8} P_{\text{Br}_2}^{\frac{1}{2}} \times \exp(-0.10 \pm 0.01 \text{ eV}/kT) \text{ mole fraction} \quad (35)$$

for the hole concentration, p , in the undoped and TlBr-doped crystal, respectively. For reasons outlined above, we can use Eq. (35) for the evaluation of K_{Br_2} . On comparing Eq. (16) with Eq. (35) we obtain with $[V_{\text{Pb}}^{\cdot}] = 4.9 \times 10^{-4}$ mole fraction the expression

$$K_{\text{Br}_2} = (7.4 \pm 0.2) \times 10^{-5} \times \exp(-0.10 \pm 0.01 \text{ eV}/kT) \text{ atm}^{-\frac{1}{2}} \quad (36)$$

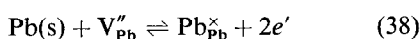
where the value $(0.10 \pm 0.01) \text{ eV}$ represents ΔH_{Br_2} . From Eqs. (6), (8) and the experimental value for ΔH_{Br_2} , we find for $\Delta H_{\text{Br}_2\text{Pb}}$ $(1.9 \pm 0.1) \text{ eV}$, and for $K_{\text{Br}_2\text{Pb}}$ the expression

$$K_{\text{Br}_2\text{Pb}} = 2.5 \times 10^{-5} \times \exp(-1.9 \text{ eV}/kT) (\text{mole fraction})^3 \text{ atm}^{\frac{1}{2}} \quad (37)$$

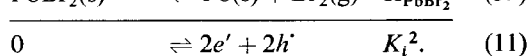
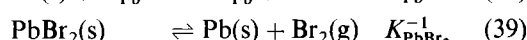
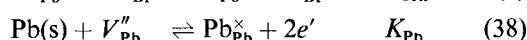
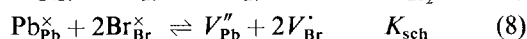
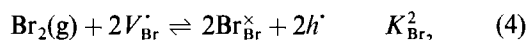
Mechanism (5) requires the formation of an immobile lead ion vacancy, whereas in mechanism (4) a bromide ion vacancy is annulled by incorporation of bromine. Mechanism (4) is energetically more favourable than mechanism (5).

The thermal band gap can be calculated with known expressions for n and p . It is assumed that the expression for K_i obtained from thermal band gap data can be directly compared to optically determined band gap data. For silver bromide the thermal and optical band gap data are in reasonable agreement in the temperature region 400–600K (7).

The thermodynamic parameters of both ionic and electronic imperfections in lead bromide as given so far enable us to predict an expression for K_{Pb} which describes the equilibrium of lead bromide in contact with metallic lead



an equilibrium, necessary to understand the behaviour of the polarization cell $-\text{Pb}|\text{PbBr}_2|\text{C}+$. The combination of Eqs. (4), (8), (38) and the equilibrium, which describes the thermal decomposition of lead bromide into solid lead and gaseous bromine gives the next scheme



From thermodynamic data (21) we calculated for the decomposition of lead bromide into solid lead and gaseous bromine

$$K_{\text{PbBr}_2}^{-1} = 5.6 \times 10^7 \exp(-3.20 \text{ eV}/kT) \text{ atm.} \quad (39)$$

We obtain for K_{Pb} from the presented scheme the expression

$$K_{\text{Pb}} = 2.5 \times 10^{+6} \times \exp(-3.8 \text{ eV}/kT) \text{ mole fraction} \quad (40)$$

where the preexponential factor must be considered as a rough estimate, since in the calculations it was assumed that $g_c = g_v = 1$, and $m_e^* = m_h^* = m$.

Nevertheless we can use Eq. (40) in our experiments on the cell $-\text{Pb}|\text{PbBr}_2|\text{C}+$, of which results will be published in due course.

Acknowledgments

The author is very much indebted to Prof. J. H. van Santen and Prof. G. Blasse for encouraging this work, and for valuable criticism during the preparation of the manuscript.

References

1. J. SCHOONMAN, *J. Solid State Chem.* **2**, 31 (1970).
2. O. STASIW AND J. TELTOW, *Nachr. Akad. Wiss. (Goettingen) Math. Phys. Kl.* **1944**, 153.
3. J. ARENDS AND J. F. VERWEY, *Phys. Status Solidi* **23**, 137 (1967).
4. A. C. H. VAN PESKI, J. SCHOONMAN, AND D. A. DE VOOS, Photo Electrochemical Phenomena. In, "Solid State Electrochemistry" (J. Hladik, ed.) Academic Press, London (in press).
5. F. A. KRÖGER, "The Chemistry of Imperfect Crystals." North-Holland Amsterdam, 1964.
6. L. M. SHAMOVSKII, A. A. DUNINA, AND M. I. GOSTEVA, *Sov. Phys. JETP* **3**, 511 (1956); *Sov. Phys. Dokl.* **1**, 124 (1956).

7. P. B. P. PHIBBS AND F. A. KRÖGER, *J. Phys. Chem. Solids* **30**, 1435 (1969).
8. J. F. VERWEY, Thesis, University of Utrecht, 1967.
9. F. E. C. SCHEFFER AND M. VOOGD, *Rec. Trav. Chim. Pays Bas* **45**, 214 (1926).
10. J. F. VERWEY AND J. SCHOONMAN, *Physica* **35**, 386 (1967).
11. J. SCHOONMAN, *J. Solid State Chem.* **4**(3) 466 (May, 1972), in press.
12. F. A. KRÖGER, *J. Phys. Chem. Solids* **26**, 901 (1965).
13. G. LIIDJA, V. PLEKHANOV AND A. MALYSHEVA, *Esti N.S.V. Tead. Akad. Toim. Fuus. Mat.* **19**, 328 (1970).
14. J. SCHOONMAN AND J. F. VERWEY, *Physica* **39**, 244 (1968).
15. P. MÜLLER, S. SPENKE, AND J. TELTOW, *Phys. Status. Solidi* **41**, 81 (1970).
16. H. DÜN WALD AND C. WAGNER, *Z. Phys. Chem.* **B24**, 53 (1934).
17. W. JOST, "Diffusion in Solids, Liquids, Gases," pp. 35-38. Academic Press, New York, 1960.
18. G. W. LUCKEY, *Discuss Faraday Soc.* **28**, 113 (1959).
19. M. GEORGIEV AND J. MALINOWSKI, *J. Phys. Chem. Solids* **28**, 931 (1967).
20. J. MALINOWSKI, *Photogr. Sci. Eng.* **15**, 175 (1971).
21. N.B.S. Circular No. 500 (1952).