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The Conductivity of Lead Bromide in a Bromine Atmosphere

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The conductivity of both pure and impurity doped single crystals of lead bromide was measured in bromine vapour.

Results of excess conductivities due to electron holes measured in the temperature region 25–350°C are presented.

The increase of the excess conductivity varies as the square root of the bromine pressure.

1. Introduction

Both ionic and electronic currents can be present in lead bromide.

Current polarisation experiments, according to the principles of Hebb (*1*) and Wagner (*2*), on lead bromide doped with potassium bromide were carried out by Wagner and Wagner (*3*). The measured conductivities could be ascribed to hole currents.

As regards the ionic component, lead bromide is characterized by the presence of Schottky defects: lead–ion vacancies and bromine–ion vacancies (*4*, *5*).

In this paper, electrical experiments, which have been performed to gain more information about the reaction of bromine with pure and impurity doped single crystals of lead bromide, are described.

2. Experimental

A detailed description of the crystal preparation and bridge circuit (*4*, *6*), has been published elsewhere.

In the next sections, crystals have got suffix *A*, or *S*. *A* denotes crystal growing according to Bridgman. Crystals with suffix *S* were grown in a zone melting apparatus. Flat discs up to about 1-mm thick were cut from the large single crystals.

Special conductivity equipments for isothermal and isobaric bromine experiments were used (more details will be published later).

During the course of these investigations, crystals were annealed in a well-defined bromine atmosphere. The annealing procedure was carried out in the same apparatus that was used for the bromine treatment of the lead bromide melt during crystal preparation (*4*).

From conductivity versus annealing-time plots we determined experimentally the time to reach the equilibrium conductivity. In the temperature region 510–625°K, and bromine pressure region 0.30–0.50 atm annealing times of 1 hr were necessary to equilibrate the crystals.

Ohmic contacts between the crystal and electrodes were established with "Aquadag", or "Leitsilber". The former was used in the isothermal and isobaric experiments. It is obvious that the latter must be used in inert atmospheres. We used platinum electrodes protected with a layer of "Aquadag" because Pt can react[1] with halogens (*8*).

3. Temperature and Bromine Pressure Dependence of the Excess Conductivity

If molecules of bromine can dissolve and diffuse as such into the lead bromide lattice the electrical conductivity would remain unchanged. If the reaction of bromine with the crystal is connected with the formation of holes, the spatial migration of

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[1] In the case of silver bromide in contact with bromine and platinum electrodes a decreased electronic (hole) current is observed (*9*). Contamination by Pt, presumably $PtBr_2$, causes this effect. By incorporation of $PtBr_2$, a shift of the cationic (Frenkel) disorder enhances the silver vacancy concentration. In lead bromide the Schottky equilibrium is not affected by a substitutional replacement of lead ions by Pt^{2+} ions.

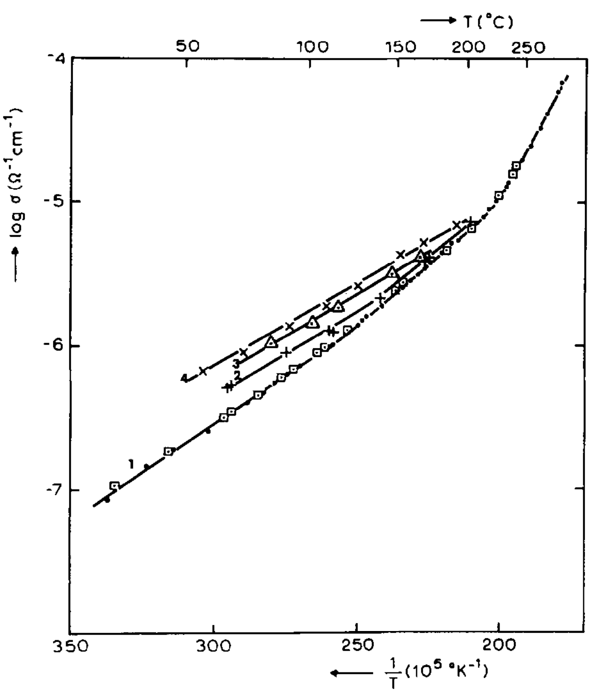


FIG. 1. Electrical conductivity, σ, of lead bromide plotted as $\log \sigma$ versus $1/T$.

1. nitrogen atmosphere
2. $P_{Br_2} = 105$ mm Hg
3. $P_{Br_2} = 150$ mm Hg
4. $P_{Br_2} = 180$ mm Hg

which is not directly related to the diffusion of bromine ions the electrical conductivity will change.

Some preliminary experiments have indicated that the conductivity of lead bromide brought into contact with bromine vapour increases.

The quantity $\Delta\sigma$ (the increase in conductivity) is calculated from the difference between the electrical conductivity of the crystal in the presence of bromine, and without it. In the calculations it is assumed that in the overall electrical conductivity, the fraction which comes from the ionic component remains unchanged in the presence of bromine.

This assumption is arbitrary, if in the process a small shift of the Schottky equilibrium results (Section 6). At elevated temperatures and small bromine pressures, however, we assume a bromine independent concentration of Schottky defects.

The increase in conductivity under isobaric circumstances as a function of temperature is limited to a certain temperature region. At high temperatures the large, strongly temperature-dependent ionic conductivity masks the comparatively smaller hole current, as can be seen in Fig. 1. In the extrinsic conductivity region two methods were used to determine the temperature dependence of the excess conductivity:

(a) isobaric method: temperature region 25–200°C (Fig. 1);
(b) isothermal method: temperature region 25–125°C (Fig. 2a and b).

In Fig. 3 the excess conductivities are plotted as a function of increasing temperature. From the $\log(\Delta\sigma)$ versus $1/T$ plot a characteristic activation heat results, which is presented in Table I.

The excess conductivities can be presented as a function of the square root of the partial bromine

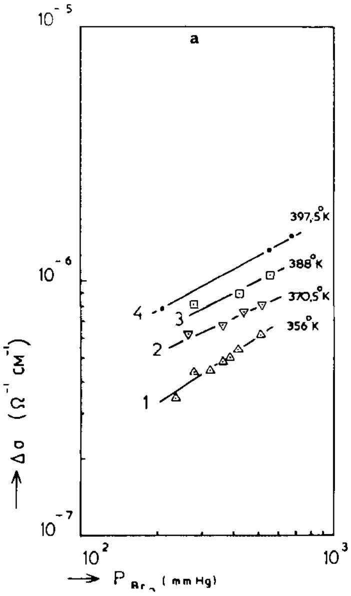
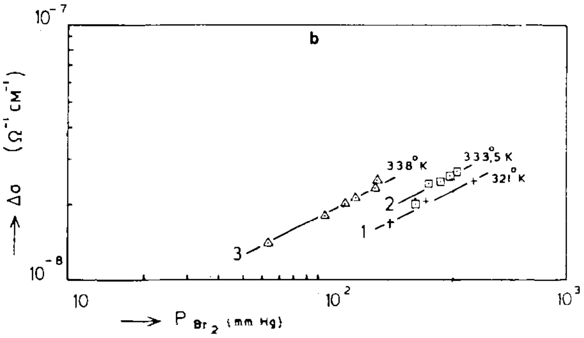


FIG. 2(a). The excess conductivity, $\Delta\sigma$, isothermally plotted as a function of the bromine pressure.

Isotherm 1–4: $PbBr_2$ (SV)



2(b). The excess conductivity, $\Delta\sigma$, isothermally plotted as a function of the bromine pressure.

Isotherm 1–2: $PbBr_2$ (A7)

Isotherm 3: $PbBr_2$ (SV)

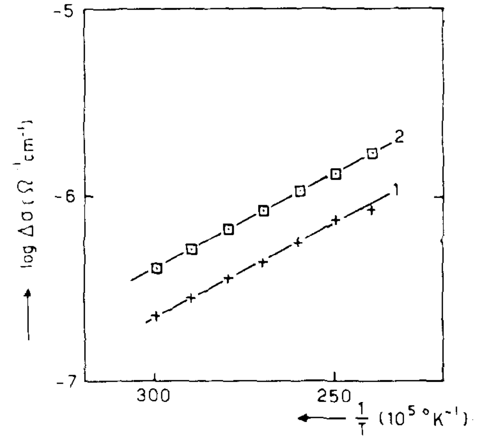


FIG. 3. Excess conductivities in pure crystals plotted as log$\Delta\sigma$ versus $1/T$.

1 and 2: $PbBr_2$ (SIII), 150 and 180 mm Hg

pressure. Equation (1) represents the results from Fig. 2a as a function of bromine pressure, and of temperature,

$$\Delta\sigma = 10^{-2}.\sqrt{P_{Br_2}}.\exp(-0.23\,\mathrm{eV/kT})\,\Omega^{-1}\,\mathrm{cm}^{-1}\,\mathrm{atm}^{1/2}. \quad (1)$$

From the low temperature slope of the logσ versus $1/T$ plot of the reference crystal, the conductivity of which was measured in nitrogen, we calculate

$$\sigma_0 = 2.0\exp(-0.44\,\mathrm{eV/kT})\,\Omega^{-1}\,\mathrm{cm}^{-1}. \quad (2)$$

So the relative excess conductivity,

$$\Delta\sigma/\sigma_0 = 5\times 10^{-3}\sqrt{P_{Br_2}}\exp(+0.21\,\mathrm{eV/kT})\,\mathrm{atm}^{1/2}, \quad (3)$$

is lowered with increasing temperature.

The conductivity of the mobile species for pure lead bromide in equilibrium with bromine vapour are plotted together with the transport numbers

$$t_h = \Delta\sigma/(\sigma_0 + \Delta\sigma)$$

in Fig. 4. The values for the calculation of the transport numbers were taken from results presented in Figs. 1 and 3 for $PbBr_2$ (SIII) crystals.

TABLE I

ACTIVATION HEAT FOR EXCESS CONDUCTION

Activation heat from	Calculated from $d(\log\Delta\sigma)/d(1/T)$
Isobaric method	0.21 ± 0.02 eV
Isothermal method	0.23 ± 0.02 eV

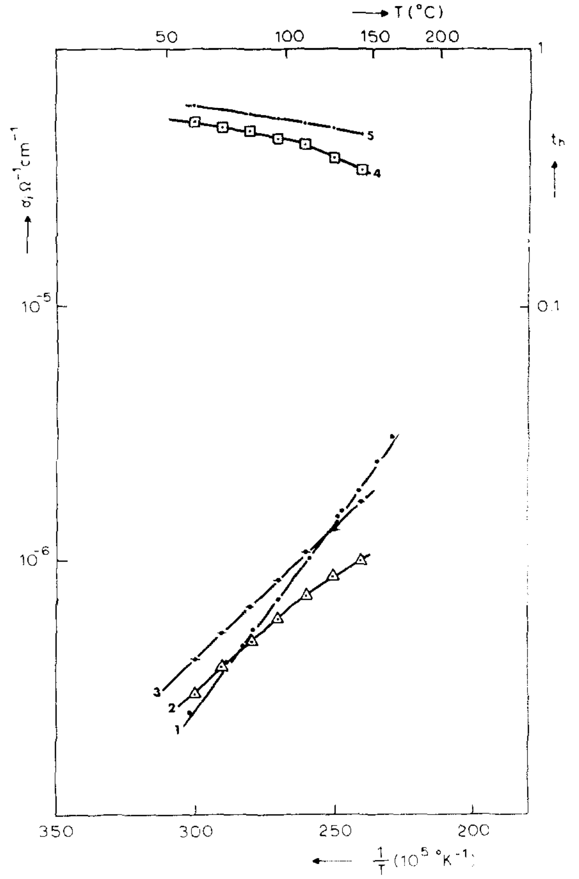


FIG. 4. Conductivities and transport numbers of the dominant defects for pure $PbBr_2$ in equilibrium with bromine vapour.

1. $\sigma_{V_{Br^-}}$
2. σ_h (150 mm Hg)
3. σ_h (180 mm Hg)
4. t_h (150 mm Hg)
5. t_h (180 mm Hg)

4. Annealing Experiments

The proposed evaluation of the excess conductivity holds for the extrinsic temperature region as was mentioned before. In our undoped crystals intrinsic conductivity usually starts at 200°C. In the temperature region 240–350°C some crystals were annealed in bromine vapour. After quenching to room temperature the conductivities were measured in air.

To check the establishment of the Schottky equilibrium after the annealing and quenching procedure some crystals were annealed in evacuated ampullae. The conductivities of these crystals equal the reference conductivities of untreated crystals. For this reason, we disregarded quenched-in Schottky defects. The results of the annealing experiments are given in Figs. 5 and 6. Experimental

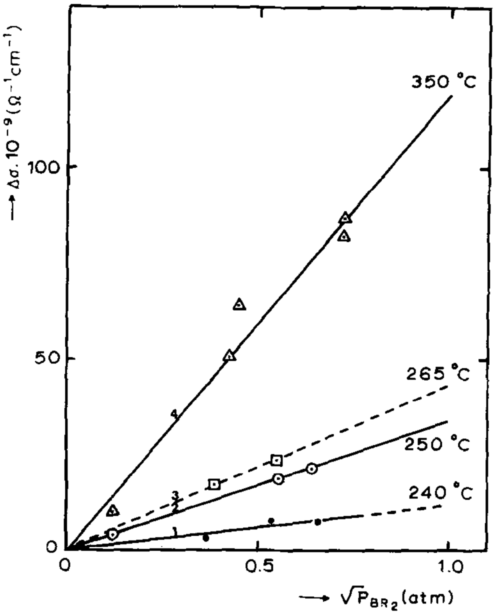


FIG. 5. Excess conductivities, $\Delta\sigma$, at room temperature for annealed and quenched crystals.

1. $PbBr_2$ (A6) 2–4. $PbBr_2$ (SIII)

points represent the average values of at least three pieces cut from a single crystal (SIII and A7).

5. Impurity Doped Crystals

In order to obtain more information about the equilibrium reaction, some impurity doped crystals were annealed for 1 hr in bromine atmospheres. Again the conductivities were measured in air after quenching to room temperature. The results are listed in Table II.

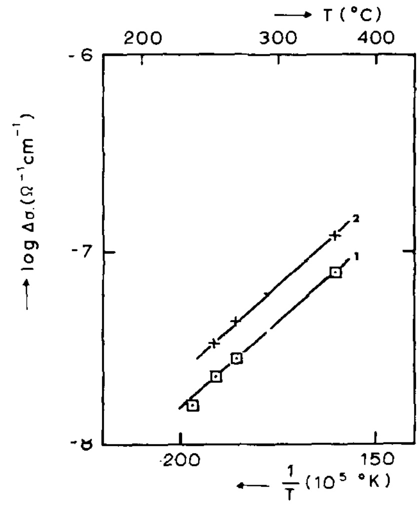


FIG. 6. Increase in conductivity plotted versus $1/T$ for crystals annealed in bromine vapour.

1. $P_{Br} = 320$ mm Hg 2. $P_{Br_2} = 760$ mm Hg

TABLE II

THE ROLE OF FOREIGN IONS ON THE EXCESS CONDUCTIVITY

Crystal	Bromine Pressure (mm Hg)	Annealing Temperature (°K)	$\Delta\sigma \times 10^{-9}$ (Ω^{-1} cm^{-1})
$PbBr_2$–AgBr	317	523	133
(S)	321	513	77
$PbBr_2$ pure	317	523	23
(SIII)	321	513	16
$PbBr_2$–$BiBr_3$	317	523	18
	321	513	14

The pure (SIII) and silver doped crystals were investigated also by the isothermal method. Some values are compared in Table III. The excess conductivities measured with the silver doped crystals varied also proportional to the square root of bromine pressure.

6. Discussion

Bromine vapour causes bleaching of lead bromide crystals in which lead colloids were present in a surface layer (*11*). Structure considerations make diffusion of molecules of bromine unlikely (*4*).

The influence of incorporating aliovalent impurities can be described by the following electroneutrality conditions (*4*, *5*):

$$[V_{Br^-}] = 2[V_{Pb^{2+}}] + [Ag^+] \tag{4}$$

and

$$[V_{Br^-}] + [Bi^{3+}] = 2[V_{Pb^{2+}}]. \tag{5}$$

The disadvantage of measuring in the extrinsic conductivity region can be readily seen in the presented figures. The conductivity of the pure crystals depends on the residual impurity content. For all the experimental results we can conclude

TABLE III

EXCESS CONDUCTIVITIES IN PURE AND SILVER DOPED CRYSTALS

Crystal	Bromine Pressure (mm Hg)	Equilibrium Temperature (°K)	$\Delta\sigma \times 10^{-8}$ (Ω^{-1} cm^{-1})
$PbBr_2$–AgBr	175	373	17.4
$PbBr_2$–AgBr	175	404	28.0
$PbBr_2$ (SIII)	175	387	6.4

that the excess conductivity is increased by impurities which enhance the concentration of the bromine ion vacancies, the mobile ionic species.

From these experimental results we conclude that lead bromide exposed to bromine vapour exhibits excess conductivities attributable to electron holes. The assumed chemical reaction for bromine incorporation in the crystal is represented by formulation (6),

$$\tfrac{1}{2}\mathrm{Br}_2 + V_{\mathrm{Br}^-} \rightleftarrows \mathrm{Br}^-_{\mathrm{lattice}} + p. \qquad (6)$$

The conductivity of lead bromide in inert atmospheres is given by the relation,

$$\sigma_0 = [V_{\mathrm{Br}^-}]_0 \cdot |e| \cdot \mu_V, \qquad (7)$$

in which square brackets denote concentration. μ_V is the mobility of the anion vacancies.

The total conductivity in a bromine atmosphere can be represented by

$$\sigma_{\mathrm{Br}_2} = p \cdot |e| \cdot \mu_p + [V_{\mathrm{Br}^-}] \cdot |e| \cdot \mu_V. \qquad (8)$$

μ_p is the hole mobility, and p denotes hole concentration. In the calculations of the excess conductivities ($\Delta\sigma = \sigma_{\mathrm{Br}_2} - \sigma_0$), it was assumed that $[V_{\mathrm{Br}^-}]_0 = [V_{\mathrm{Br}^-}]$.

According to the chemical formulation (6), and including the shift of the Schottky equilibrium, we find that

$$\Delta\sigma = p \cdot |e| \cdot (\mu_p - \mu_V). \qquad (9)$$

The mobility of the bromine ion vacancies has been given in a previous paper (*5*).

$$\mu_V = \left(\frac{10^2}{T}\right) \exp\left(\frac{-0.2g\ \mathrm{eV}}{\mathrm{kT}}\right) \frac{\mathrm{cm}^2}{\mathrm{V\ sec}}. \qquad (10)$$

The measured square-root dependence on bromine pressure indicates a well-defined mass-action effect of bromine pressure on hole concentration and suggests that the hole mobility is only a function of temperature. The apparent diffusion coefficient of the holes at room temperature was calculated from the rate of attaining the equilibrium conductivity, by using the rate-formula given by Dünwald and Wagner (*10*).

Via the well-known Einstein relation and using the room temperature value of μ_V, calculated with Eq. (10), for μ_V/μ_p the value 10^{-2} is obtained. This reduces Eq. (9) to

$$\Delta\sigma = p \cdot |e| \cdot \mu_p. \qquad (11)$$

From Figs. 5 and 6 we calculate

$$\Delta\sigma = 8.3 \times 10^{-4} \sqrt{P_{\mathrm{Br}_2}} \exp(-0.34\ \mathrm{eV/kT})\, \Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{atm}^{1/2}. \qquad (12)$$

The high-temperature equilibrium was frozen in and all crystals were measured at room temperature. If the hole mobility is independent of hole concentration we may accept for μ_V/μ_p, in all the annealed and quenched crystals, the value 10^{-2}. So from Figs. 5 and 6 the temperature coefficient of the hole concentration is obtained:

$$p \propto \exp(-0.34\ \mathrm{eV/kT}). \qquad (13)$$

Combining Eq. (1) and (12) leads to

$$\mu_p \propto \exp(+0.11\ \mathrm{eV/kT}). \qquad (14)$$

If more experimental facts, concerning the temperature dependence of the hole mobility are known, more quantitative calculations can be presented.

Our experiments are in quantitative agreement with the proposed reaction scheme (*6*, *7*) for the photodecomposition of lead bromide. In this reaction scheme a photohole diffuses to the surface and is trapped at a surface halogen ion. Probably two neutral bromine atoms give a bromine molecule, which desorbs from the surface.

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