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The Ionic Conductivity of Pure and Doped Lead Bromide Single Crystals

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The ionic conductivity data of pure and doped lead bromide are used to evaluate the defect parameters: entropy (ΔS_m) and enthalpy (ΔH_m) of motion of an anion vacancy, entropy (ΔS_f) and enthalpy (ΔH_f) of formation of a Schottky defect trio. The expression for the mobility of the bromide ion vacancies was recalculated from the conductivity of different thallium (I) bromide-doped crystals. The experimental expression is

$$\mu_{V_{Br}^{\cdot}} = \left(\frac{5.0 \pm 0.2}{T}\right) \exp\left(\frac{-0.25 \pm 0.01 \text{ eV}}{kT}\right) \text{cm}^2 \text{ V}^{-1} \text{ sec}^{-1}.$$

From conductivity isotherms (σ/σ_0 vs dopant concentration) the experimental relation for the intrinsic bromide ion-vacancy concentration was calculated to be

$$[V_{Br}^{\cdot}]_0 = (21 \pm 2) \exp\left(\frac{-0.57 \pm 0.03 \text{ eV}}{kT}\right) \text{ mole fraction.}$$

A comparison between the ionic conductivity and a self-diffusion experiment shows that in the conductivity experiments the displacement of the bromide ion vacancies is measured.

1. Introduction

A pure stoichiometric crystal can only show an increase in the concentration of cation vacancies, if there is an increase in the concentration of either anion vacancies, or cations at interstitial sites, or both. A stoichiometric amount of anion and cation vacancies is called Schottky disorder. In the case of Frenkel disorder equal concentrations of ion vacancies and interstitial ions of the same type occur.

In practice the intrinsic defects are predominantly of one of these limiting types. Since, as a result of thermal activation, these defects can jump from place to place through the lattice, they are responsible for matter-transport processes in these crystals, e.g., electrolytic conductivity, diffusion rates, etc.

The defect parameters of the predominant lattice disorder of ionic crystals can be investigated by measuring the ionic conductivity of crystals containing known concentrations of aliovalent cations or anions. These aliovalent dopants change the concentration of the intrinsic lattice defects, preserving charge neutrality and therefore influencing the ionic conductivity. A recent review of this subject has been given by Barr and Lidiard (*1*).

It has been known for a long time that the transport number of the bromide ions in lead bromide is unity up to the melting point (*2*). In previous papers (*3*, *4*) we reported ionic conductivity results on pure and doped lead-bromide single crystals. Substitutional replacement of lead ions by monovalent cations increased the conductivity, whereas a decreased conductivity was measured after incorporation of trivalent bismuth ions. Together with structural considerations (*3*) we omitted the occurrence of Frenkel defects and introduced the following electroneutrality conditions

$$[Me_{Pb}'] + 2[V_{Pb}''] = [V_{Br}^{\cdot}] \tag{1}$$

and

$$[Me_{Pb}^{\cdot}] + [V_{Br}^{\cdot}] = 2[V_{Pb}'']. \tag{2}$$

Me_{Pb}' is a monovalent cation at a lead ion site (effective charge −) and $Me_{Pb}^{\cdot}$ is a trivalent cation at a lead ion site (effective charge +). Square brackets denote concentrations. We consider anion and cation vacancies to be the only intrinsic point defects in lead bromide. Their thermal generation is given by

$$PbBr_2 \rightleftharpoons V_{Pb}'' + 2V_{Br}^{\cdot}. \tag{3}$$

The aim of the present paper is to present more elaborate conductivity results and to extend the quantitative discussion of these results.

2. Experimental

The pure and doped lead-bromide samples were cleaved from single crystals perpendicular to the *c* axis. The single crystals were grown either according to the Bridgman technique, i.e., lowering a sealed ampulla containing purified material through a temperature gradient, or directly obtained from the zone-refining apparatus after about 30 zone passes (*3*). The lead bromide was doped with thallium by adding thallium (I) bromide before the zone melting procedure under vacuum. Bismuth or silver was introduced by placing a small amount of the metal at the beginning of the tube, followed by zone-refining under bromine pressure (*3*).

It was necessary to remeasure the conductivity of trivalent bismuth-doped crystals, since the impurity-controlled conductivity region, although showing a decrease (*3*) as expected from Eq. (2), could not unambiguously be correlated to anion conduction.

When the crystal conductance was less than $10^{-8}\ \Omega^{-1}$, dc measurements were performed on a Bruel & Kjoer Megohm-meter, when the crystal conductance exceeded $10^{-8}\ \Omega^{-1}$, a General Radio impedance bridge (type 1608A), with external oscillator (type 1210C), and an amplifier-null-detector (type 1232A) was used. In the experiments flat disks were used with thickness 0.1–0.3 cm and a surface area of about 1 cm^2. Good contacts on the crystals were obtained with either Aquadag, or Leitsilber. The conductivity at constant frequency (1 kc/sec) was independent of voltage up to 45 V. At constant voltage (range 1–45 V) the conductivity was independent of frequency, ranging from 0.1 to 50 kc/sec. In these ranges the painted electrodes behave like ohmic contacts. The frequency used throughout the experiments was 1 kc/sec. At this frequency the inaccuracy of the bridge is about 0.1%.

The conductivity of the crystals was measured as a function of increasing as well as a function of decreasing temperature in a dry nitrogen atmosphere. In both cases the same conductivity values were obtained.

The temperature was measured with a calibrated chromel–alumel thermocouple mounted near an electrode. The actual crystal temperature was checked by melting a calibrated chromel–alumel thermocouple into a single-crystal specimen and measuring with both thermocouples the temperature in the range 300–620°K.[1] This procedure yielded an experimental correction formula of the type

$$T(\text{crystal}) = C_1\, T(\text{cell}) + C_2.$$

For various conductivity cells in our laboratory C_1 values are close to unity and $0 < C_2 < 10°\mathrm{K}$. No preliminary heat treatment was necessary for the pure and doped crystals in order to obtain reproducible conductivity data.

3. Conductivity Results

The plots of $\log \sigma T$ vs $1/T$ of lead bromide doped with silver bromide, thallium (I) bromide or bismuth (III) bromide are shown in Fig. 1. $\mathrm{Me}'_{\mathrm{Pb}}$ ($\mathrm{Me} = \mathrm{Tl}, \mathrm{Ag}$) incorporation is followed by a shift of the Schottky equilibrium [cf. Eq. (3)] and corresponds to an increased bromide ion-vacancy concentration according to Eq. (1). As a result the conductivity, σ, increases. According to Eq. (2) incorporation of $\mathrm{Me}^{\cdot}_{\mathrm{Pb}}$ ($\mathrm{Me} = \mathrm{Bi}$) decreases the bromide ion-vacancy concentration. A decreased conductivity results with respect to the undoped crystal.

From the impurity-controlled conductivity region we obtain the same conductivity-activation energies, indicating that in all crystals the conduction is due to anion vacancies. The intrinsic conductivity, σ_0, represents in the $\log \sigma T$ vs $1/T$ plot a straight line. This corresponds to the formation of a Schottky defect trio and the motion of an anion vacancy.

From the conductivity plots of the thallium (I) bromide-doped crystals we constructed conductivity isotherms, i.e., σ/σ_0 vs dopant concentration. From these isotherms, presented in Fig. 2, we can calculate values of the intrinsic bromide ion-vacancy concentration. In addition the linearity of these isotherms allows us to exclude associated defects of the type $(\mathrm{Tl}_{\mathrm{Pb}}.\mathrm{V}_{\mathrm{Br}})^{\times}$. Furthermore the absence of these associated defects include the possibility to determine very accurately the bromide ion-vacancy mobility as a function of temperature.

The relationship between the conductivity and the mobility in the case of one mobile charge carrier is given by

$$\sigma = ne\mu \tag{4}$$

in which n is the concentration, e the charge and μ the mobility of the charge carrier. In general the

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[1] I am indebted to Mr. G. J. Dirksen of this Laboratory, who carried out the calibration of the thermocouples against PTB standards. Use was made of a Heraeus calibration furnace type T.P.K., and a Dieselhorst potentiometer (Bleeker).

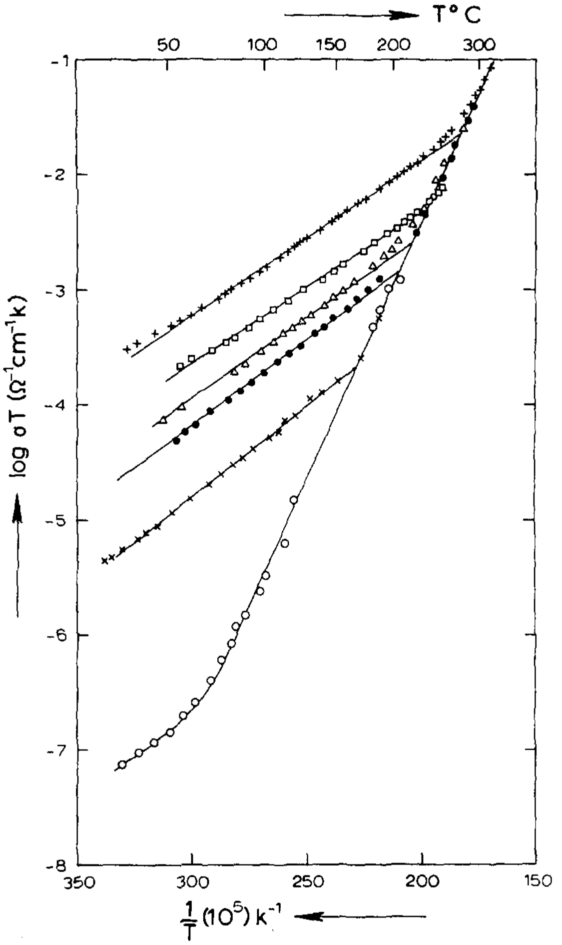

FIG. 1. The ionic conductivity, σ, of pure and doped lead bromide crystals, plotted as $\log \sigma T$ vs $1/T$. ○○ $PbBr_2$–$BiBr_3$ (1.9×10^{-2} mole %), ×× $PbBr_2$–$BiBr_3$ (8×10^{-4} mole %), .. $PbBr_2$ undoped, △△ $PbBr_2$–AgBr (~2×10^{-3} mole %), □□ $PbBr_2$–TlBr (1×10^{-2} mole %), ++ $PbBr_2$–TlBr (2×10^{-2} mole %).

mobility is proportional to the jump frequency, ν, to a particular site: $\mu = C\nu/T$, in which C is a constant, determined by the lattice involved. Upon doping with monovalent cations we may arrive considering Eq. (1), at the situation

$$[V_{Br}^{\cdot}] \gg [V_{Br}^{\cdot}]_0 \gg [V_{Pb}'']. \qquad (5)$$

This means that the concentration of the intrinsic thermally generated bromide ion vacancies, $[V_{Br}^{\cdot}]_0$, can be neglected with respect to the extrinsic concentration generated by thallium (I) bromide incorporation (*4*), i.e., since $[V_{Pb}''] \simeq 0$, $n = [Tl_{Pb}']$. If we plot $\log(\sigma T/[Tl_{Pb}']e)$ [$= \log \mu T$] vs $1/T$ for the different thallium (I) bromide-doped crystals, we must obtain one straight line in the absence of associated defects. It is assumed that μ is independent of the anion vacancy concentration. The result is presented in Fig. 3.

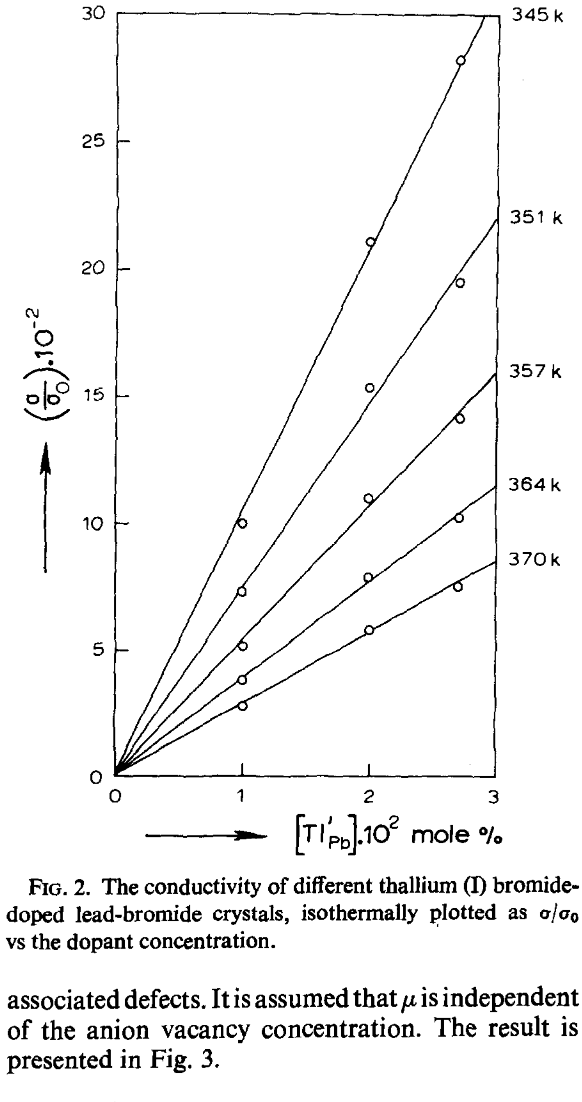

FIG. 2. The conductivity of different thallium (I) bromide-doped lead-bromide crystals, isothermally plotted as σ/σ_0 vs the dopant concentration.

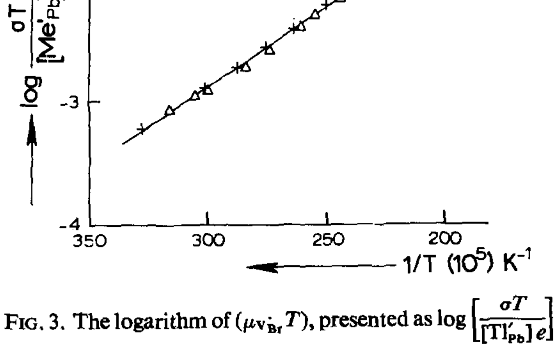

FIG. 3. The logarithm of ($\mu_{V_{Br}^{\cdot}} T$), presented as $\log \left[\frac{\sigma T}{[Tl_{Pb}']e}\right]$ vs $1/T$ for crystals doped with □□ 1×10^{-2} mole %, ++ 2×10^{-2} mole %, △△ 2.7×10^{-2} mole % TlBr.

4. Ionic Conductivity

The ionic conductivity in lead bromide (*3*, *4*) is analogous to the ionic conductivity in lead chloride (*5–7*, *9–10*). With the usual formulas (*8*) the following expressions for the temperature and concentration dependence of the ionic conductivity in lead chloride were derived by De Vries (*6*). These expressions are also applicable for describing the conductivity behaviour of lead bromide, since the thermal disorder in lead bromide appeared to be of the same type as in lead chloride.

In the extrinsic-conductivity region, σ is given by

$$\sigma = \frac{[V_{Br}^{\cdot}]\nu_0 a^2 e^2}{kT} \exp\left(\frac{\Delta S_m}{k}\right) \exp\left(\frac{-\Delta H_m}{kT}\right), \tag{6}$$

where ΔS_m and ΔH_m are the entropy and enthalpy of motion, respectively, ν_0 is an effective vibrational frequency, usually equated to the Debye frequency, and a is the jump distance.

In the intrinsic-conductivity region, σ_0 is represented by Eq. (7),

$$\sigma_0 = \frac{\sqrt[3]{(2N\nu_0 a^2 e^2)}}{kT} \exp\left(\frac{\Delta S_f/3 + \Delta S_m}{k}\right) \times \exp\left[\frac{-(\Delta H_f/3 + \Delta H_m)}{kT}\right], \tag{7}$$

where ΔS_f and ΔH_f denote the formation entropy and formation enthalpy, respectively, of a Schottky defect trio. N is the number of anions per unit volume. As usual T denotes the absolute temperature and k the Boltzmann constant.

From the extrinsic-conductivity regions obtained with the doped crystals (Fig. 1) we calculated for ΔH_m the value (0.29 ± 0.04) eV. From the intrinsic part of the conductivity plot ($\log \sigma T$ vs $1/T$) of undoped and doped crystals we calculate

$$\sigma_0 T = 1.69 \times 10^5 \exp\left(\frac{-0.77 \pm 0.04\ \text{eV}}{kT}\right) \quad \Omega^{-1}\ \text{cm}^{-1}\ \text{K}. \tag{8}$$

From Eq. (8) we obtain for one third of the heat of formation of a Schottky defect trio, $\Delta H_f/3$, the value (0.48 ± 0.06) eV.

5. Concentration of Defects in Lead Bromide

5.1. Temperature Dependence

The general relation governing the concentration of the Schottky defects in lead bromide is in accordance with Eq. (3) given by

$$K_{sch} = [V_{Pb}''][V_{Br}^{\cdot}]^2 = \exp(\Delta S_f/k)\exp(-\Delta H_f/kT), \tag{9}$$

where K_{sch} is the Schottky equilibrium constant. The validity of this equation is not affected upon doping with, for instance, thallium (I) bromide. The increase of the anion vacancy-concentration results in a decrease in the lead ion-vacancy concentration in such a way that Eq. (9) holds, i.e., $[V_{Pb}''] = K_{sch}/[Tl_{Pb}']^2$. In the lead bromide crystals doped with thallium (I) bromide we can neglect the presence of associated defects of the type $(Tl_{Pb}.V_{Br})^{\times}$ (Fig. 2). From Eq. (5) we may exclude the occurrence of vacancy pairs, $(V_{Pb}.V_{Br})'$, in the extrinsic-conductivity region, since $[V_{Pb}'']$ is practically zero.

The evaluation of the slopes of the isotherms presented in Fig. 2 yields, according to Eqs. (4) and (5), the values of the intrinsic bromide ion-vacancy concentration in pure lead bromide. When $\log [V_{Br}^{\cdot}]_0$ is plotted against $1/T$, a straight line is obtained, the equation of which is

$$[V_{Br}^{\cdot}]_0 = (21 \pm 2)\exp\left(\frac{-0.57 \pm 0.03\ \text{eV}}{kT}\right) \quad \text{mole fraction.} \tag{10}$$

In his original paper on lead-chloride conduction Simkovich (*9*) plotted $[\sigma/\sigma_0 - (\sigma/\sigma_0)^{-2}]$ vs $\Delta\gamma = [Me_{Pb}'] - [Me_{Pb}^{\cdot}]$ to evaluate $[V_{Cl}^{\cdot}]_0$. Isotherms of this type can also be used for the evaluation of $[V_{Br}^{\cdot}]_0$. If Eq. (5) holds $[\sigma/\sigma_0 - (\sigma/\sigma_0)^{-2}]$ reduces in good approximation to σ/σ_0. The term $(\sigma/\sigma_0)^{-2}$ cannot be neglected for very low dopant concentrations. Simkovich used for σ_0 the conductivity data of undoped lead chloride, which means

$$[\sigma/\sigma_0 - (\sigma/\sigma_0)^{-2}] = 0 \qquad \text{for } \Delta\gamma = 0.$$

From the conductivity isotherms σ/σ_0 vs $[Me_{Pb}']$ the intrinsic bromide ion-vacancy concentrations can be calculated directly, if the values of σ_0 used are those extrapolated from the intrinsic-conductivity region to the low-temperature region as was pointed out by Schoonman and Verwey (*4*). In this case $\sigma/\sigma_0 = 1$ for $[Me_{Pb}'] = 0$. We prefer the use of these isotherms, since the extrinsic conductivity of the undoped crystals is strongly dependent on the remainder impurity content.

In a recent study of the ionic conductivity of pure and doped lead-chloride crystals Hoshino and coworkers (*10*) also used this method, i.e., extrapolated σ_0 values in constructing the σ/σ_0 vs $[Me_{Pb}']$ isotherms. Their high-temperature isotherms show $\sigma/\sigma_0 = 1$ for $[Me_{Pb}'] = 0$, whereas the low-temperature isotherms show $\sigma/\sigma_0 \gg 1$ for $[Me_{Pb}'] = 0$. This can be understood if we accept the presence of the associates $(Me_{Pb}.V_{Cl})^{\times}$.

From the Eqs. (3) and (9) we obtain a theoretical expression for the intrinsic concentration of the bromide ion vacancies

$$[V_{Br}^{\cdot}]_0 = \sqrt[3]{2}\exp(\Delta S_f/3k)\exp(-\Delta H_f/3kT). \quad (11)$$

This expression is compared with Eq. (10). For $\Delta H_f/3$ we now obtain the value (0.57 ± 0.03) eV. From the pre-exponential factor we calculate for $(\Delta S_f/3k)$ the value 2.8 ± 0.1, so the formation entropy ΔS_f has the value (16.7 ± 0.6) cal/deg mole.

The Schottky constant describing the thermal equilibrium can now be represented by

$$K_{sch} = (4.5 \pm 0.1) \times 10^3 \exp\left(\frac{-1.71 \pm 0.09\ \text{eV}}{kT}\right) \text{(mole fraction)}^3. \quad (12)$$

In Fig. 4 we have plotted the temperature dependence of the intrinsic-vacancy concentrations in lead bromide as obtained from Eq. (10) and the relation $[V_{Pb}''] = \frac{1}{2}[V_{Br}^{\cdot}]$. In addition extrinsic bromide ion-vacancy concentrations in an undoped and in TlBr doped crystals, assuming $[V_{Br}^{\cdot}] = [Me_{Pb}']$, are presented, showing indeed that intrinsic concentrations can be neglected here.

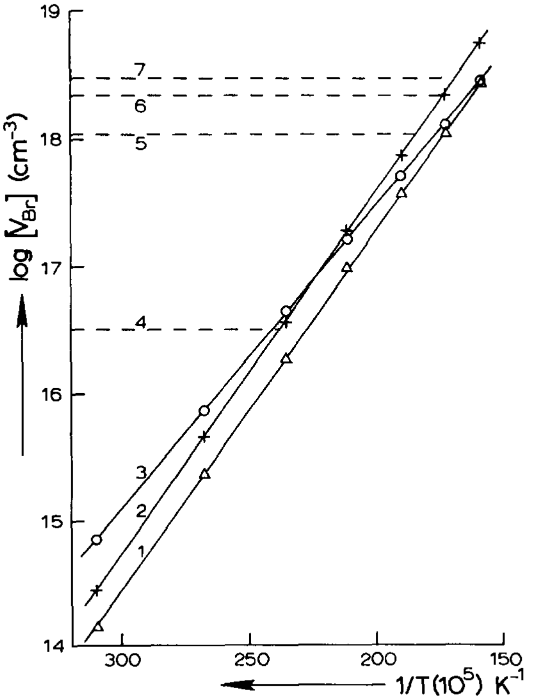

FIG. 4. Intrinsic and extrinsic concentrations of lattice defects in lead bromide. 1 $[V_{Pb}'']_0 = \frac{1}{2}[V_{Br}^{\cdot}]_0$, Eq. (10), 2 $[V_{Br}^{\cdot}]_0$, Eq. (10), 3 $[V_{Br}^{\cdot}]_0$, Eq. (3) in Ref. (*4*), 1 $[V_{Br}^{\cdot}]$ as calculated from the extrinsic conductivity of an undoped crystal (remainder impurity content). 5, 6, 7 $[V_{Br}^{\cdot}] = [Tl_{Pb}']$, 1×10^{-2}, 2×10^{-2} and 2.7×10^{-2} mole % TlBr, respectively.

Anion-vacancy concentrations as presented in Ref. (*4*) were obtained with the assumption $\Delta S_f = 0$, and are presented by curve 3 in Fig. 4. ΔS_f influences only the magnitude of $[V_{Br}^{\cdot}]_0$ and not the temperature coefficient. It must be pointed out, however, that the value 0.48 eV $(\Delta H_f/3)$, obtained from the intrinsic-conductivity region is used in calculating curve 3, whereas curve 2 is based on Eq. (10).

5.2. The Pre-exponential Factor

The pre-exponential factor in Eq. (10) represents the variation in vibrational entropy upon formation of the vacancies (*18*). In Table I we compare the mean change in vibrational entropy associated with the formation of vacancies in several ionic crystals and metals.

In general it appears that ΔS_f(metals) < ΔS_f(ionic crystals). Attempts to calculate ΔS_f for vacancies in metals have been rather successful (*14*) and yield approximated values of 1.3 ± 0.4 for vacancy formation in simple cubic, bcc and fcc structures.

The vibrational frequencies of a solid are affected by the formation of vacancies. The general equation which relates the entropy to the lattice frequencies is to a first approximation given by (*8*, *18*)

$$\exp(\Delta S/k) = (\nu_0/\nu)^{\times}, \quad (13)$$

where ν_0 is roughly equal to the Debye frequency, and ν is the vibrational frequency of the lattice perturbed by a vacancy. × denotes the number of ions adjacent to the vacancy. If we assume that the bromide ion vacancies affect the entropy of the crystal by changing the vibrational frequencies of the nearest lead ions only, i.e.,

$$S(V_{Br}^{\cdot}) = (\times_{Br^-})k\ln(\nu_0/\nu_{Pb^{2+}})$$

and that lead ion vacancies affect the vibrational frequencies of the adjacent bromide ions only, i.e.,

$$S(V_{Pb}'') = (\times_{Pb^{2+}})k\ln(\nu_0/\nu_{Br^-})$$

TABLE I

FORMATION ENTROPIES OF VACANCIES

Crystal	Defect	$\Delta S_f/k$	$\Delta S_f/2k$	$\Delta S_f/3k$	Ref.
NaCl	V_{Na}'		3.1 ± 0.9		(*11*)
KCl	V_K'		3.5 ± 1.2		(*11*)
$PbCl_2$	$V_{Cl}^{\cdot}$			5.4 ± 0.3[a]	(*10*)
$PbBr_2$	$V_{Br}^{\cdot}$			2.8 ± 0.1	this work
Au	V_{Au}	1 (±0.3)			(*12*, *14*)
Ag	V_{Ag}	1.5 (±0.5)			(*13*, *14*)

[a] Hoshino et al. (*10*) calculated from their experimental results for $\Delta S_f/k$ the value 5.4 ± 0.3. Actually $\Delta S_f/3k$ has the value 5.4 ± 0.3.

we can calculate from Eq. (12)

$$\nu_0{}^2 = 2.54\nu_{Br^-}\nu_{Pb^{2+}} \qquad (14)$$

since the lead ions are surrounded by nine bromide ions, $\times_{Pb^{2+}} = 9$, and bromide ions are surrounded either by four or five lead ions (*17*), $\times_{Br^-} = 4$, or 5. Equation (14) was calculated, assuming an average coordination number $\times_{Br^-} = 4.5$.

According to Mott and Gurney (*8*) for vacancies $\nu < \nu_0$. From Eq. (14) it is not obvious that $\nu_{Br^-} < \nu_0$, since we may well have the situation

$$\nu_{Br^-} < (\text{or} >)\nu_0$$

and

$$\nu_{Pb^{2+}} > (\text{or} <)\nu_0$$

with

$$\nu_{Br^-}\nu_{Pb^{2+}} < \nu_0{}^2$$

or in other words, bromide ion vacancies decrease (or increase) the entropy, and lead ion vacancies increase (or decrease) the entropy of the crystal.

Since vacancy formation implies that ions near the vacancies are bound with fewer bonds than ions in the unperturbed lattice we might indeed expect overall decreased vibrational frequencies, i.e., Eq. (14). The situation described is only an approximation since more ions than just the nearest neighbours are affected. In addition the lattice around the vacancy relaxes (Section 8).

6. Mobility of the Bromide Ion Vacancies

6.1. Temperature Dependence

During the ionic-conduction process the bromide ion vacancies migrate through the lattice, and as a consequence the bromide ions move into the opposite direction. In Section 3 we mentioned the proportionality between the mobility, μ, and the frequency, ν, of the ion jump to a particular site.

In accordance with Eq. (6)

$$\mu_{V_{Br}^{\cdot}} = \frac{\nu_0 a^2 e}{kT}\exp(\Delta S_m/k)\exp(-\Delta H_m/kT). \qquad (15)$$

More accurate conductivity results obtained with lead-bromide crystals doped with different amounts of thallium (I) bromide were used to recalculate the temperature dependence of the mobility. Since $\mu T = \sigma T/[\mathrm{Tl}'_{Pb}]e$ the straight line as presented in Fig. 3 represents the temperature dependence of the anion-vacancy mobility in crystals in which impurity-vacancy associates are absent. From the experimental results we found

$$\mu_{V_{Br}^{\cdot}} = \left(\frac{5.0 \pm 0.2}{T}\right)\exp\left(\frac{-0.25 \pm 0.01\ \text{eV}}{kT}\right)$$
$$\text{cm}^2\ \text{V}^{-1}\ \text{sec}^{-1}. \qquad (16)$$

For the enthalpy of motion, ΔH_m, we have now the value (0.25 ± 0.01)eV. The same parameter calculated from the extrinsic-conductivity region of the doped crystals is given in Section 4: i.e., (0.29 ± 0.04) eV. Both values are in good agreement.

6.2. The Pre-exponential Factor

From the pre-exponential factor in Eq. (16) we obtain on comparing with Eq. (15)

$$\nu_0\exp(\Delta S_m/k) = 2.8 \times 10^{11}\ \text{sec}^{-1}. \qquad (17)$$

For the jump distance, a, the value 3.9 Å (*3*, *17*) is used. Assuming for ν_0 the value 8.6×10^{13} sec^{-1} as calculated from the infrared absorption region (*4*, *16*) we obtain for $\Delta S_m/k$ the value -5.7 ± 0.2. Schoonman and Verwey (*4*) neglected the entropy term in the equation for the mobility and compared directly the experimental value for ν_0 (5.5×10^{12} sec^{-1}) obtained from their pre-exponential factor ($10^2/T$), with the infrared absorption frequency (8.6×10^{13} sec^{-1}). Since actually $\nu_0\exp(\Delta S_m/k)$ has the value 5.5×10^{12} sec^{-1}, $\Delta S_m/k$ approximates the value -3. We believe that the present value -5.7 ± 0.2 is more accurate since it was calculated from the conductivity results of three different TlBr doped crystals, whereas the value -3 is based on a single conductivity run (*4*), using the extrinsic conductivity-activation energy.

The entropy of migration results from changes in lattice vibrational modes during the jumping process. The frequency of the nearest-neighbour vibrations, assuming an average coordination number 4.5 at a bromide ion site, is approximately given by (Section 5.2),

$$S(V_{Br}^{\cdot}) = k\ln(\nu_0/\nu_{Pb^{2+}})^{4.5}. \qquad (18)$$

On behalf of this simple model we obtain from Eqs. (14), (17) and (18) $\nu_{Pb^{2+}} > \nu_0$ and $\nu_{Br^-} < \nu_0$, with $\nu_{Br^-}\nu_{Pb^{2+}} < \nu_0{}^2$ as was mentioned in Section 5.2.

In the bromide ion-vacancy jump process the entropy is lowered. Similar situations exist in silver bromide (*1*), lead sulphide (*18*) and sodium chloride (*18*, *28*). In silver bromide the silver ion vacancy has a negative entropy of motion. In lead sulphide lead ion vacancies cause an increase of the entropy, whereas sulphur vacancies have the opposite effect. The reversed situation, with respect to the situation in lead sulphide, exists in sodium chloride, i.e., the mobile vacancy, V'_{Na}, decreases the entropy of the crystal.

7. Diffusion in Lead Bromide

Information about the actual transport mechanism in a crystal can be obtained from a comparison of self-diffusion and conductivity experiments. The principal requirement is that one type of defect mechanism contributes to both ionic conductivity and diffusion. Ionic conductivity and diffusion are related on a microscopic scale by the Einstein relation for each type of defect. On a macroscopic scale, however, it is necessary to introduce a correlation factor, f, for diffusion. The factor f depends on the crystal lattice as well as on the mechanism of ionic transport (*19–22*).

The experimental correlation factor is obtained by measuring the total conductivity, σ, and calculating the diffusion coefficient, D_σ, with the normal macroscopic Einstein relation, $D_\sigma = (kT/\mathrm{Ne}^2)\sigma$. The value of D_σ is compared with the diffusion coefficient $D^\ddagger$ measured with radioactive tracers.

For the bromide ions in lead bromide we can write $f_{\mathrm{Br}} = D^\ddagger_{\mathrm{Br}}/D_\sigma$. The tracer diffusion coefficient of the bromide ions is directly comparable to D_σ calculated from the measured conductivity. The occurrence of mobile neutral impurity-vacancy associates [for example $(\mathrm{O_{Br}} \cdot \mathrm{V_{Br}})^\times$, next paper] which would be unnoticed in a conductivity experiment may contribute considerably to bromide tracer diffusion. The importance of the impurity-vacancy associates can be minimized by working at high temperatures. In the temperature region 225–350°C (intrinsic-conductivity region) Dr. L. W. Barr measured on our undoped lead-bromide crystals the diffusion coefficient of the bromide ions (*4*, *23*), using the bromine isotope ^{82}Br (*31*). As a result he obtained a linear Arrhenius plot: $\log D^\ddagger_{\mathrm{Br}}$ vs $1/T$. From his experimental results we calculated for $D^\ddagger_{\mathrm{Br}}$ the expression

$$D^\ddagger_{\mathrm{Br}} = 2.82 \times 10^{-3} \exp\left(\frac{-0.73 \pm 0.01\ \mathrm{eV}}{kT}\right) \quad \mathrm{cm^2\ sec^{-1}}. \tag{19}$$

From the intrinsic conductivity of the undoped crystal we calculated

$$D_\sigma = 3.50 \times 10^{-3} \exp\left(\frac{-0.74 \pm 0.02\ \mathrm{eV}}{kT}\right) \quad \mathrm{cm^2\ sec^{-1}} \tag{20}$$

giving for the correlation factor f_{Br} the value 0.81. If we compare this single tracer experiment with intrinsic-conductivities as measured on both pure and doped crystals during the course of conductivity investigation in our laboratory we obtain for f_{Br} the range 0.70–0.81.

The anion sublattice in lead bromide consists of a disturbed hexagonal packing (*17*). The theoretical correlation factor for diffusion of free vacancies in a hexagonal closed-packed structure has the value 0.78146 (*19*). In the diffusion experiment the displacement of the tracer is measured. On account of the value 0.81 it is obvious that in lead bromide a tracer migrates by a bromide ion vacancy, giving us further support that in the conductivity experiments we have measured the displacement of the bromide ion vacancies.

8. Discussion

The defect parameters of the dominant lattice disorder, i.e., Schottky defects, in lead bromide as deduced from ionic conductivity and diffusion experiments are presented in Table II. From Table II we may conclude that the activation enthalpies in the intrinsic conductivity region ($\Delta H_f/3 + \Delta H_m$) are in reasonable agreement. An increase in the value for ΔH_m lowers the value for $\Delta H_f/3$.

The values for ΔH_m and $\Delta H_f/3$ are within the experimental error isotropic. Smakula (*24*) found the value 0.28 eV for all three directions, and 0.53 eV ($\Delta H_f/3$) for the *a* and *b* direction. The equations for the intrinsic bromide ion-vacancy concentration [Eq. (10)] and their mobility [Eq. (16)] are mainly obtained from extrinsic-conductivity data. The experimental expression describing the intrinsic conductivity, i.e., Eq. (8),

$$\sigma_0 T = 1.69 \times 10^5 \exp\left(\frac{-0.77 \pm 0.04\ \mathrm{eV}}{kT}\right) \quad \Omega^{-1}\ \mathrm{cm^{-1}\ K} \tag{8}$$

can be obtained on substituting Eqs. (10) and (16) into Eq. (4). As a result we get

$$\sigma_0 T = 1.85 \times 10^5 \exp\left(\frac{-0.82 \pm 0.04\ \mathrm{eV}}{kT}\right) \quad \Omega^{-1}\ \mathrm{cm^{-1}\ K}. \tag{21}$$

Both expressions are in very good agreement.

Barsis and Taylor (*26*), in discussing the conductivity results of De Vries (*5*, *6*) on lead chloride, have pointed out that conductivity isotherms of the type presented in Fig. 2 are characteristic of either Schottky disorder, or Frenkel disorder with a relatively immobile interstitial anion. The same ambiguity should therefore exist in lead bromide. From the lead-bromide structure we can derive that interstitial ions with radius < 0.94 Å may occur (*3*). The Pauling radius of the bromide ion is 1.95 Å. Therefore we omit the occurrence of interstitial bromide ions.

TABLE II

DEFECT PARAMETERS FROM CONDUCTIVITY AND DIFFUSION (FOR THE *c* DIRECTION)

Source	$\Delta S_f/3k$	$\Delta S_m/k$	$\Delta H_f/3$	ΔH_m
Conductivity:				
Smakula (*24*)			0.64 eV	0.28 eV
Verwey, Schoonman (*3*)			0.48 ± 0.06 eV	0.29 ± 0.04 eV
Schoonman, Verwey (*4*)[a]		−2.8		
This work	2.8 ± 0.1	−5.7 ± 0.2	0.57 ± 0.03 eV	0.25 ± 0.01 eV
Anion diffusion:				
Barr (*23*)			0.40 eV	0.33 eV

[a] Calculated from Ref. (*4*).

On using Eq. (13) to calculate Eq. (14), thus accepting only a change of vibrational frequencies of ions adjacent to the vacancy, we obtained as a net effect decreased frequencies, since we measured a positive value for the formation entropy of a defect trio. This is to be expected if a vacancy disorder is predominant. For Frenkel defects the expression for $\exp(\Delta S_f/k)$ is more complicated, but in general $\exp(\Delta S_f/k)$ is less than unity, since the frequency of an interstitial ion and that of its neighbours will be greater than that of a normal lattice ion (*8*, *25*). We showed in Section 6.2 that $\nu_{Br^-} < \nu_0$ and $\nu_{Pb^{2+}} > \nu_0$ with $\nu_{Br^-}\nu_{Pb^{2+}} < \nu_0^2$. Furthermore it was exemplified in Section 6.2 that such situations do occur in substances with Frenkel disorder as well as in substances with Schottky disorder. Therefore the entropy change caused by a single defect has by no means a diagnostic value concerning the predominant disorder. As has been mentioned before the situation described is only an approximation, since more ions than just the nearest neighbours are affected. Actually all lattice vibrations are reduced by a vacancy and this combined effect of all these small frequency changes may exceed the nearest neighbour effect, i.e., Eq. (13) (*27*). Therefore the model used in Section 6.2 represents a lower limit.

In addition the lattice around the vacancy relaxes. According to Theimer (*28*) the displacements of the nearest neighbours is quite important and may even produce a net increase in the frequencies, which can be larger than the decrease, according to Mott and Gurney, by the vacancy itself. Using the displacements of the ions produced by the electric field of a vacancy as calculated by Tosi and Fumi (*29*), Theimer calculated, neglecting ionic polarizations, for vacancy formation in NaCl $\Delta S_f = -0.085\ k$. However, it must be pointed out that the ionic displacements are strongly influenced by polarization of the ions in the field of the vacancy. On drastically reducing the ionic displacements Theimer could arrive at a positive entropy, in accordance with the experimental value (Table I). Faux and Lidiard (*30*) calculated, accepting only polarizable anions, for vacancy formation in NaCl an inward radial displacement of the ions surrounding a vacancy, which accounts directly for a positive entropy of formation. In metal systems the contribution of small relaxations associated with vacancies can in general be neglected (*14*). Therefore the feature ΔS_f (metals) < ΔS_f (ionic crystals) can be qualitatively understood from the fact that when an ion is removed from an ionic lattice larger relaxations occur than in case of vacancy formation in metal systems (*15*).

In view of Eq. (14) and the results of Section 6.2 we may assume that the bromide ions around the lead ion vacancy have found equilibrium positions closer to the vacancy and that the lead ions around the bromide ion vacancy have found equilibrium positions farther away from the vacancy (*32*).

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