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Association of Defects in Lead Chloride and Lead Bromide: Ionic Conductivity and Dielectric Loss Measurements

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The ionic conductivity data of pure and doped lead bromide without associated defects are used in order to explain the anomalous conductivity behaviour of copper (I) bromide and lead oxide-doped lead-bromide crystals. In these crystals precipitated dopant and associated defects are present. The association enthalpy, and enthalpies| of solution for free defects and for associated defects in lead bromide are calculated from the concentration and temperature dependence of the ionic conductivity, respectively. A detailed comparison has been made between the ionic conductivity data and dielectric loss measurements on both lead chloride and lead bromide. Associated defects of the type $(\mathrm{Me_{Pb}.V_X})^\times$ and $(\mathrm{O_X.V_X})^\times$, (X = Cl, Br) as found from the conductivity data, are confirmed by the dielectric loss measurements. For the copper (I) bromide-doped lead-bromide crystals a relaxation process is proposed because of hopping electrons.

1. Introduction

The ionic conductivity of pure and doped lead-chloride and lead-bromide single crystals has been interpreted in terms of anionic conduction (*1–5*). In general the enthalpy of motion of the halide ion vacancy can be obtained from the extrinsic-conductivity region of, for example, thallium (I) halide-doped lead-halide crystals, $\mathrm{PbX_2}$–TlX (X = Cl, Br), (*6*, *10*), if associated defects are absent.

If doped crystals are grown from the melt, the impurity concentration at lower temperatures may exceed the solubility limit. If the crystals are kept at room temperature for sufficiently long times, the dopant precipitates, forming a second phase. The precipitation of the impurity can be schematically represented by the sequence

Free defects → impurity-vacancy associates → precipitate.

The defect parameters concerning precipitation of the dopant and association of free defects can be studied in conductivity experiments, since because of these effects departures from linearity in the extrinsic region of the $\log \sigma$ vs $1/T$ plots do occur. In that case several conductivity activation energies can be derived from the experimental conductivity data. As a result one obtains not only the enthalpy of motion of the vacancies, but also the association enthalpy and enthalpies of solution for free and for associated defects.

De Vries (*6*) reported slight departures from the linear plot of $\log \sigma$ vs $1/T$ in the extrinsic-conductivity region, due to thallium (I) chloride ion-vacancy associates. The extrinsic-conductivity region clearly consists of two linear parts. The low-temperature conductivity-activation energy (0.43 ± 0.02) eV leads to the enthalpy of motion, ΔH_m, and the association enthalpy, ΔH_a, whereas the high-temperature activation energy (0.35 ± 0.02) eV can be directly related to the motion of the chloride ion vacancies. On increasing the temperature the conductivity behaves intrinsically.

In lead-bromide crystals doped with copper (I) bromide, or with lead oxide more pronounced departures were measured (*4*). The conductivity behaviour in the low-temperature region of the extrinsic conduction is typical of a precipitation phenomenon (*7*). As has been pointed out by Breckenridge (*8*) the existence of associated ionic defects may give rise to dielectric losses.

In this paper we shall discuss the quantitative results of the conductivity experiments and dielectric

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loss measurements on both pure and doped lead-chloride and lead-bromide crystals. Furthermore it will be shown that in the copper (I) bromide-doped lead-bromide crystal two relaxation modes are present. The relaxation time of the first mode can be correlated with associated ionic defects, whereas the relaxation time of the second mode seems to be characteristic of hopping electrons.

2. Experimental

Both lead-chloride and lead-bromide samples used in this work, were cleaved from single crystals perpendicular to the *c* axis. The crystal purification, the growing technique, and the conductivity bridge used, have been described previously (*4*, *6*, *9*).

The conductivity and dielectric losses were measured on freshly prepared single crystals, except for the copper (I) bromide-doped lead-bromide crystal. The ampulla containing this crystal was opened about one year after preparation. Cloudiness due to precipitation was observed with an optical microscope in the upper part of the ampulla. In lead-oxide-doped lead-bromide, cloudiness was observed directly after preparation. In the doped lead chloride and the thallium (I) bromide-doped lead-bromide samples no second phase was present. The impurity content of the crystals was determined spectrochemically at the Philips Research Laboratories (*4*). The total amount of incorporated oxygen is unknown, since no analytical determination method was available. However, experiments are in progress to determine the oxygen content with activation analysis at "Reactor Centrum Nederland."

The dielectric measurements were performed on a General Radio Capacitance Bridge (type 706 C), the auxiliary apparatus, i.e., oscillator, tuned null-detector and balancing capacitors of the same manufacturer.

The crystals were mounted in a cryostat which was evacuated before the measurements. In order to eliminate the contribution of the cables to the capacitance and the loss, we used a switch in the cryostat very close to the crystal. Good contacts on the crystals were obtained by means of a silver paint ("Leitsilber" Degussa 200).

3. Anomalous Conductivity of Copper (I) Bromide- and Lead-Oxide-Doped Lead Bromide

Assuming a substitutional replacement of lead ions by monovalent copper ions, $\mathrm{Cu}'_{\mathrm{Pb}}$, and of bromide ions by oxygen, $\mathrm{O}'_{\mathrm{Br}}$, respectively, (*4*) it follows from the lattice reactions (1) and (2) that in both crystals electroneutrality is maintained by an enhanced bromide ion-vacancy concentration, $[\mathrm{V}^{\cdot}_{\mathrm{Br}}]$

$$\mathrm{CuBr} \rightarrow \mathrm{Cu}'_{\mathrm{Pb}} + \mathrm{V}^{\cdot}_{\mathrm{Br}} + \mathrm{Br}^{\times}_{\mathrm{Br}} \tag{1}$$

and

$$\mathrm{PbO} \rightarrow \mathrm{O}'_{\mathrm{Br}} + \mathrm{V}^{\cdot}_{\mathrm{Br}} + \mathrm{Pb}^{\times}_{\mathrm{Pb}} \tag{2}$$

in which $\mathrm{Pb}^{\times}_{\mathrm{Pb}}$ and $\mathrm{Br}^{\times}_{\mathrm{Br}}$ denote a lead ion and a bromide ion in their normal lattice positions, respectively. Compared to the undoped crystals we measured a higher conductivity for both doped crystals. The conductivity results of several copper (I)-doped crystals are presented in Fig. 1. From the conductivity isotherms (σ/σ_0 vs impurity content) presented in Fig. 2, we conclude that the measured conductivity is too low with respect to the incorporated amount of copper (I) bromide.

The anomalous extrinsic conductivity of the copper (I)-doped crystals can be represented by Eqs. (3) and (4)

$$\sigma T = 3.4 \times 10^3 \exp\left(\frac{-0.54 \pm 0.04\ \mathrm{eV}}{kT}\right)\ \Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{K} \tag{3}$$

and

$$\sigma T \sim \exp\left(\frac{-0.34 \pm 0.03\ \mathrm{eV}}{kT}\right)\ \Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{K} \tag{4}$$

in the temperature regions 80–140°C and 140–200°C, respectively. At temperatures, above about 200°C the conductivity becomes intrinsic. The experimental data can be described by Eq. (5)

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

Let us assume the following equilibria (*4*, *7*),

$$\begin{array}{lll} & \underset{\Delta H_s}{\overset{\longrightarrow}{\longleftarrow}} & \mathrm{Cu}'_{\mathrm{Pb}} + \mathrm{V}^{\cdot}_{\mathrm{Br}} + \mathrm{Br}^{\times}_{\mathrm{Br}} \\ \mathrm{CuBr\ (precipitate)} & & \qquad \uparrow\downarrow \Delta H_a \\ & \overset{\Delta H_s^*}{\overset{\longrightarrow}{\longleftarrow}} & (\mathrm{Cu}_{\mathrm{Pb}}.\mathrm{V}_{\mathrm{Br}})^{\times} + \mathrm{Br}^{\times}_{\mathrm{Br}} \end{array} \tag{6}$$

Application of the law of mass action then gives, for the solubility for unassociated defects

$$K_s = [\mathrm{Cu}'_{\mathrm{Pb}}][\mathrm{V}^{\cdot}_{\mathrm{Br}}] = K_s{}^0 \exp(-\Delta H_s/kT), \tag{7}$$

for the solubility for associated defects

$$K_s{}^* = [(\mathrm{Cu}_{\mathrm{Pb}}.\mathrm{V}_{\mathrm{Br}})^{\times}] = K_s^{*0} \exp(-\Delta H_s{}^*/kT), \tag{8}$$

and for the association of defects

$$K_a = \frac{[(\mathrm{Cu}_{\mathrm{Pb}}.\mathrm{V}_{\mathrm{Br}})^{\times}]}{[\mathrm{Cu}'_{\mathrm{Pb}}][\mathrm{V}^{\cdot}_{\mathrm{Br}}]} = ZK_a{}^0 \exp(\Delta H_a/kT), \tag{9}$$

where square brackets denote concentrations.

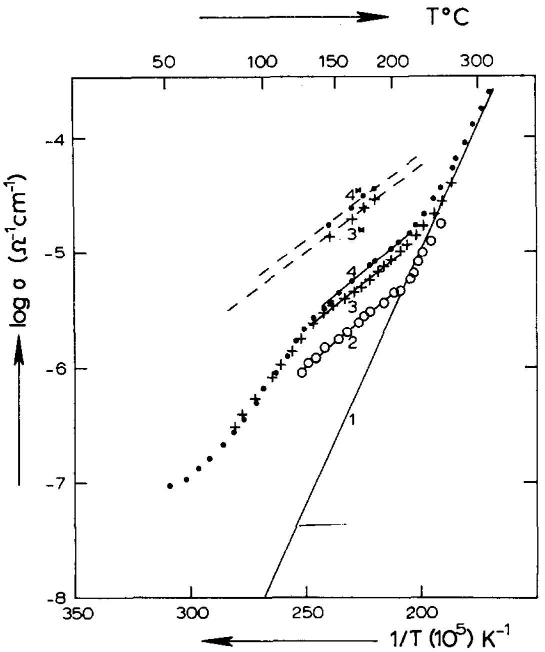

FIG. 1. The ionic conductivity, σ, of pure and copper (I) bromide-doped lead-bromide crystals. 1—intrinsic conductivity, 2—$PbBr_2$–CuBr 1.7×10^{-5} (mole fraction), 3—$PbBr_2$–CuBr (2.3×10^{-4} mole fraction), 4—$PbBr_2$–CuBr (2.9×10^{-4} mole fraction). The curves 3* and 4* represent calculated conductivities in the case that all copper (I) ions (3 and 4) had replaced lead ions.

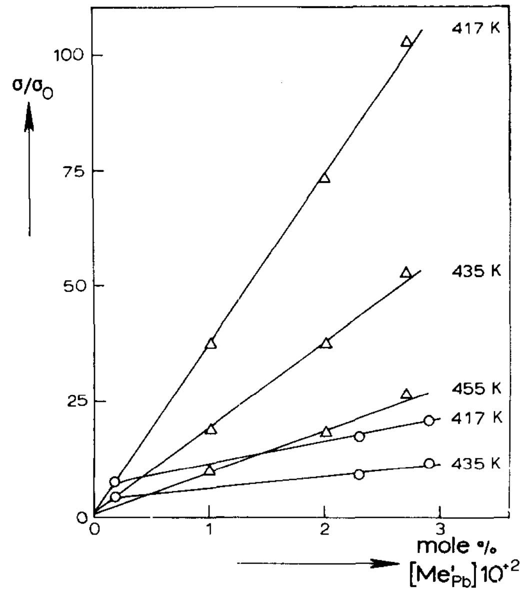

FIG. 2. The conductivity of thallium (I) bromide (△△) and copper (I) bromide (○○)-doped lead-bromide crystals, isothermally plotted as σ/σ_0 vs the amount of impurity. In the $PbBr_2$–TlBr crystals associated defects were not present.

The equilibrium constants are interrelated by the following equations

$$\Delta H_s = \Delta H_a + \Delta H_s^*$$

and

$$K_s^{*0} = ZK_a^0 K_s^0. \tag{10}$$

ΔH_s is the enthalpy of solution for free defects, ΔH_s^* is the enthalpy of solution for associated defects, and ΔH_a is the enthalpy of association for free defects. The pre-exponential factors originate from the change in the vibrational entropy (*10*, *19*). Z denotes the number of possible orientations of the associate, and originates from the configurational part of the entropy variation due to the association of defects.

On introducing into Eq. (11)

$$\sigma = [V_{Br}^{\cdot}]\, e\mu_{V_{Br}^{\cdot}}, \tag{11}$$

the relation for the bromide ion-vacancy concentration as obtained from Eq. (7), i.e.,

$$[V_{Br}^{\cdot}] = (K_s^0)^{1/2} \exp(-\Delta H_s/2kT) \text{ mole fraction} \tag{12}$$

and the bromide ion-vacancy mobility as obtained from Ref. (*10*),

$$\mu_{V_{Br}^{\cdot}} = \left(\frac{5.0 \pm 0.2}{T}\right) \exp\left(\frac{-0.25 \pm 0.01 \text{ eV}}{kT}\right) \text{cm}^2\, \text{V}^{-1}\, \text{sec}^{-1} \tag{13}$$

we obtain

$$\sigma T = 5Ne(K_s^0)^{1/2} \exp\left[-\left(\frac{\Delta H_s + 0.50}{2kT}\right)\right] \Omega^{-1}\, \text{cm}^{-1}\, \text{K}, \tag{14}$$

where N ($= 2.2 \times 10^{22}$ cm^{-3}) denotes the number of bromide ions per cm^3.

In the temperature region 80–140°C Eq. (3) represents the experimental conductivity. On comparing Eqs. (3) and (14) we find for ΔH_s the value (0.58 ± 0.08) eV and for K_s^0 the value 0.4 ± 0.1.

The association enthalpy, ΔH_a, can be calculated from the concentration dependence and the temperature dependence of the conductivity in the temperature region 140–200°C. In this temperature region the total amount of copper (I) bromide, [CuBr], is dissolved and present in free and in associated form

$$[\mathrm{CuBr}] = [(\mathrm{Cu_{Pb}}.\mathrm{V_{Br}})^{\times}] + [\mathrm{Cu'_{Pb}}]. \tag{15}$$

Combination of Eqs. (9) and (15), bearing in mind $[\mathrm{Cu}'_{\mathrm{Pb}}] = [\mathrm{V}^{\cdot}_{\mathrm{Br}}]$, then gives

$$\Delta H_a = kT \ln \left[\frac{[\mathrm{CuBr}] - [\mathrm{V}^{\cdot}_{\mathrm{Br}}]}{ZK_a{}^0 [\mathrm{V}^{\cdot}_{\mathrm{Br}}]^2} \right] \quad (16)$$

if we neglect the intrinsic bromide ion-vacancy concentrations, which is allowed in the temperature region involved here (*10*).

From the conductivity isotherms, σ/σ_0, for the thallium (I) bromide- and copper (I) bromide-doped crystals (Fig. 2) we calculate with Eq. (16) for the association enthalpy the expression

$$\Delta H_a = [(0.18 \pm 0.02) - kT \ln K_a{}^0]\ \mathrm{eV}. \quad (17)$$

For Z the value 9 (coordination number of a lead ion in lead bromide) was used (*19*). If we neglect the vibrational part of the entropy variation, i.e., $K_a{}^0 = 1$ (*21*), Eq. (17) reduces to $\Delta H_a = (0.18 \pm 0.02)$ eV.

If we compare the conductivity isotherms for the copper (I) bromide-doped crystals with those for the thallium (I) bromide-doped crystals we see

$$[\mathrm{Cu}'_{\mathrm{Pb}}] < [\mathrm{CuBr}] \quad (18)$$

or in other words a high degree of association. If we introduce Eq. (18) into the combination of Eqs. (9) and (15) we obtain for the bromide ion-vacancy concentration

$$[\mathrm{V}^{\cdot}_{\mathrm{Br}}] \simeq \left(\frac{[\mathrm{CuBr}]}{ZK_a{}^0} \right)^{1/2} \exp \left(\frac{-\Delta H_a}{2kT} \right) \text{ mole fraction.} \quad (19)$$

Substitution of Eqs. (13) and (19) into Eq. (11) then gives

$$\sigma T \simeq 5Ne \left(\frac{[\mathrm{CuBr}]}{ZK_a{}^0} \right)^{1/2} \exp \left[- \left(\frac{\Delta H_a + 0.50}{2kT} \right) \right] \Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{K}. \quad (20)$$

This conductivity equation closely resembles the equation for defect interactions in silver chloride and silver bromide as derived by Müller (*11*). It must be compared to Eq. (4) for the evaluation of ΔH_a. From the temperature dependence of the conductivity we obtain in this way for ΔH_a the value (0.18 ± 0.06) eV in good agreement with the value for ΔH_a calculated from the concentration dependence of the conductivity. We are now able to determine the enthalpy of solution for associated defects, $\Delta H_s{}^*$. Introducing the experimental values for ΔH_a and ΔH_s into relation (10) we get $\Delta H_s{}^* = (0.40 \pm 0.08)$ eV. Since we assumed $K_a{}^0 = 1$, the value for K^{*0} approximates (4 ± 1).

In the temperature range 140–200°C there exists a high degree of association as was mentioned before [cf. Eq. (18)]. A comparison of Eq. (12) with Eq. (19) shows approximately that the impurity will remain in solution at temperatures such that (*20*)

$$(K_s{}^0)^{1/2} \exp(-\Delta H_s/2kT) > \left(\frac{[\mathrm{CuBr}]}{ZK_a{}^0} \right)^{1/2} \exp(-\Delta H_a/2kT). \quad (21)$$

In Fig. 1, curves 3 and 4 represent the conductivity of crystals doped with 2.3×10^{-4} and 2.9×10^{-4} mole fraction copper (I) bromide. Inserting these concentrations, $K_a{}^0 = 1$ and the experimental defect parameters into Eq. (21) we obtain for the lowest temperatures, T_p, satisfying Eq. (21) about 170 and about 190°C, respectively. Below these temperatures precipitation will start. From Fig. 1 we see that the temperatures, T_p, of the intersections of precipitation ranges with association ranges are 135 and 145°C, respectively. The agreement is reasonable if we take into account the experimental errors in the defect parameters.

The maximum solubility of copper (I) bromide in the presence of association is obtained on introducing Eqs. (12) and (8) into relation (15),

$$[\mathrm{CuBr}] = (K_s{}^0)^{1/2} \exp(-\Delta H_s/2kT) + K_s^{*0} \exp(-\Delta H_s{}^*/kT) \text{ mole fraction.} \quad (22)$$

The total uptake of copper (I) bromide by the crystal is greater in the presence of association than it would be if ΔH_a was zero, cf. Eq. (12). The total solubility was calculated in the temperature region 80–140°C with Eq. (22). Some values are collected in Table I. The conductivity vs $1/T$ plots, obtained with lead oxide-doped lead-bromide crystals are similar to curves 3 and 4, as presented in Fig. 1 Assuming in these crystals, in which a precipitated phase was present, the existence of the associates $(\mathrm{O}_{\mathrm{Br}}.\mathrm{V}_{\mathrm{Br}})^{\times}$ we can make use of the above-mentioned theoretical considerations to calculate ΔH_a, ΔH_s,

TABLE I

THE TOTAL SOLUBILITY OF COPPER (I) BROMIDE AS A FUNCTION OF TEMPERATURE

Temperature °K	[CuBr] mole fraction from Eq. (22)
353	5.8×10^{-5}
373	9.9×10^{-5}
393	1.6×10^{-4}
413	2.6×10^{-4}

and ΔH_s^*. The anomalous conductivity of the lead-oxide-doped lead-bromide crystals can be represented also by two relations. In the temperature region 70–130°C, the precipitation range, we obtained

$$\sigma T = 5.5 \times 10^3 \exp\left(\frac{-0.56 \pm 0.05 \text{ eV}}{kT}\right) \Omega^{-1}\text{ cm}^{-1}\text{ K}. \tag{23}$$

In the temperature region 130–200°C, the association range, we calculated from the experimental conductivity data

$$\sigma T \sim \exp\left(\frac{-0.35 \pm 0.03 \text{ eV}}{kT}\right) \Omega^{-1}\text{ cm}^{-1}\text{ K}. \tag{24}$$

From Eqs. (14) and (23) we obtain for the enthalpy of solution for free defects, ΔH_s, the value (0.6 ± 0.1) eV, and for K_s^0 the value 0.6 ± 0.1.

If we compare Eq. (24) with Eq. (20) we obtain for the association enthalpy, ΔH_a, the value (0.20 ± 0.06) eV. It was impossible until now to calculate ΔH_a from the concentration dependence of the conductivity, since the amount of oxygen is unknown. Introduction of the values for ΔH_s and ΔH_a into relation (10) gives for the enthalpy of solution for associated defects, ΔH_s^*, the value (0.4 ± 0.1) eV, and for K_s^{*0} the value 5 ± 1.

In Table II we have collected the different enthalpies, concerning migration of anion vacancies, ΔH_m, and solution of impurities, together with association enthalpies. In this table we have also included some literature values for lead-chloride crystals, since the next section deals with both pure and doped lead-chloride and lead-bromide crystals.

4. Dielectric Loss Measurements

If the Debye model (*12*) applies to the associated ionic defects the real and imaginary part of the dielectric constant are

$$\begin{aligned} \epsilon' &= \epsilon_\sim + [(\epsilon_s - \epsilon_\sim)/(1 + \omega^2\tau^2)], \\ \epsilon'' &= (\epsilon_s - \epsilon_\sim)[\omega\tau/(1 + \omega^2\tau^2)], \end{aligned} \tag{25}$$

in which ω denotes the frequency of the applied field (radians per second) and τ denotes the relaxation time of the dipoles involved. ϵ_s and $\epsilon_\sim$ are the dielectric constants for frequencies ω with $\omega \ll \tau^{-1}$ and $\omega \gg \tau^{-1}$, respectively. Assuming $\epsilon_s - \epsilon_\sim \ll 1$ the dielectric loss is given by

$$\tan\delta = C[\omega\tau/(1 + \omega^2\tau^2)] + (\sigma/\omega\epsilon_\sim). \tag{26}$$

The first term of the right-hand side of Eq. (26) describes the relaxation loss, whereas the second term gives the ionic-conductivity contribution to the loss, and

$$C = (\epsilon_s' - \epsilon_\sim')/\epsilon_\sim' = \beta N_d p^2/\epsilon_\sim kT, \tag{27}$$

where N_d and p are the concentration and the moment of the dipoles involved, and β is a factor taking into account local field corrections.

From the behaviour of $\tan\delta$ for frequencies far outside the relaxation region, i.e., $\omega \ll \tau^{-1}$, the contribution due to the conductivity to the loss could be eliminated. In order to reduce this contribution as much as possible the measurements were performed in the temperature region 80–300°K. We investigated lead-chloride as well as lead-bromide crystals, both pure and doped.

4.1. Lead Chloride

Crystals of nominally pure and KCl-doped lead chloride exhibited dielectric loss. The same was the case with $BeCl_2$-doped crystals which we had at our disposal; these crystals show the same value for the conductivity with respect to the undoped lead-chloride crystals, indicating that the beryllium ion had replaced the lead ion. The relaxation time can be described in all three cases by

$$\tau = \tau_0 \exp(\Delta H_r/kT) \tag{28}$$

with $\tau_0 = (1.50 \pm 0.5) \times 10^{-13}$ s and the activation enthalpy $\Delta H_r = 0.37 \pm 0.02$ eV.

From high-temperature conductivity experiments (300–500°K) and the relation for the chloride ion-

TABLE II

DEFECT PARAMETERS (IN eV) CONCERNING SOLUTION OF PRECIPITATED DOPANT AND MIGRATION AND ASSOCIATION OF DEFECTS IN LEAD CHLORIDE AND LEAD BROMIDE

Crystal	ΔH_m	ΔH_a	ΔH_s	ΔH_s^*	Ref.
$PbCl_2$–TlCl	0.35 ± 0.02	0.21 ± 0.07			(*6*)
$PbBr_2$–CuBr		0.18 ± 0.02	0.58 ± 0.08	0.40 ± 0.08	this work
$PbBr_2$–PbO		0.20 ± 0.06	0.6 ± 0.1	0.4 ± 0.1	this work
$PbBr_2$–TlBr	0.25 ± 0.01	0.16 ± 0.03[a]			(*10*)

[a] Section 4.2.

vacancy mobility (*6*) we derived for the chloride ion-vacancy concentrations the values 10^{-5}, 10^{-2} and 10^{-5} mole fraction in the pure, KCl and $BeCl_2$-doped crystals, respectively. In the case of a $LaCl_3$-doped crystal ($[V_{Cl}^{\cdot}] = 10^{-7}$ mole fraction) we could not detect any relaxation loss. The maximum value of the relaxation loss $\tan\delta_m = \frac{1}{2}C$ is just the same for pure and $BeCl_2$-doped lead chloride, whereas doping with KCl was found to increase $\frac{1}{2}C$ (by a factor of about 4).

Since, according to Eq. (27), C depends on the concentration of the dipoles the conclusion seems justified that the dipoles involved are associates between chloride ion vacancies and impurities present in our crystals. Moreover, the activation enthalpy, ΔH_r, as obtained from Eq. (28) equals within the experimental error the enthalpy, ΔH_m, for the chloride ion-vacancy migration (Table II). Therefore we assume the chloride ion vacancy to be the mobile part of the dipole.

4.2. Lead Bromide

Lead bromide exhibits similar loss features as the lead chlorides (Fig. 3). The value of $\tan\delta_m$ could be increased or decreased upon doping with TlBr and $BiBr_3$, respectively. These dopants lead to an increase, or decrease in the number of the bromide ion vacancies, respectively (*5*, *10*).[1] The relaxation time behaves as indicated by Eq. (28) with $\tau_0 = (7.0 \pm 0.5) \times 10^{-11}$ s and $\Delta H_r = (0.20 \pm 0.02)$ eV. We have plotted $\log\tau$ as a function of $1/T$ as can be seen in Fig. 4 (curve I). For reasons similar to the lead chloride case we conclude that we are dealing with an associate of a bromide ion vacancy and an impurity, the bromide ion vacancy being the mobile part of the dipole, although ΔH_r has a somewhat lower value than the enthalpy, ΔH_m, for bromide ion-vacancy migration as given in Table II. It must be pointed out, however, that it is not *a priori* necessary for reorientation enthalpies and migration enthalpies to have exactly the same value. One reason for a possible discrepancy between these values may be, for example, a local lattice deformation due to the incorporated impurity ion in which neighbourhood the vacancy moves. Indeed we expect a somewhat larger lattice deformation in the case of a Tl^+ ion (radius 1.47 Å) than in the case of a K^+ ion (radius 1.33 Å), since the radius of the lead ion is 1.21 Å.

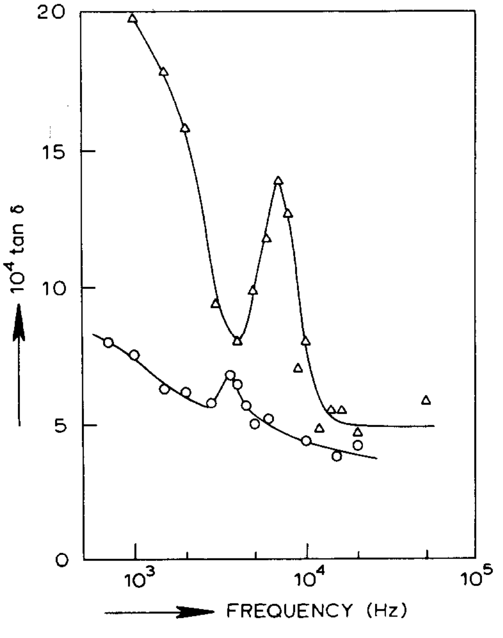

FIG. 3. The dielectric loss $\tan\delta$, plotted vs the frequency, of a nominally pure (○○) and TlBr (△△)-doped lead-bromide crystal, measured at 175°K and 180°K, respectively.

4.3. Copper (I) Bromide-Doped Lead Bromide

The CuBr-doped lead-bromide crystals behave like the above mentioned lead bromides in the temperature region above 180°K only. Below this temperature a new relaxation process appears as can be seen in Fig. 4 (curve II). Its values for ΔH_r and τ_0 are (0.028 ± 0.002) eV and $(3.0 \pm 0.3)10^{-6}$ s, respectively. Note the strong difference between these values and the corresponding ones of curve I. The value $\frac{1}{2}C$ of the maximum loss is of the same order of magnitude as in the undoped lead-bromide case.

In Table III we have summarized the dielectric loss features, i.e., ΔH_r and τ_0, for $PbCl_2$ and $PbBr_2$ (both pure and doped), and for PbBr–CuBr below 180°K. In addition we have included by way of comparison the corresponding values of the enthalpy for vacancy migration (Table II), and the infrared absorption frequency ν_0.

5. Discussion

In the temperature region 80–140°C the experimental results showed a conductivity which is independent of the total amount of copper (I) bromide, and in the temperature region 140–200°C

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[1] In some highly TlBr-doped crystals, without precipitated dopant material, associated defects were present, as was concluded from conductivity experiments: $\Delta H_a = (0.16 \pm 0.03)$ eV. These crystals were used in the dielectric investigations.

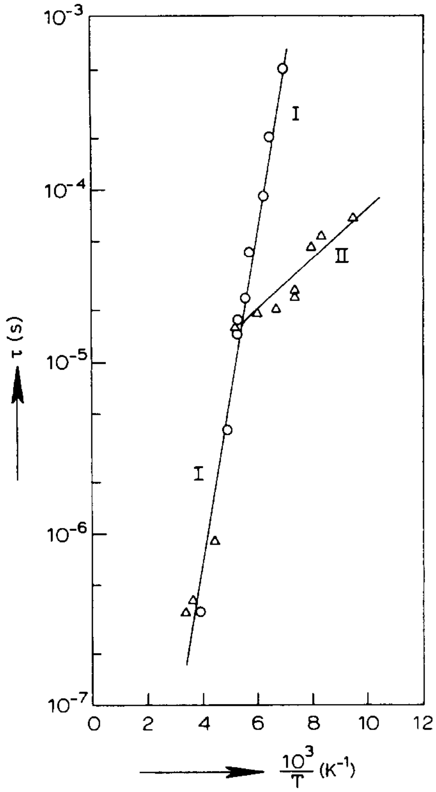

FIG. 4. The relaxation time, τ, of nominally pure and doped lead-bromide crystals vs $1/T$. The values for the CuBr-doped crystals are indicated by Δ.

a conductivity indicating a high degree of association. We conclude that the associates $(\mathrm{Cu_{Pb}.V_{Br}})^{\times}$ are precursors to CuBr precipitation in lead bromide. The temperatures, T_p, of the intersection of precipitation ranges with association ranges as calculated with Eq. (21) are in reasonable agreement with the experimental values for T_p. We should expect somewhat higher values for T_p from the maximum solubility of the unassociated impurity ions, cf. Eq. (12), setting $[\mathrm{CuBr}] = [\mathrm{V}_{\mathrm{Br}}^{\cdot}]$, since association actually increases the solubility of copper (I) bromide. However, the given error ranges exclude an accurate analysis based on the T_p values. The magnitude of the T_p values obtained with Eq. (12) is comparable to that obtained with Eq. (21).

One lead-bromide unit in the crystal can be replaced by the unit $(\mathrm{Cu_{Pb}.V_{Br}})^{\times}\mathrm{Br}_{\mathrm{Br}}^{\times}$. Clusters of these units can be considered to be a separate phase of CuBr. In addition, the bromide ion vacancies involved in these units supply the space necessary in the precipitation of CuBr as a separate phase.

In lead-bromide crystals doped with lead oxide the associates $(\mathrm{O_{Br}.V_{Br}})^{\times}$ are precursors to precipitation of PbO as a separate phase. In the precipitation range (70–130°C) the conductivity is also independent of the total amount of lead oxide. Association does occur in the temperature region 130–200°C, but since an accurate oxygen analysis is still lacking, the degree of association is unknown. However, the degree of association must be considerable, since the total amount of dopant in, and the extrinsic conductivities of lead oxide and copper (I) bromide-doped crystals are of the same order of magnitude.

The pre-exponential factors in Eqs. (7) and (8) originate from the change in the vibrational entropy as was mentioned already. The general equation, which relates the entropy to the lattice frequencies is to a first approximation given by $\exp(\Delta S/k) = (\nu_0/\nu)^{\times}$ [preceding paper, Eq. (13)]. We assume here also that a vacancy or an impurity ion affects the entropy of the crystal by changing the vibrational frequencies of its nearest-neighbour ions.

With the copper (I) bromide-doped crystals we obtained for the pre-exponential factor, $K_s^0 = \exp(\Delta S_s/k)$, viz. upper part of Eq. (6) and equilibrium constant (7), the value 0.4 ± 0.1. The entropy of solution for free defects, ΔS_s, has the value $(-0.9 \pm 0.3)k$. From $\Delta S_s = S(\mathrm{V}_{\mathrm{Br}}^{\cdot}) + S(\mathrm{Cu}_{\mathrm{Pb}}')$ we calculate

$$\nu_{\mathrm{Pb}^{2+}}(\nu_{\mathrm{Br}^-})^2 = (1.2 \pm 0.2)\,\nu_0{}^3. \tag{29}$$

From the results presented in Section 6.2 of the preceding paper we calculate $\nu_{\mathrm{Pb}^{2+}} = 3.6\ \nu_0$. Inserting this value into Eq. (29) then gives $\nu_{\mathrm{Br}^-} = 0.6\ \nu_0$, or in other words the bromide ions around the $\mathrm{Cu}_{\mathrm{Pb}}'$ ions have found equilibrium positions closer to the impurity ion (*10*, *19*). This result is reasonable since the radius of the copper (I) ion (0.96 Å) is smaller than the radius of a lead ion (1.21 Å) (*22*).

Lead oxide dissolves in unassociated form according to reaction (30)

$$\mathrm{PbO} \rightleftharpoons \mathrm{O}_{\mathrm{Br}}' + \mathrm{V}_{\mathrm{Br}}^{\cdot} + \mathrm{Pb}_{\mathrm{Pb}}^{\times}. \tag{30}$$

From the precipitation range in the $\log \sigma T$ vs $1/T$ plot the value 0.6 ± 0.1 is obtained for $K_s{}^0$. ΔS_s has the value $(-0.5 \pm 0.2)k$. Since $\Delta S_s = S(\mathrm{O}_{\mathrm{Br}}') + S(\mathrm{V}_{\mathrm{Br}}^{\cdot})$ we calculate $\nu_{\mathrm{Pb}^{2+}} = 0.3\ \nu_0$, or in other words the lead ions around the $\mathrm{O}_{\mathrm{Br}}'$ ions have found equilibrium positions closer to the impurity ion. We believe that this is also a reasonable result since the effective charge of the $\mathrm{O}_{\mathrm{Br}}'$ ion is negative, whereas the effective charge of the bromide ion vacancy is positive. In addition, the radius of the oxide ion (1.32 Å) is smaller than the radius of the bromide ion.

The possible associates, giving rise to the dielectric loss are $(\mathrm{Me_{Pb}.V_X})^{\times}$ and $(\mathrm{A_X.V_X})^{\times}$, wherein $\mathrm{Me}_{\mathrm{Pb}}'$ represents a monovalent cation and $\mathrm{A_X}'$ a divalent anion (we exclude for the present the second process

TABLE III

DIELECTRIC RELAXATION PARAMETERS OF LEAD CHLORIDES AND LEAD BROMIDES

Crystals	ΔH_r (eV)	ΔH_m (eV)	τ_0 (s)	ν_0 (s^{-1})
$PbCl_2$	0.37 ± 0.02	0.35 ± 0.02	$(1.5 \pm 0.5) \times 10^{-13}$	1.8×10^{13}
$PbBr_2$	0.20 ± 0.02	0.25 ± 0.02	$(7.0 \pm 0.5) \times 10^{-11}$	8.6×10^{13}
$PbBr_2$–CuBr[a]	0.028 ± 0.002		$(3.0 \pm 0.3) \times 10^{-6}$	

[a] Below 180°K.

in $PbBr_2$–CuBr). The losses measured in undoped lead chloride and lead bromide may be attributed, at least partly, to dissolved oxide impurity associated with anion vacancies. Although we are at the moment unable to present quantitative results of an oxygen analysis, as was mentioned already, it should be noted that oxygen was detected in the pure crystals. From a preliminary analysis we calculated $O'_{Br} < 5 \times 10^{-4}$ mole fraction.[2] The remainder impurity content in undoped lead chloride as determined from ionic-conductivity data expressed as chloride ion-vacancy concentration equals 10^{-5} mole fraction. In addition to reorientation of the dipole by means of diffusion of the anion vacancy via nearest neighbours, reorientation must also be possible in the case of the $(O_X.V_X)^{\times}$ associate by means of a direct jump of the oxide ion into the halide ion vacancy.

Usually the value $\nu = (2\pi\tau_0)^{-1}$ is related to the Reststrahlen-frequency ν_0. In general this relation is

$$\nu = A_S A_E \nu_0, \qquad (31)$$

where symmetry properties of the dipole and entropy effects associated with the dipole orientation have been taken into account by means of the factors A_S and A_E, respectively. Relaxation processes wherein ions or ion vacancies are involved usually lead to values of ν in the infrared region. Comparison of the values of τ_0 and ν_0 given in Table III, supports this experience. We note that at a first glance the difference between the value of ν and ν_0 in the case of lead bromides indicates a negative entropy change; writing A_E as $\exp(\Delta S/k)$ in analogy to the results of the preceding paper (*10*) for the conductivity.

The background of Eq. (31) and also of Eq. (28), is the interpretation of the relaxation process as a (classic) rate process. In general, quantum-mechanical analysis (*13*) confirms this interpretation in the case of ions, but indicates also a second way for relaxation which seems to be especially important in the case of electrons. The transition rate between equilibrium positions separated by a potential barrier is determined by a tunneling process, leading to a larger value for τ_0 and a smaller activation enthalpy than one would expect in the case of ions. In this model the activation enthalpy has to be interpreted as the energy necessary for the excitation of an electron from the ground state to an excited state inside a potential well. Several experiments (*14*, *15*) concerning relaxation losses due to electrons strongly confirm this concept.

On account of these considerations we believe that the relaxation process below 180°K in copper (I) bromide-doped lead bromide (curve II in Fig. 4) can be attributed to hopping (or, more precisely: tunneling) electrons. Since the process appears to be present in the case of copper (I)-doped crystals only, it must also be related to the copper ions. A possible explanation would then be electron hopping between a monovalent and a neighbouring divalent copper ion, viz.

$$Cu'_{Pb_1} + Cu^{\times}_{Pb_2} \rightleftharpoons Cu^{\times}_{Pb_1} + Cu'_{Pb_2}. \qquad (32)$$

This implies that we have to make two assumptions.

(1) In addition to the monovalent copper some divalent copper is present too. It is known that copper (I) ions in silver halides act as a hole trap (*16*, *17*). Recently one of the authors (*18*) showed hole conduction in lead bromide treated in a bromine atmosphere. Therefore it is not unreasonable to accept the conversion $Cu'_{Pb} \rightarrow Cu^{\times}_{Pb}$ up to a few percent, since according to the crystal-growing technique used the lead-bromide–copper (I)-bromide mixture was exposed to a bromine atmosphere (this conversion has little influence on the interpretation of the conductivity results, given in Section 3).

(2) It must also be assumed that the copper concentration is high enough to assure the existence of a sufficiently large number of copper-ion pairs.

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[2] Thanks are due to Dr. Ir. H. A. Das of "Reactor Centrum Nederland" for this preliminary analysis.

This seems reasonable, since dopant precipitation was already present in most of these crystals. In view of this we believe that the hopping process takes place, especially in the close surroundings of the copper-bromide clusters in the crystal.

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