

Diffusion and Ionic Conductivity in Cesium Bromide and Cesium Iodide*

DAVID W. LYNCH†

Department of Physics, University of Illinois, Urbana, Illinois

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The diffusion coefficients of the constituent ions were measured in CsBr and CsI single crystals between 300°C and 550°C by means of radioactive tracers and were compared with electrical conductivity measurements. Approximate satisfaction of the Nernst-Einstein equation indicates that the conductivity is nearly completely ionic and the diffusion measurements show that the halogen ion defects are the more mobile. Attempts to identify the mechanisms for ionic transport by means of the Bardeen-Herring correlation factor are discussed. Schottky defects seem likely but the assumption of an additional mechanism for cationic transport is required. If Schottky defects are predominant their formation enthalpies are 2.0 eV and 1.9 eV in CsBr and CsI respectively, and the activation enthalpies for halogen vacancy motion are 0.27 eV and 0.3 eV respectively, while the cesium vacancy activation enthalpy is about 0.58 eV for both salts.

1. INTRODUCTION

SINCE diffusion and ionic conductivity in ionic crystals occur by means of mobile lattice defects, studies of these phenomena frequently yield information about the defects in the crystals studied. Previous work on some of the alkali halides of the NaCl structure and on AgBr and AgCl has led to an apparently adequate model for ionic transport in these salts.¹ Little work has been done on the alkali halides of the CsCl structure.

The conductivities of CsBr and CsI have been measured previously² but they do not agree with the results of the present investigation and are believed to be in error due to a surface effect. Diffusion and conductivity have been studied in CsCl,²⁻⁴ but there is evidence of an appreciable electronic contribution to the conductivity of this salt. The chlorine ion diffuses more rapidly than the cesium ion in CsCl, but cesium diffusion is not negligible, being about one-fifth as rapid as chlorine diffusion throughout the entire temperature range including the high-temperature region where CsCl possesses the NaCl structure. Little can be said about the lattice defects in CsCl.

TlCl has the CsCl structure and seems to contain Schottky defects with chlorine vacancies considerably more mobile than thallium vacancies.^{5,6}

A more extensive study of CsBr and CsI was under-

taken to compare the lattice defects of alkali halides with the CsCl and NaCl structures.

2. THEORY

The electrical conductivity due to j -type ions moving by the m th defect mechanism is

$$\sigma_j = \alpha_m (Ne^2/kT) a_0^2 \nu_{jm} \exp[-(g_{jm} + \Delta g_{jm})/kT], \quad (1)$$

where N is the number of j -ion sites per unit volume, a_0 is the lattice parameter and ν_{jm} is a constant with the dimensions of a frequency. α_m is a geometrical parameter relating the jump distance of the charged defect to the lattice parameter. g_{jm} is (or is related to) the Gibbs free energy required to form the defect involved in the conduction process and Δg_{jm} is the Gibbs free energy of the activated system (defect in the position of highest free energy along its jump path) minus the Gibbs free energy of the system with the defect in its equilibrium position.⁷ Both g_{jm} and Δg_{jm} are composed of an entropy term and an enthalpy term, and the enthalpy terms are referred to as the formation and activation enthalpies. For the case of Schottky defects in the CsCl lattice $\alpha = 1$, g_{jm} is half the free energy to form a Schottky defect, and Δg_{jm} is the activation energy for the type of vacancy being considered. The total ionic conductivity may consist of a sum of terms like (1) for each of the two types of ions.

The diffusion coefficient for a radioactive tracer of ion j moving by mechanism m is

$$D_{Tj} = \alpha'_m \beta_m a_0^2 \nu_{jm} \exp[-(g_{jm} + \Delta g_{jm})/kT], \quad (2)$$

where α'_m is a geometrical factor which may not always equal α_m for the same mechanism. β_m is the Bardeen-Herring correlation factor which accounts for the fact that tracer diffusion is not always random even though the defect responsible for the diffusion may jump randomly. β depends on the lattice geometry and on the mechanism for diffusion. For the vacancy mecha-

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† Union Carbide Fellow. Present address: Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa.

¹ A general reference on diffusion and conductivity with an extensive bibliography is the review by A. B. Lidiard, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XX, pp. 246-349.

² W. W. Harpur, R. L. Moss, and A. R. Ubbelohde, Proc. Roy. Soc. (London) A232, 196 (1955).

³ W. W. Harpur and A. R. Ubbelohde, Proc. Roy. Soc. (London) A232, 310 (1955).

⁴ J. F. Laurent and J. Benard, J. Phys. Chem. Solids 3, 7 (1957).

⁵ K. Hauße and A. L. Griessbach-Vierck, Z. Elektrochem. 57, 248 (1953).

⁶ R. J. Friauf, Bull. Am. Phys. Soc. 3, 127 (1958).

⁷ C. Wert, Phys. Rev. 79, 601 (1950).

nism in the CsCl lattice $\alpha'=1$ and $\beta=0.655$.⁸ Tracer j may move by several mechanisms so D_{Tj} may be a sum of terms like (2).

If conduction and tracer diffusion occur by means of the same single mechanism one expects the Nernst-Einstein relation to be valid for each ion:

$$\frac{t_j \sigma}{D_{Tj}} = \frac{\alpha}{\alpha' \beta} \frac{Ne^2}{kT}. \quad (3)$$

If t_j , the transport number, is unknown, then since $t_a + t_c = 1$,

$$\frac{\alpha' \beta}{\alpha} \frac{kT \sigma}{Ne^2} = \frac{\alpha' \beta}{\alpha} D_o = D_{Ta} + D_{Tc}, \quad (4)$$

where c and a refer to cations and anions. For the more general case in which many mechanisms may be involved the Nernst-Einstein relation in the absence of transport numbers becomes

$$D_o = \sum_{j=a,c} D_{Tj} \frac{\sum_m \alpha_m \nu_{jm} \exp[-(g_{jm} + \Delta g_{jm})/kT]}{\sum_m \alpha_m' \beta_m \nu_{jm} \exp[-(g_{jm} + \Delta g_{jm})/kT]}. \quad (5)$$

These expressions are not correct if some diffusion occurs by a mechanism which contributes nothing to the conductivity. Any electrically neutral, mobile entity permits such a mechanism, and the most likely ones are cation-anion vacancy pairs and cation vacancy-divalent cation impurity complexes. Diffusion by a ring mechanism⁹ also contributes nothing to the conductivity. In this event the measured D_{Tj} must have subtracted from it the diffusion coefficient of the tracer via this neutral mechanism before using (3), (4), or (5). The diffusion coefficient of the tracer via the neutral mechanism cannot be measured by itself but must be inferred from the disagreement between D_{Tj} and $t_j D_o$.

Attempts will be made to fit the data to Eqs. (4) and (5) by assuming a few mechanisms. This is not a very reliable procedure since even in cases where Eq. (3) is believed to be appropriate the uncertainty in the experimental data is usually as large as the variations in $\alpha' \beta / \alpha$ for the various possible mechanisms. In these cases experiments on crystals doped with aliovalent impurities have been the means of identifying successfully the mode of ionic transport.¹ The effects of aliovalent impurities in CsBr and CsI can be discussed only tentatively.

Another means of identifying the mechanism for transport is to compare calculated values of the formation and activation energies with the experimentally obtained enthalpies. However accurate calculations are tedious and, in the case of the cesium halides, may not be straightforward because of large polarization effects and close packing. Rough estimates of relative

energies have been made in the manner of Jost and Nehlep¹⁰ and these were used to eliminate from consideration mechanisms involving interstitials because of the large energy required to place an interstitial in the crowded lattice. A crowdion configuration was not examined.

3. EXPERIMENTAL PROCEDURE

Crystals

Single crystals of CsBr and CsI were obtained from the Harshaw Chemical Company and from Dr. Karl Korth, Hegelstrasse 37, Kiel, Germany. Conductivity measurements were also made on crystals obtained from other sources. A CsI crystal grown in argon by the Bridgeman technique was kindly supplied by Professor A. Smakula of the Massachusetts Institute of Technology. Several CsBr and CsI crystals were grown in air by the Kyropoulos technique from salts supplied by the Dow Chemical Company and A. D. Mackay, Inc. Semiquantitative spectrographic analyses and ultraviolet absorption measurements revealed that the crystals contained many impurities, the most common being Mg, Al, Ca, and Si. The total concentration of impurities was of the order of 0.01%.

Conductivity

Carbon electrodes were painted on a polished slab of the crystal which was then placed between the platinum electrodes of a sample holder in a regulated furnace with a helium atmosphere. The resistance of the sample was measured with a General Radio 716-C capacitance bridge at 1 kc/sec. No systematic frequency dependence of the resistance was observed between 800 cps and 16 kc/sec. The temperature of the sample was measured with a Pt-Pt+10% Rh thermocouple.

Diffusion

Thin (usually less than $\frac{1}{2}$ micron) layers of salts containing radioisotopes were vacuum evaporated onto surfaces of the crystals previously cut with a microtome. Cs¹³⁴ was obtained by pile irradiation of chips of CsBr and CsI. NaI¹³¹ and KBr⁸² were obtained from Oak Ridge and used as received except that some CsI was usually added to the NaI solution. Conductivity measurements and one Br⁸² diffusion coefficient measurement on a CsBr+1% KBr sample indicated that the potassium in the evaporated layer had no effect on the Br⁸² diffusion coefficient measurements on pure crystals.

Diffusion occurred while the crystals were in vycor and platinum holders with helium atmospheres which were placed in regulated furnaces. The diffusion time t was chosen so that $Dt \sim 10^{-5}$ cm. Temperatures were measured with a Pt-Pt+10% Rh thermocouple and

⁸ K. Compaan and Y. Haven, Trans. Faraday Soc. 52, 786 (1956).

⁹ C. Zener, Acta Cryst. 3, 346 (1950).

¹⁰ W. Jost and G. Nehlep, Z. physik. Chem. 34, 1 (1936).

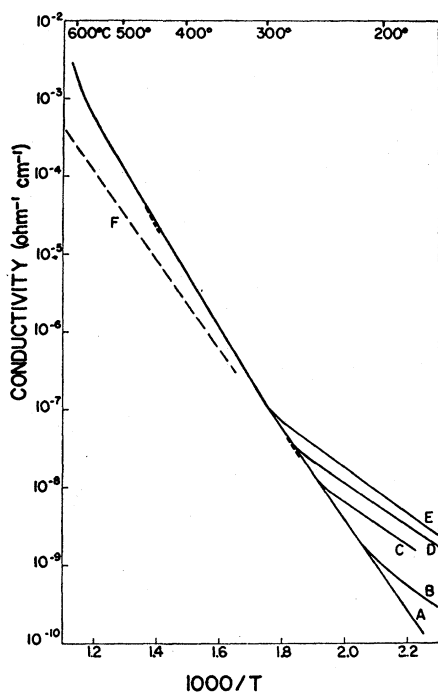


FIG. 1. Conductivity of cesium bromide vs reciprocal absolute temperature. A. Harshaw I, Dow; B. Korth I; C. Korth III; D. Harshaw "special" (center of their ingot); E. Harshaw "special" after HBr anneal; and F. Harpur, Moss, and Ubbelohde (reference 2).

corrections were applied for temperature fluctuation and for diffusion during the heating period.

From 15 to 40 slices about 5 microns thick were subsequently cut from the crystal on a microtome and removed on scotch tape. Slice thicknesses were measured with an interferometer during the slicing. Alignment of the surface prior to slicing was accomplished with an optical lever and in a few cases a correction due to Shirn, Wajda, and Huntington¹¹ was applied.

The slices were placed on plastic holders and the activity of each was measured with a G.M. tube and scaler. Appropriate corrections were made for the short half-lives of Br^{82} and I^{131} , and for varying slice thicknesses, background activity, and tube dead time. Plots of the logarithm of the corrected activity per standard slice vs the square of the depth of the slice center from the surface were straight lines with slopes of $-2.303/4Dt$.

Errors

The conductivities are believed to be correct to within 6% for temperatures above about 350°C, and within 10% for lower temperatures. The diffusion coefficient error is believed to be less than 10% at the higher temperatures and less than 15% at the lower temperatures. These estimates are largely based on

¹¹ G. A. Shirn, E. S. Wajda, and H. B. Huntington, *Acta Met.* **1**, 513 (1953).

estimated systematic errors in temperature measurement and are larger than the observed average deviations of the data.

4. RESULTS

Conductivity

The conductivities of many samples of CsBr and CsI are given in Figs. 1 and 2.¹² The first striking feature of these curves is that the two salts have nearly identical conductivities. Both show a slight change in slope at about 480°C and both have similar low-temperature "impurity regions." The conductivity data are best fitted by expressions of the form $\sigma = \sigma_0 \exp(-E/kT)$ where the constants are given in Table I. Between the highest temperatures listed and the melting point the conductivity curves arc upward and are not fitted by any simple expression. In the impurity regions the slopes correspond to enthalpies of from 0.51 to 0.59 eV for both CsI and CsBr.

There is marked disagreement with the conductivity data of Harpur, Moss, and Ubbelohde.² It is believed that their data are in error because of a surface effect. They poured molten salt into a heated quartz cell fitted with platinum electrodes, then cooled slowly. In the present work it was found that the cesium halides attack both platinum and Vycor when molten. Furthermore the diffusion measurements reported in this paper

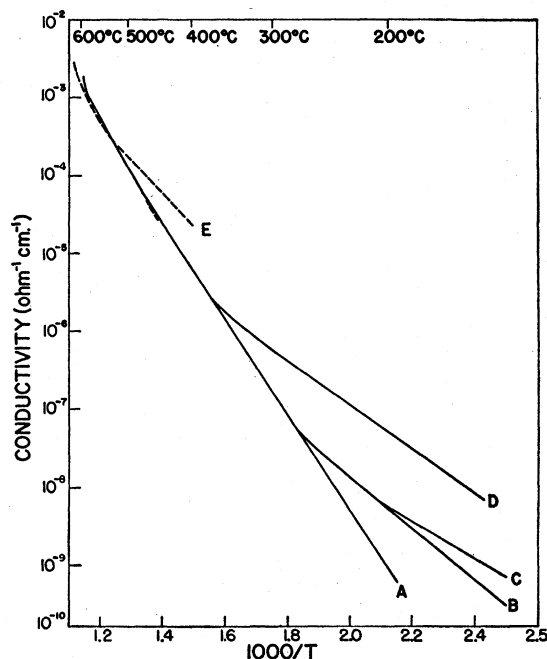


FIG. 2. Conductivity of cesium iodide vs reciprocal absolute temperature. A. Harshaw I; B. Harshaw II; C. Korth II, Smakula; D. Korth I; and E. Harpur, Moss, and Ubbelohde (reference 2).

¹² Tables of numerical conductivity and diffusion data are available in Technical Report No. 1, Contract NONR-1834 (19), Office of Naval Research, Washington, D. C. (unpublished); or D. W. Lynch, thesis, University of Illinois (unpublished).

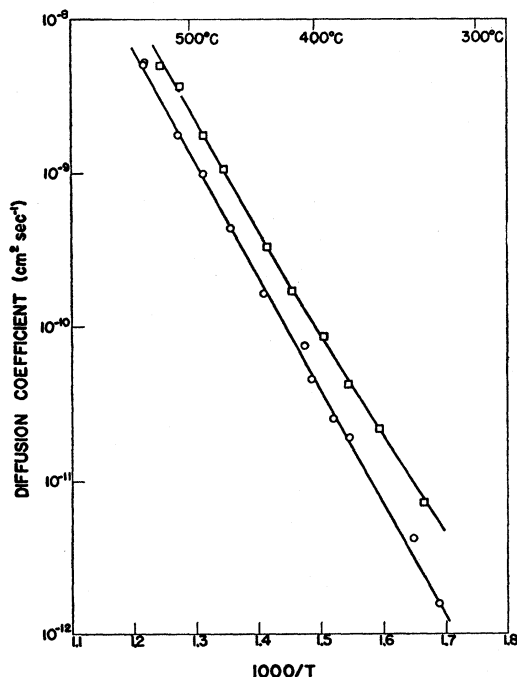
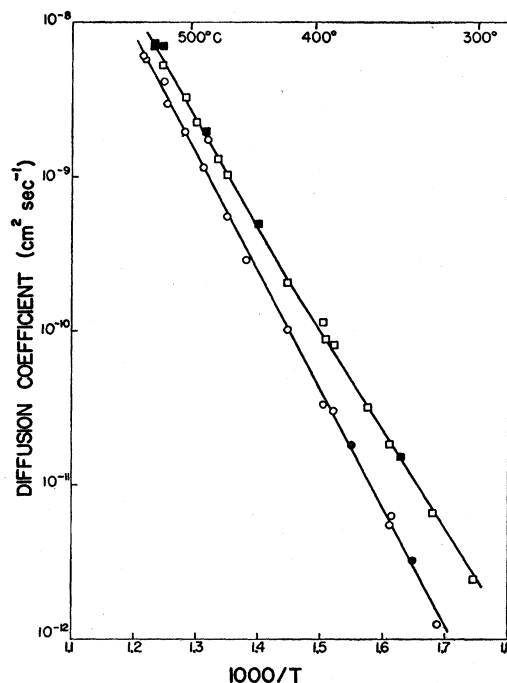
TABLE I. Experimentally determined parameters for the conductivity $\sigma = \sigma_0 \exp(-E/kT)$.

Material	Temperature region (°C)	σ_0 (ohm ⁻¹ cm ⁻¹)	E (ev)
CsBr	475-590	2.48×10^8	1.435
CsBr	impurity region-475	2.51×10^4	1.285
Harshaw CsBr "I"	below 290	1.87×10^3	1.165
CsI	480-595	2.21×10^8	1.43
CsI	impurity region-480	1.38×10^4	1.25

do not agree with the conductivities of Ubbelohde and co-workers.

Figure 1 also shows the change in conductivity produced by heating CsBr to about 550°C for an hour in an atmosphere of HBr. This anneal also caused the conductivity near the melting point to decrease below the extrapolated linear portion of the plot and to become concave downward, instead of concave upward (not shown). Harpur and Ubbelohde found that heating CsCl in HCl vapor reduced the conductivity by as much as a factor of 3 over the entire temperature range of their measurements, and they suggest that the HCl anneal removed oxygen from the crystal. They give several mechanisms by which oxygen could lead to electronic conductivity. Their measurements of the stoichiometry of CsCl as a function of treatment support their interpretation of the effect of HCl vapor.

Attempts were made to grow doped crystals. A crystal grown from a melt of CsBr containing 0.02 mole % Cs₂S had a conductivity curve with a low-temperature slope corresponding to an enthalpy of 0.27 ev. The

FIG. 3. Tracer diffusion coefficients in cesium bromide vs reciprocal absolute temperature. \circ —Cs¹³⁴; \square —Br⁸².FIG. 4. Tracer diffusion coefficients in cesium iodide vs reciprocal absolute temperature. \circ —Cs¹³⁴; \square —I¹³¹. Solid points are less reliable.

high conductivity in this low-temperature region decreased while the crystal was at room temperature overnight, disappearing after three days, although no change in conductivity was observed during periods of about an hour at several temperatures in the region of enhanced conductivity. This sulfur-induced conductivity could not be restored by annealing near the melting point then quenching. A CsBr crystal containing about 0.01 mole % BaBr₂ was grown, but it was supersaturated with Ba⁺⁺ as the conductivity was time-dependent in the low-temperature region and the thermal history determined the direction in which the conductivity changed.

Diffusion

Tracer diffusion coefficients are plotted in Figs. 3 and 4. (Neither these nor the conductivities have been corrected for thermal expansion.) The crystals were from Harshaw and Korth and no difference was found in the diffusion coefficients for crystals from these two sources. In particular for Korth I CsI neither the I¹³¹ nor the Cs¹³⁴ tracer diffusion coefficients were larger than those for the other crystals even in the temperature range in which the Korth I CsI had a much larger conductivity. The diffusion coefficients are fitted by the expression $D = D_0 \exp(-E/kT)$ where the constants are given in Table II. Both CsI and CsBr halogen tracer diffusion coefficient curves exhibit a slight change in slope.

TABLE II. Experimentally determined parameters for the diffusion coefficients $D = D_0 \exp(-E/kT)$.

Material	Tracer	Temperature region (°C)	D_0 (cm ² sec ⁻¹)	E (ev)
CsBr	Br ⁸²	415–530	3.92	1.42
CsBr	Br ⁸²	330–415	0.441	1.29
CsBr	Cs ¹³⁴	320–550	15.1	1.54
CsI	I ¹³¹	410–540	2.05	1.37
CsI	I ¹³¹	300–410	0.487	1.28
CsI	Cs ¹³⁴	320–550	14.24	1.53

Comparison of Diffusion and Conductivity

At the present writing no reliable transport numbers have been obtained.¹³ Without these important data the diffusion coefficients cannot be compared directly with the conductivity with any certainty. To test Eq. (4) $D_{Ta} + D_{Tc}$ was plotted vs T^{-1} along with D_σ for CsBr in Fig. 5. These should agree if all transport occurs by means of direct jumps of interstitial ions ($\alpha'/\beta/\alpha = 1$). $0.655D_\sigma$ is also plotted and should agree with $D_{Ta} + D_{Tc}$ if all transport is via vacancies. If the transport occurs by means of the interstitialcy mechanism¹ correlation effects may become very large¹⁴ and $\alpha'/\beta/\alpha$ is expected to be quite small, giving poorer agreement between $D_{Ta} + D_{Tc}$ and the conductivity. A similar set of curves results for CsI.

5. DISCUSSION

(1) There are qualitative differences between ionic transport in CsBr and CsI and ionic transport in the alkali and silver halides of the NaCl structure. In CsBr and CsI both ions contribute significantly to ionic transport phenomena and the anionic diffusion coefficients are larger than those for the cation while in the other alkali and silver halides ionic transport is almost entirely cationic at temperatures well below the melting point.

(2) From the approximate satisfaction of Eq. (4) by the data it appears that ionic transport accounts for most of the conductivity in the temperature range of the diffusion measurements. This conclusion is further supported by the sample-to-sample reproducibility of the conductivity in this region. There is anomalous behavior in the Korth I CsI crystals. Here neither diffusion coefficient curve had a small slope at low temperatures although the conductivity of the same samples had a low slope at these temperatures. It may be that the "impurity controlled" CsI conductivity is electronic in nature. From the HBr anneal there is no evidence for electronic conductivity in CsBr except

¹³ N. L. Laurance (private communication). It appears that whenever the transport numbers are not nearly unity or zero complicated effects occur at the crystal or tablet interfaces which produce considerable scatter in the results of transport number measurements and which also may produce a large systematic error. For CsBr t_σ is between 0.3 and 0.5 in the temperature range 350°C–450°C.

¹⁴ A. B. Lidiard, Suppl. Nuovo cimento 7, 620 (1958).

possibly near the melting point where there are no diffusion data. The increase in the low-temperature conductivity may have been due to the dispersion of impurities by the anneal. Although there are impurity-induced absorption bands near the tail of the fundamental absorption band, these crystals are not photoconductive for wavelengths in these bands.¹⁵

(3) The supposition that Schottky defects predominate seems reasonable and yields formation enthalpies for Schottky defects of about 2.0 ev and 1.9 ev in CsBr and CsI respectively, activation enthalpies for halogen vacancy motion of about 0.27 ev and 0.3 ev respectively, and a cesium vacancy activation enthalpy of 0.58 ev for both salts. Figure 5 shows that, except at the highest temperature, agreement between $D_{Ta} + D_{Tc}$ and $(\alpha'/\beta/\alpha)D_\sigma$ is within the estimated limits of experimental error for the two cases in which transport is assumed to be due only to vacancies and only to interstitials moving by direct jumps. From energy considerations the former is preferred. If interstitials occurred they would probably occur in a crowdion configuration or at least jump by the interstitialcy mechanism, each of which would lead to large correlation effects, and these effects were not observed.

By assuming that the low-temperature conductivity results from cesium vacancies introduced by divalent

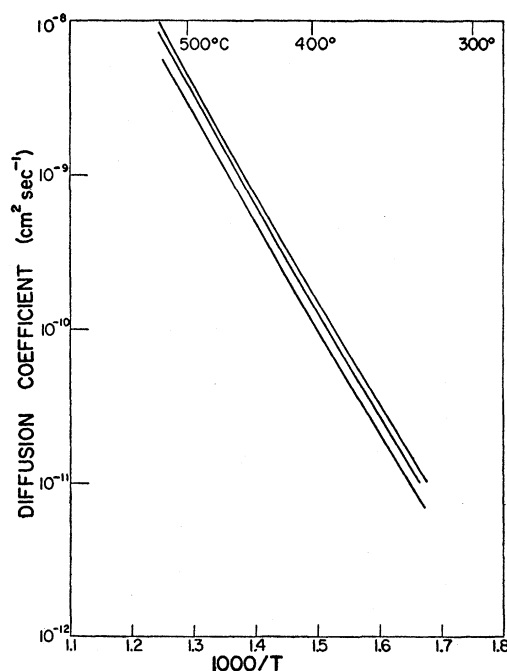


Fig. 5. Comparison of diffusion and conductivity in cesium bromide. The upper curve is the diffusion coefficient curve calculated from the total conductivity, using $\alpha'/\beta/\alpha = 1$. The lower curve is the diffusion curve calculated from the total conductivity using $\alpha'/\beta/\alpha = 0.655$, appropriate for vacancies. The middle curve is $D_{Cs} + D_{Br}$ taken from the smooth curves of Fig. 3.

¹⁵ An examination for room temperature photoconductivity was kindly made by Professor F. C. Brown.

metallic impurities the activation enthalpy for these vacancies is obtained from the slope of the low-temperature conductivity curve, using Eq. (1) with $N \exp(-g_s/2kT)$ replaced by the constant density of impurity-introduced vacancies. The slope of the Cs¹³⁴ diffusion curve then gives a value for the Schottky defect formation enthalpy. For CsBr the slope of the low-temperature conductivity curve of the crystal doped with Cs₂S yields a value for the activation enthalpy of a bromine ion vacancy. The Br⁸² diffusion coefficient curve gives the same numerical value for the Schottky defect formation enthalpy as the Cs¹³⁴ diffusion coefficient curve if the portion below the slight change in slope of the Br⁸² curve is used. For CsI the iodine vacancy activation enthalpy was obtained from the slope of the I¹³¹ diffusion curve below its slope change, using the formation enthalpy found from the Cs¹³⁴ curve. The fact that the diffusion of both tracers in CsBr leads to the same formation enthalpy supports the hypothesis of the predominance of Schottky defects.

(4) At least one additional diffusion mechanism occurs for the halogen tracers. This can be seen from the slight change in the slope of D_{Ta} , and is also suggested by the fact that Eq. (3) for vacancies is not satisfied within experimental errors at high temperatures. If it is assumed that diffusion of the halogen tracer by some electrically neutral mechanism becomes appreciable in the high-temperature region, then in this region $0.655D_s$ should be compared with $D_{Tc} + D_{Ta}'$, where D_{Ta}' is approximately the extrapolation of the low-temperature diffusion coefficient. This improves the agreement at high temperatures.

Since the region of intrinsic conductivity is under consideration the likely neutral mechanisms are Zener rings in the halogen sub-lattice and cation-anion vacancy pairs, but not impurity-vacancy complexes. (There is not necessarily equal augmentation of the cation and anion diffusion coefficients by the pairs.⁸)

If one were to require a closer fit to Eq. (3) with $\alpha'\beta/\alpha = 0.655$ (although closer agreement is not justified if the errors are considered) it could be obtained by the addition of another neutral mechanism for D_{Ta} or D_{Tc} or both. It is here that transport numbers are invaluable in deciding to which ion one should ascribe discrepancies in the Einstein relation.

In connection with the present discussion it is interesting to note that if all the conductivity is ascribed to halogen vacancies there is good agreement between $0.655D_s$ and D_{Ta} over the entire range for both salts. No significance is believed to be attached to this agreement since it is known that $t_c > 0$.¹³

(5) Divalent impurities are not very soluble in CsBr and CsI, but if possible, experiments on doped crystals of these salts should be performed to permit a more definite assignment of diffusion mechanisms. Even for Ba⁺⁺ whose ionic radius is nearly equal to that of Cs⁺ the solubility limit at room temperature must be less than 0.01 mole %.

Since the slope of the Cs₂S-influenced region of the conductivity curve is not equal to the slope of the impurity region of undoped crystals, divalent anionic impurities are not the impurities preponderant in undoped crystals. Thus because of solubility effects the conductivity in the impurity region is due to cesium defects, although the halogen defects seem to be the larger source of conductivity in the intrinsic region.

ACKNOWLEDGMENTS

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