Effective Volumes of Vacancies of Divalent Ions and Their Diffusion Coefficients in Alkali Halides*

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(Received 17 October 1968; revised manuscript received 10 March 1969)

Photoelastic effects induced by divalent ions Sr^{++} and Ba^{++} diffused into KCl have been observed and measured experimentally. The theoretical analysis allows the calculations of the diffusion coefficients $D(Sr^{++})$ $=9.0\times10^{-5}\ e^{-0.77/kT}$ cm²/sec and $D(Ba^{++})$ $=2.5\times10^{-2}\ e^{1.1/kT}$ cm²/sec, and of volume changes due to impurity-vacancy complexes. By following the thermal dissociation of these complexes, it was possible to conclude that the isolated vacancy causes a lattice expansion larger than the contraction due to the isolated divalent ion.

I. INTRODUCTION

BIREFRINGENCE in alkali-halide crystals induced by irradiation has been first used by Primak, Delbecq, and Yuster,[1] for measuring volume changes caused by defects generated by radiation. Wiegand and Smoluchowski[2] have modified this technique using a half-bombarded crystal. Mascarenhas *et al.*,[3] Costa Ribeiro,[4] Lüty, Ribeiro, Mascarenhas, and Sverzut,[5] and Ritz and Mascarenhas[6] have extended the use of the technique to color-center investigations, modifying the experimental methods in several ways.

In the present work we have measured the induced birefringence due to defects introduced in KCl by diffusion of divalent metal ions. It is known, since the work of Pick and Weber,[7] that introduction of divalent ions Sr^{++} and Ca^{++} into KCl causes a density change corresponding to a fractional volume contraction $\delta \equiv \Delta V/V$. Pick and Weber's measurements have been made at a temperature where the divalent ions are associated with the vacancy, giving δ/C-0.086 for a Sr^{++}-vacancy pair and $\delta/C=0.075$ for a Ca^{++}-vacancy pair (C is the molar fraction of the impurity).

In this paper we show that it is possible to apply the photoelastic technique to (i) measure the volume expansion of impurities and associated complexes; (ii) follow quantitatively the dissociation of metal-vacancy complexes as a function of temperature; and (iii) obtain a new method for the measurement of diffusion coefficients and associated activation energies.

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II. EXPERIMENTAL

Samples of a typical size 1.0×1.0×1.5 cm were cut from Harshaw crystals. A square (100) face of each crystal was sprayed with a saturated solution of the impurity ion and dried at about 200°C. No evidence of OH^- was found after diffusion as monitored in a spectrophotometer.

The diffusion was done in a quartz-tube furnace in a N_2 atmosphere. The diffusion time was adequate to produce a penetration $(2Dt)^{1/2}$ of the order of 1.0 mm. At the end of the diffusion the temperature was decreased about 100°C in the first hour and after that a slower rate of 15°C/h. This precaution prevented spurious stresses.

Plates 1.5 mm thick were cleaved out of these blocks parallel to the diffusion direction. The uniformity and depth of penetration was ascertained by x-raying control plates, because F centers grow faster in the vicinity of divalent impurities. This technique was used by Mascarenhas in his study of diffusion coefficients.[8]

The plates were attached to a holder and the birefringence measured in a photoelastimeter as described
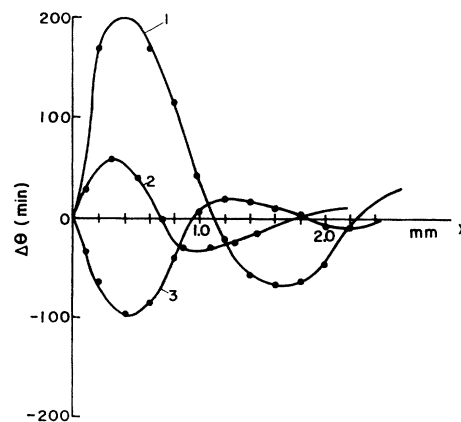

FIG. 1. Photoelastic profiles due to diffusion of impurities in NaCl and KCl single crystals. Curve 1 corresponds to diffusion of Sr^{++} in NaCl, curve 2 to Rb^+ in KCl, and curve 3 to Sr^{++} in KCl.

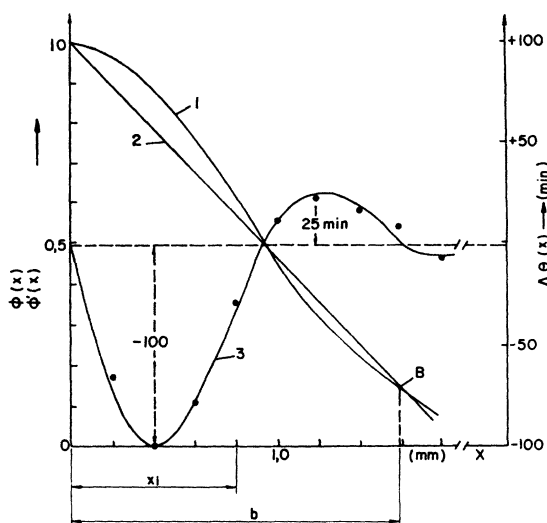[8] S. Mascarenhas, Bull. Am. Phys. Soc. **12**, 467 (1967).

FIG. 2. Fitting of theoretical curves to the experimental points for diffusion of Sr^{++} in KCl at 470°C during 3.5×10^6 sec: (1) $\phi(x) = e^{(-x^2/4Dt)}$, (2) straight line $\phi'(x) = (1-0.86x)/b$, and (3) $\Delta\theta(x) = A(1-0.86/b - e^{x^2/4Dt}) = A[\phi(x) - \phi'(x)]$, where x_i is the abscissa of the inflection point of the $e^{(-x^2/4Dt)}$ curve and b the abscissa of the third interception of the straight line with the $e^{(-x^2/4Dt)}$ curve.

in detail elsewhere.[4] Briefly, the birefringence is measured by the rotation of the plane of polarized light ($\Delta\theta$) that traverses the crystal. The photoelastimeter had a 0.1 mm slit width, and $\Delta\theta$ could be measured to $\pm 60''$ of arc. 572-μ light was used for the measurements which were made in the central portion of the plate to avoid edge effects.

Figure 1 shows patterns obtained for $KCl:Sr^{++}$, $NaCl:Sr^{++}$, and $KCl:Rb^+$. NaCl has a photoelastic constant of opposite sign to KCl and thus gives reversed signs in the profiles. The same reversal must occur for $KCl:Rb^+$, because the Rb^+ ion is larger than K^+ and gives a local expansion instead of a contraction as in the case of Sr^{++}.

The pattern is localized in that region in which subsequent x raying shows more F centers. Plates in which diffusion did not occur do not show a photoelastic profile after a similar treatment.

The amount of Sr^{++} and Ba^{++} diffused in each sample was measured by neutron activation analysis. The concentration at each point was calculated, using the distribution function of impurities found by Chemla,[9] $C = C_0 e^{(-x^2/4Dt)}$, for the diffusion of divalent ions in NaCl.

The error of the average temperature values was $\sim 8\%$.

III. THEORETICAL

The photoelastic patterns of Fig. 2 can be quantitatively interpreted by extending the approach given first by Primak, Delbecq, and Yuster[1] for the tensions

⁹ M. Chemla, Ann. Phys. (Paris) 1, 959 (1956).

generated in a crystal bombarded with deuterons. A similar calculation has been done by Wiegand and Smoluchowski[2] for the crystal half-irradiated with x rays.

Let e_{xx}, e_{yy}, e_{xy}, $\cdots$, be the strains, σ_{xx}, σ_{yy}, σ_{xy} the stresses, and δ the relative dilatation due to the impurities. If we assume, following the results of Pick and Weber,[7] that δ is a linear function of concentration of impurities, we can write

$$\delta(x) = \delta(0)e^{-x^2/4Dt}, \tag{1}$$

where $\delta(0)$ is the dilatation corresponding to concentration $C(0)$. Using the equilibrium equation, the compatibility equation for the strains, and the relations between stresses and strain

$$\sigma_{xx} = C_{11}e_{xx} + 2C_{12}e_{yy} - \beta\delta(x),$$
$$\sigma_{yy} = (C_{11}+C_{12})e_{yy} + C_{12}e_{xx} - \beta\delta(x), \tag{2}$$
$$\sigma_{xy} = C_{44}e_{xy},$$

where

$$\beta = \tfrac{1}{3}(C_{11}+2C_{12}),$$

we get for the strains

$$e_{xx} = K_2/C_{11} + \beta\delta(x)/C_{11} - 2(C_{12}/C_{11})e_{yy},$$
$$e_{yy} = K_3 x + K_4, \tag{3}$$
$$e_{xy} = K_1.$$

In this derivation it is assumed that $e_{yy} = e_{zz}$, in spite of the fact that these two directions are not completely equivalent because of the dimensions of the sample.[2]

Here, K_1, K_2, K_3, and K_4 are constants which can be determined as follows: Using the boundary condition $\sigma_{xx}(0) = 0$, $\sigma_{xy}(0) = 0$, we find that $K_1 = 0$ and $K_2 = 0$. It follows that the difference between the two principal strains is

$$e_{yy} - e_{xx} = [(2C_{12}+C_{11})/3C_{11}][3K_4 + 3K_3 x - \delta(x)].$$

The K_3 and K_4 constants can be determined by fitting theory to experimental data or by the method developed by Wiegand.[10] Fitting theory to experimental data (see Fig. 2), we found

$$K_4 = \tfrac{1}{3}\delta(0) \quad \text{and} \quad K_3 = -0.86\delta(0)/3b.$$

Weigand's method minimizes the strain energy relative to each constant:

$$\frac{\partial}{\partial K_4}\int_0^l \epsilon(x)dx = 0, \quad \frac{\partial}{\partial K_3}\int_0^l \epsilon(x)dx = 0.$$

Using the strain-energy density function for this problem with $e_{yy} = e_{zz}$,

$$\epsilon(x) = \tfrac{1}{2}C_{11}[(\tfrac{1}{3}e_{xx} - \delta)^2 + 2(\tfrac{1}{3}e_{yy} - \delta)^2]$$
$$+ C_{12}[2(\tfrac{1}{3}e_{xx} - \delta)(\tfrac{1}{3}e_{yy} - \delta) + (\tfrac{1}{3}e_{yy} - \delta)],$$

¹⁰ D. Wiegand (private communication).

we get

$$\tfrac{1}{2}K_3 l^2 + K_4 l = \tfrac{1}{3}\delta(0)\int_0^l e^{-x^2/4Dt}dx,$$

$$\tfrac{1}{3}K_3 l^3 + \tfrac{1}{2}K_4 l^2 = \tfrac{1}{3}\delta(0)\int_0^l e^{-x^2/4Dt}x\,dx.$$

If we take the l value as that where the photoelastic pattern becomes negligible ($\simeq 2.8x_i$), we get

$$K_4 = 1.03\tfrac{1}{3}\delta(0)\quad\text{and}\quad K_3 = -0.84\delta(0)/3b.$$

It follows that

$$e_{yy} = e_{xx} = [(2C_{12}+C_{11})/3C_{11}]\delta(0)$$
$$\times(1.03-0.84/b-e^{(-x^2/4Dt)}).$$

We have made the hypothesis that the crystals may be considered as infinite in the z direction. However, if it is considered as a plate—that is, if e_{zz} is just equal to zero from the start—we got the same final result for $e_{yy}-e_{xx}$ as when the crystal is supposed to be infinite in the z direction.

When using Wiegand's conditions for the determination of K_3 and K_4, we chose the "effective length" of the sample as $l = 2.8x_i$. Experimentally it is found that the photoelastic profile does not depend on the crystal length if it is larger than $2.8x_i$. The values of K_3 and K_4 calculated using this l value—that also agree with those obtained by adjusting theory with experimental data—predict large strains in the end of the crystal plate. However, Fig. 2 shows that these strains for $x>b$ are much smaller than those predicted by the theory. This may mean that slip has taken place at this part of the crystal or that the application of this simple theory to large crystals ($x\gg b$) is only an approximation in that part of the crystal. In any one of these two cases one should use the effective rather than the actual length.

With the known photoelastic constant C_λ, the crystal thickness d, and the elastic constants S_{11} and S_{12}, the retardation $\Delta\theta$ is given by

$$\Delta\theta = \frac{(e_{yy}-e_{xx})C_\lambda d}{3(S_{11}-S_{12})}$$

and, finally,

$$\Delta\theta(x) = A\,(1-0.86xb^{-1}-e^{-x^2/4Dt}),\qquad(4)$$

where

$$A = \frac{\delta(0)dC_\lambda}{3(S_{11}+S_{12})}.$$

From (4) it follows that the inflexion point x_i of the $\Delta\theta$-versus-x-curve is the same as that of the function $e^{(-x^2/4Dt)}$. Thus the determination of the diffusion coefficient is independent of the straight line $1-0.86x/b$ and can be done directly from the $\Delta\theta(x)$ curve, using $D = x_i/2t$. Knowing D and fitting the experimental points to the theory, we can find the value of A.

TABLE I. Relative volume changes in KCl at room temperature due to IV complexes.

Ion	Molar fraction (C_0)	Relative volume change $\delta(0)$	K_{IV}
Sr^{++}	1.8×10^{-3}	3.0×10^{-4}	0.17 ± 0.03
Ba^{++}	1.2×10^{-3}	1.9×10^{-4}	0.16 ± 0.03

IV. DIFFUSION MEASUREMENTS

Using the technique described above, we have determined the diffusion coefficients of Ba^{++} and Sr^{++} at several temperatures. These divalent ions have a rather high diffusion coefficient, which induces a prominent strain profile in a relatively short time. In our measurements the penetrations were such as to give $x_i \simeq 1.0$ mm.

On a plot of $\log D$ versus $1/T$, the experimental points fell on a straight line within an accuracy of 8% in the measured range of 480–700°C.

The diffusion coefficients found for Sr^{++} and Ba^{++} ions in KCl as a function of the temperature can be described by the functions

$$D_{Ba^{++}} = 2.5\times10^{-2}e^{(-1.1/kT)}\ \text{cm}^2/\text{sec},$$

$$D_{Sr^{++}} = 9.0\times10^{-5}e^{(-0.77/kT)}\ \text{cm}^2/\text{sec},$$

where the activation energy is given in eV.

We have checked these results using the previously mentioned technique[8] of measuring D from the F-center concentration gradient along the crystal slab.

Our results show an increase in the activation energies and diffusion coefficients as the ionic radii of the impurities increase. A small number of measurements made in the temperature range 480–700°C of the diffusion of Ca^{++} and Mg^{++} in KCl showed lower diffusion coefficients and activation energies. The same behavior has been observed by Arai and Mullen[11] for the diffusion of Rb$^+$ in NaCl, KCl, and RbCl.

V. VOLUME CHANGES

The results above can be expressed in terms of the relative volume change K_{IV} per molar fraction δ/C of associated impurity-vacancy complexes (IV) as found first by Pick and Weber.[7] Table I shows the results in which error in K_{IV} arises mainly from the photoelastic constant, fitting data to theory and chemical analysis. Our values of K_{IV} for Sr^{++}-doped KCl, when compared with those of Pick and Weber, have the same sign and the same order of magnitude. However, our values are systematically higher. This discrepancy may arise from the measurement of the impurity concentration in both experiments.

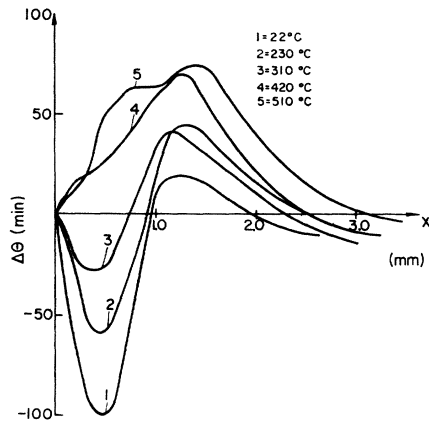[11] G. Arai and J. Mullen, Phys. Rev. **143**, 663 (1966).

FIG. 3. Photoelastic pattern for Sr^{++} diffused in KCl measured at several temperatures (in °C): (1) 22, (2) 230, (3) 310, (4) 420, and (5) 510.

Figure 3 shows the photoelastic pattern measured at different temperatures. In order to explain this behavior, the photoelastic constant C_λ was measured with no appreciable change in the temperature interval in which we worked. The temperature dependence of $S_{11}+S_{22}$ cannot account, either, for the changes observed, as shown in Fig. 4. Thus, in order to explain the reversal in the sign of the pattern, we propose that at higher temperatures the impurity-vacancy complexes dissociate, generating free vacancies and free impurities, and that $|K_V| > |K_{M^{++}}|$. If C is the total molar fraction of divalent ions and α the degree of dissociation of the IV complex, we can write

$$\delta(\alpha) = C|\alpha K_{M^{++}} + \alpha K_V + (1-\alpha)K_{IV}|,$$

where K_V, K_{IV}, and $K_{M^{++}}$ are the fractional volume changes per molar fraction associated with isolated vacancies, isolated IV complexes, and isolated divalent ions, respectively.

Figure 4 shows $\delta(\alpha)/C_0$ as a function of α which was calculated as a function of the temperature using Lidiard's model[12] with $C=10^{-3}$ and $\xi=0.55-4\times10^{-4}T$ for the Gibbs free energy as given by Jacobs and Maycock.[13] From Fig. 4 the value of α for which $\delta=0$ is $\alpha=0.55$. It follows that

$$0.55(K_{M^{++}}+K_V) = -0.45K_{IV} = -0.076,$$

$$K_{M^{++}}+K_V = -0.14.$$

[12] A. Lidiard, in Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1957).
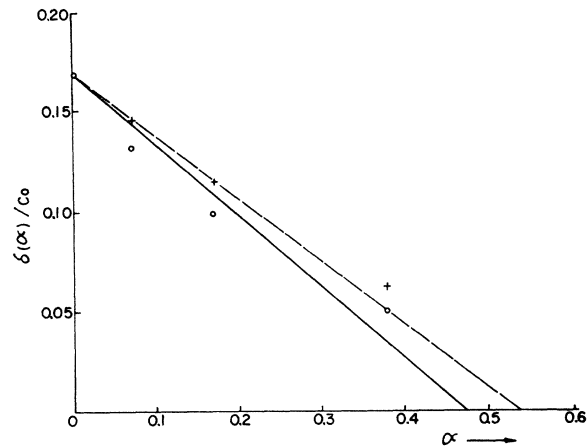[13] P. M. Jacobs and N. Maycock, J. Phys. Chem. Solids 24, 1693 (1963).

FIG. 4. Relative volume change per total number of divalent ions $\delta(\alpha)/C_0$ as a function of the degree of dissociation α of the IV complexes. Open circles are points taken directly from the curves of Fig. 3. Crosses are the same as the open-circle points but corrected for the change of $S_{11}+S_{22}$ with temperature. α values are calculated using Lidiard's model.

This result shows that the positive vacancy induces a volume expansion larger than the contraction due to the divalent ion. If we use Eshelby's theory[14] and the calculations of Bassani and Fumi,[15] we obtain $K_V=0.70$, and using our results, we get $K_{M^{++}}=0.56$.

Although the measurements of K are not very precise, it is clear that

$$|K_V| > |K_{M^{++}}| \quad \text{for Sr}^{++} \text{ in KCl.}$$

It is known that impurity-vacancy complexes associate in aggregates, as had been shown by Dryden and Cook.[16] We have not found detectable volume changes due to that aggregation in KCl/Sr^{++} crystals annealed for 60 h at 80°C.

Some of the changes in the shape and position of peaks in Fig. 4 may be the result of the change of orientation of elastic strain dipoles surrounding impurity-vacancy pairs in various degrees of association produced by the over-all strain field.

ACKNOWLEDGMENTS

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[15] F. Bassani and F. Fumi, Nuovo Cimento 7, 95 (1958).
[16] J. S. Cook and J. S. Dryden, Proc. Phys. Soc. (London) 80, 479 (1962).