Diffusion Processes in TlCl *

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Pure single crystals have been used for measurements of ionic conductivity (160° − 425 °C), Cl diffusion (275° − 415 °C), and Tl diffusion (290° − 400 °C). Conductivity measurements were made with a capacitance bridge at 1 to 10 kHz, and diffusion coefficients were obtained with radioactive tracers and the sectioning technique. It is found that $D^*(\mathrm{Cl})$ is 10 to 40 times larger than $D^*(\mathrm{Tl})$. An empirical fit gives

$$D^*(\mathrm{Cl}) = 0.031 \ \exp[-(0.771 \pm 0.010)/k\,T] \,,$$
$$D^*(\mathrm{Tl}) = 0.62 \ \ \exp[-(1.101 \pm 0.020)/k\,T]$$

with D in cm^2/s and the energy in eV. The conductivity has an activation energy of 0.76 eV for 230° − 330 °C, increasing to 0.87 eV for 375° − 425 °C. For several reasons the conductivity is believed to be entirely ionic. The Nernst-Einstein relation is generally well obeyed, but there is a significant excess diffusion of 10 to 15%.

The results show that the defect structure consists primarily of Schottky defects with highly mobile anion vacancies. The excess diffusion can be accounted for by the presence of up to 20% of either vacancy pairs or next nearest neighbor jumps into single vacancies; there is no clear preference for either mode. With a Schottky formation energy of 1.36 ± 0.03 eV from other work, the mobility energies are 0.104 ± 0.005 eV for Cl for either model, and 0.56 ± 0.04 or 0.44 ± 0.02 eV for Tl, respectively. Comparisons are made to observations of conductivity and diffusion by other workers near room temperature and in the melt.

I. Introduction

Extensive studies of ionic conductivity and diffusion in alkali halides with the NaCl structure (fcc) have revealed the presence of Schottky defects [1]. The ionic transport processes involve jumps of nearest neighbor (nn) ions into single cation and anion vacancies, with the cation usually being more mobile and therefore tending to dominate the conductivity. Recent work has shown that there may also be appreciable contributions from bound vacancy pairs at temperatures near the melting point [2, 3]. In AgCl and AgBr, on the other hand, which also have the NaCl structure, many investigations have confirmed the presence of cation Frenkel defects. Diffusion measurements have shown that the transport processes involving cation vacancies are the same as in the alkali halides, but that those involving interstitial ions occur by a combination of collinear and non-collinear interstitialcy jumps [4]. Thus the difference in the type of defect for the silver halides, which is undoubtedly due to the larger polarizability of the silver ion, leads to a profound difference in the nature of the ionic transport processes.

In contemplating the possible diffusion mechanisms for the thallium halides, two major factors need to be considered. The general similarity of these compounds to the silver halides in many respects — melting points between 400° and 500 °C, high dielectric constants, plasticity of the crystals at room temperature, general chemical behavior — would suggest that cation Frenkel defects might be favored. But TlCl, TlBr, and the high temperature phase of TlI have the CsCl structure (sc) rather than the NaCl structure of most of the silver and alkali halides. The difference in structure introduces many different intriguing possibilities for transport mechanisms — two different interstitial sites, six nn instead of twelve, a different geometry for vacancy pairs, and even the possibility of next nearest neighbor (nnn) as well as nn jumps into single vacancies.

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[1] A. B. LIDIARD, in: Handb. der Physik (ed. by S. FLÜGGE), Vol. **20**, p. 246, Springer-Verlag, Berlin 1957.

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For CsCl [5], CsBr [6], and CsI [6], for instance, the anion diffusion is comparable to, but somewhat larger than, the cation diffusion, suggesting Schottky defects again, but now with the anion more mobile. For these reasons an investigation of the intrinsic transport properties of the thallium halides, starting with TlCl, was thought to be interesting.

The experimental evidence and analysis presented in this paper show the following results for ionic transport mechanisms in TlCl. There is ample reason to believe that the conductivity is exclusively ionic. Schottky defects are predominant, with anion vacancies having a mobility 10 to 100 times larger than cation vacancies. Furthermore the existence of any appreciable concentration of cation Frenkel defects is definitely excluded by the experimental results. Thus there is no correspondence of the defect structure to that of the silver halides, despite the general similarity of chemical and bulk properties. There is a general analogy to the diffusion behavior of the cesium halides, but the mobility ratio is much more extreme in TlCl, probably because of the larger polarizability of Tl. The relatively small amount of excess diffusion can be acounted for by rather modest contributions either from bound jumps into vacancy pairs or from nnn jumps into single vacancies, with no obvious discrepancy or decided preference for either possibility. Comparisons are also made to diffusion results near room temperature obtained from NMR experiments and to the behavior of the liquid at temperatures slightly above the melting point.

II. Experimental Procedures

TlCl was produced by precipitation from dilute solutions (1 molar) of analytical reagent grade $TlNO_3$ and HCl and was purified by several stages of recrystallization from solution. After the powder was dried in vacuum at 150 °C for at least 10 hours, single crystals were grown in an evacuated, sealed-off quartz tube with a pointed tip by lowering out of a furnace at the rate of several mm/hr. Individual samples were machined in a lathe to cylinders 1 cm in diameter and 0.5 to 1.5 cm long.

The sample holder for high temperature measurements has been described in detail elsewhere [7]. The primary requirements are provisions for evacuation at room temperature, a sealed-off region of small volume, and an insulated electrical lead operating up to 450 °C. These features were obtained in a stainless steel sample holder with a removable 0-ring seal for the valve spindle, a positive thermal expansion between the spindle and the valve seat, and a stupakoff insulator silver-soldered in place. The sample holder was filled with about 1 atm of argon to retard sublimation of the sample and to improve thermal contact, and a chromel-alumel thermocouple was attached to the outside of the sample holder near the sample position. The same thermocouple was used for all conductivity and diffusion measurements in order to avoid temperature errors in the comparison of these quantities.

For conductivity measurements a stainless steel spring inside the sample holder held thin platinum disks against dag electrodes (colloidal graphite) on the sample. Observations were taken for increasing temperatures at intervals of 15 to 25 °C. An a.c. capacitance bridge was used with a General Radio resistance box at frequencies of 1 to 10 kHz in order to avoid complications from polarization effects. Extensive conductivity runs were made on six samples from three different crystals, and results were consistent within 0.6 to 1.2%. This error represents roughly comparable contributions from uncertainties in sample dimensions and from reproducibility of temperature measurements.

The time for each diffusion anneal was chosen to make the root-mean-square penetration length

$$x_{\mathrm{rms}} = \sqrt{2\,D\,t}$$

equal to 100 to 150 μ for Tl diffusion and 200 to 600 μ for Cl diffusion. The actual time varied from 7 hours at the highest temperatures for Cl to 4 days at the lowest temperatures for Tl, with typical values of 20 to 40 hours. Corrections for temperature variations were made by finding an effective time according to

$$t_0 = [D(T_0)]^{-1} \int_0^{\infty} D(T)\,\mathrm{d}t\,. \tag{1}$$

Temperature readings were taken every minute during heating and cooling and every 10 minutes to 2 hours during the steady temperature (T_0), and the integral was evaluated by trapezoidal integration on a computer. Typical heating and cooling times between $D(T)/D(T_0) = 0.01$ to 1 were 30 minutes, with corrections amounting to approximately 15 minutes each for heating and cooling and 10 minutes for small fluctuations during the long time at steady temperature. The total correction represents 1% of the total time for the longest anneals and up to 5% for the shortest anneals; one-fifth of this correction was included as random error in D.

After an anneal the sample was mounted in a teflon collet in a sliding-knife microtome and was oriented by means of an optical lever. Thin slices of 8 to 12 μ were cut with the microtome, and sections of 8 to 60 μ, amounting to approximately 0.1 x_{rms}, were collected in 1 inch diameter planchets. The mass in each plan-

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[5] P. J. HARVEY and I. M. HOODLESS, Phil. Mag. **16**, 543 [1967].

[6] D. W. LYNCH, Phys. Rev. **118**, 468 [1960].

[7] R. J. FRIAUF, Rev. Sci. Instrum. **31**, 1161 [1960].

chet was determined with a semi-micro balance (sensitivity 0.01 mg) in order to calculate the actual section thickness and the activity per unit volume. The combined influence of finite section thickness s and tilt error m (typically 20 to 50 μ) is given for a circular cross section by [8]

$$\% \text{ error in } D = (1/12)\,(s/x_{\text{rms}})^2 + (1/16)\,(m/x_{\text{rms}})^2 . \quad (2)$$

For most samples this error was 0.1 to 0.5%, but was occassionally as large as 1 to 2%.

Radioactive isotopes used were ^{204}Tl (100 mCi/g of Tl) and ^{36}Cl (3.3 mCi/g of Cl). The appropriate isotope was precipitated as TlCl in a small platinum cup and then evaporated in vacuum onto one end of the sample. With 0.2 μCi on each sample the total thickness of the radioactive layer was less than 1 μ even for Cl, making the correction for the finite thickness of the source layer negligible in all cases. Counting was done with a Geiger-Müller tube with a minimum of 10,000 counts for each section. In order to obtain uniform counting geometry from section to section, the material in each planchet was dissolved in 2 ml of water, frozen, and vacuum-evaporated to dryness.

Counts were made for 10 to 20 sections until the activity per section had decreased to one-tenth of the initial value. The solution of the diffusion equation for a thin source of initial strength Q_0,

$$\ln n(x,t) = \ln(Q_0/\sqrt{\pi D t}) - x^2/4 D t\,, \quad (3)$$

was fit with a least squares straight line by a computer program. The diffusion coefficient was calculated from the slope of the line in Eq. (3) and the effective time from Eq. (1). Errors in the slope varied between 0.5 and 2.0%, reflecting both fluctuations in counting and errors in weighing. The overall error in D amounted to 1.0 to 4.0%, with typical values of 1.5 to 2.5%.

III. Experimental Results

The conductivity for several samples from all three crystals is shown in Fig. 1; many of these same samples were later used for diffusion runs. Agreement is very good with the recent data of JACKSON and YOUNG [9]. All of the earlier measurements [10, 11], including some not shown on the graph [12], agree moderately well for W (± 0.05 eV) but give magnitudes smaller by 25 to 40 to 60%, probably because of uncertainties in the geometry of the conductivity cell. An empirical representation of the data is possible for restricted temperature intervals by

$$\sigma T = A \exp\{-W/kT\}\,. \quad (4)$$

The parameters for least squares fits are given in Table 1. It is noticeable that there is an appreciable upward curvature at the higher temperatures, the significant point being that there must be at least two mechanisms with different activation energies contributing to the conductivity.

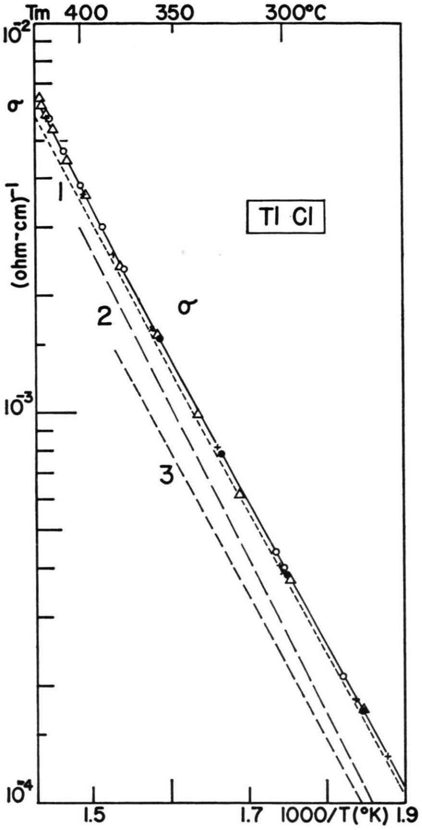

Fig. 1. Ionic conductivity of TlCl. There are several samples from each of three different crystals, which are denoted by +, ○, and △; × and ● represent two or more closely spaced points for the same crystal. The solid line is the sectional least squares fit to the combined data. Earlier results are shown by curve 1 from JACKSON and YOUNG [9], curve 2 from LEHFELDT [11], and curve 3 from PHIPPS and PARTRIDGE [10].

For several reasons it is believed that the conductivity is predominantly ionic rather than electronic [13]. There is no indication in the conductivity measurements of decomposition of the sample even at prolonged periods at high temperatures (74 hrs at 360° to

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[8] G. A. SHIRN, E. S. WAJDA, and H. B. HUNTINGTON, Acta Met. **1**, 513 [1953].

[9] B. J. H. JACKSON and D. A. YOUNG, Trans. Faraday Soc. **63**, 2246 [1967].

[10] T. E. PHIPPS and E. G. PARTRIDGE, J. Amer. Chem. Soc. **51**, 1331 [1929].

[11] W. LEHFELDT, Z. Phys. **85**, 717 [1933].

Table 1. Parameters for empirical data fits for ionic conductivity and diffusion in TlCl.

Quantity	T Range [°C]	Pre-exponential	W [eV]
Conductivity	160—240	0.60×10^6 °K/ohm cm	0.732 ± 0.004
Conductivity	235—330	1.15×10^6 °K/ohm cm	0.762 ± 0.007
Conductivity	325—380	2.3×10^6 °K/ohm cm	0.797 ± 0.007
Conductivity	375—425	8.8×10^6 °K/ohm cm	0.872 ± 0.010
JACKSON and YOUNG[a]	80—325	—	0.750 ± 0.005
Diffusion of Cl	275—415	3.1×10^{-2} cm²/s	0.771 ± 0.010
Diffusion of Tl	290—400	6.2×10^{-1} cm²/s	1.101 ± 0.020
Diffusion ratio R_{Cl}	275—415	0.457	-0.023 ± 0.011
Diffusion ratio R_{Tl}	290—400	8.03	0.300 ± 0.016
Diffusion ratio $R_{\mathrm{Cl}} + R_{\mathrm{Tl}}$	275—415	0.615	-0.009 ± 0.009

[a] Reference [9].

420 °C) [13], large polarization effects are observed at low frequencies as observed in other ionic conductors [9], and the upward curvature in the conductivity at high temperatures is typical of ionic conductors. Furthermore Hauffe and Griessbach-Vierk have obtained approximate verification of Faraday's law of mass transport for electrolysis [12]. Finally the diffusion measurements also tend to support this contention, for if any significant part of the conductivity were attributed to electronic motion, there would be an even larger excess diffusion to be accounted for by additional diffusion mechanisms. Hence it will be assumed in the remainder of this paper that all of the conductivity is ionic.

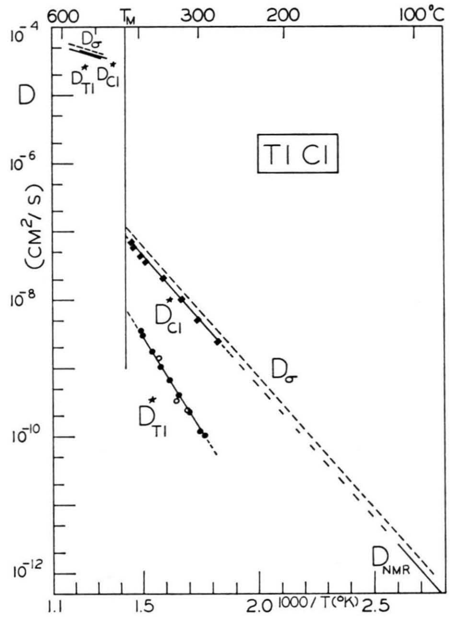

Fig. 2. Summary of diffusion in TlCl. D^*_{Cl} and D^*_{Tl} are from this work, and the straight lines are least squares fits, with the three open points excluded from D^*_{Tl}. D_σ is from JACKSON and YOUNG [9]. D_{NMR} at low temperatures is from AILION and SAMUELSON [28]; the magnitude has been adjusted to match the extrapolation of D^*_{Cl} from higher temperatures. For the liquid D_σ and D^*_{Tl} are from BERNE and KLEMM [29], and D^*_{Cl} is from ANGELL and TOMLINSON [30].

The tracer diffusion coefficients are shown in Fig. 2 and listed in Table 2. It is immediately evident that $D^*(\mathrm{Cl})$ is more than the times greater than $D^*(\mathrm{Tl})$ at all temperatures. Within the number and accuracy of the available experimental points, the best empirical fit is obtained for

$$D = D_0 \exp\{-W/k\,T\}; \tag{5}$$

the parameters from the least squares fit of this relationship are included in Table 1. The measurements of BEUTHE [14] for $D^*(\mathrm{Cl})$ and $D^*(\mathrm{Tl})$ on polycrystalline samples between 200° and 350 °C show the same general behavior ($W_{\mathrm{Cl}} = 0.82$ eV, $W_{\mathrm{Tl}} = 1.01$ eV) and agree in magnitude to ±30%. Also shown for comparison in Fig. 2 is D_σ as calculated from the conductivity by means of the Nernst-Einstein relation,

$$D_\sigma = (k\,T/N\,e^2)\;\sigma = 3.059 \times 10^{-8} \times \sigma\,T, \tag{6}$$

where N is the number of Tl^+ or Cl^- ions per unit volume.

It is convenient to compare the measured diffusion coefficients to the ionic conductivity by defining a *diffusion ratio* R for each ion.

$$R_{\mathrm{Cl}} = D^*(\mathrm{Cl})/D_\sigma, \qquad R_{\mathrm{Tl}} = D^*(\mathrm{Tl})/D_\sigma. \tag{7}$$

For this purpose σ is obtained at each diffusion temperature either by averaging conductivity measurements during the diffusional anneal (Tl at 298°, 331 °C and Cl at 385° to 415 °C) or by interpolat-

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[12] K. HAUFFE and A. L. GRIESSBACH-VIERK, Z. Elektrochem. **57**, 248 [1953].

[13] R. J. FRIAUF, J. Phys. Chem. Solids **18**, 203 [1961].

[14] C. B. BEUTHE, Thesis, Technische Universität Berlin 1961.

Table 2. Diffusion coefficients and diffusion ratios in TlCl.

	T (°C)	D^* (cm²/s)	Error[a] in D^*	D_σ (cm²/s)	Error[a]	R in D_σ	Error[a] in R
Diffusion of Cl		[$\times 10^{-8}$]	[%]	[$\times 10^{-8}$]	[%]		[%]
	274.0	0.241	2.2	0.336	0.6	0.718	2.2
	301.5	0.517	2.5	0.733	0.6	0.6	2.6
	325.25	0.997	2.0	1.359	0.9	0.733	2.2
	354.25	2.05	1.7	2.75	1.2	0.744	2.1
	385.4	3.62	1.9	5.57	2.2	0.649	2.9
	395.5	4.39	3.9	7.11	3.7	0.618	5.4
	406.0	5.85	3.0	8.93	1.5	0.655	3.4
	415.0	7.06	1.6	10.59	0.6	0.666	1.7
Diffusion of Tl		[$\times 10^{-10}$]	[%]	[$\times 10^{-10}$]	[%]		[%]
	292.0	1.038	2.1	56.8	0.6	0.0183	2.2
	298.0	1.198	2.6	65.4	1.0	0.0183	2.8
	316.5	2.28	1.9	109.6	0.8	0.0208	2.0
	319⊕	2.4	3.	116.	13⊕	0.021	13⊕
	331.0	4.00	2.7	157.8	0.4	0.0253	2.8
	335⊕	3.2	4.	143.	8⊕	0.022	9⊕
	346.0	6.74	2.2	230.	1.1	0.0293	2.5
	360.6	10.38	1.1	326.	1.2	0.0318	1.7
	364.0⊕	14.22	2.7⊕	347.	1.0	0.0410	3.0⊕
	376.0	17.31	2.0	454.	1.2	0.0382	2.4
	394.0	30.1	1.9	694.	1.2	0.0435	2.2
	397.0	35.9	1.8	745.	1.2	0.0483	2.1

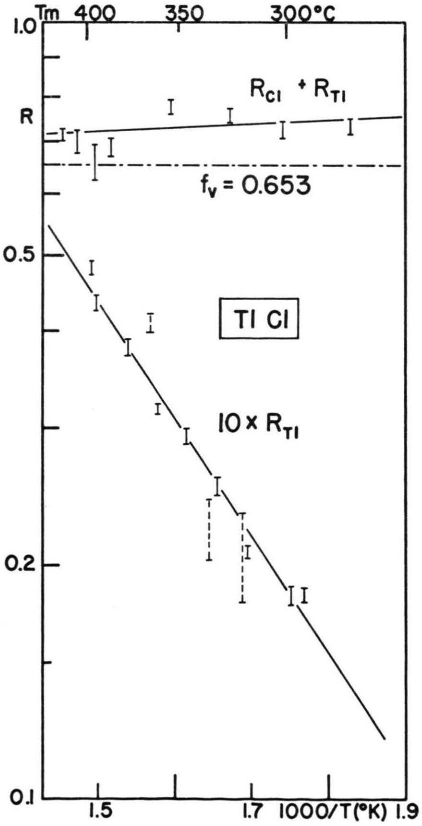
[a] Errors are given as standard deviations.

⊕ Because of large errors or other uncertainties, these points are excluded from further calculations.

ing from all conductivity data for samples cut from the same crystal. Room temperature measurements of the sample dimensions are used in evaluating both the conductivity and the diffusion coefficients; when the room temperature density $\varrho = 7.00$ g/cm³ is used to calculate N in Eq. (6), the influence of thermal expansion cancels out exactly in Eq. (7).

Experimental values for R_{Cl} and R_{Tl} are listed in Table 2 and shown in Fig. 3. It is seen that the sum of $R_{\mathrm{Cl}} + R_{\mathrm{Tl}}$ is, indeed, approximately equal to the theoretical value $f_{\mathrm{v}} = 0.653$ for single vacancies on a sc lattice[15, 16]. There is, however, a small but significant excess diffusion, which is nearly independent of temperature (see Table 1). Furthermore R_{Tl} is much smaller than R_{Cl}, indicating a rather small transport number for Tl.

Since much of the following analysis depends on the rather small difference between $R_{\mathrm{Cl}} + R_{\mathrm{Tl}}$ and f_{v} in Fig. 3, it is important to consider the experimental significance of this difference. First of all the random errors of 2 to 3% for most cases in Table 2 are ap-



← Fig. 3. Diffusion ratios for TlCl. The straight lines are least squares fits, with the three dotted points for R_{Tl} excluded. f_{v} is the theoretical value of the correlation factor for diffusion by single vacancies on a sc lattice[15].

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[15] K. Compaan and Y. Haven, Trans. Faraday Soc. **53**, 786 [1956].

[16] R. J. Friauf, J. Appl. Phys. **33**, 494 [1962].

preciably smaller than $(R_{\mathrm{Tl}}+R_{\mathrm{Cl}}-f_{\mathrm{v}})/f_{\mathrm{v}}$, that is the 10 to 15% of excess diffusion in Fig. 3. Secondly it is experimentally assured that the diffusion coefficient and conductivity are compared at the same temperature by using the same sample holder and thermocouple arrangement for all measurements. Finally a check against systematic error in the absolute comparison of tracer diffusion coefficients and electrical conductivity has been provided by measurements on AgCl:Cd, where agreement within 1 to 2% was found using the same techniques and often the same pieces of apparatus as in the present work [17].

IV. Analysis of Diffusion Processes

A) *Schottky Defects*

Let $x_{\mathrm{a}}=x_{\mathrm{c}}=x_0=$ mole fraction of Schottky defects, $a_0=$ jump distance $=$ unit cell edge, $\nu_{\mathrm{a}}=$ frequency for jump of a nn anion into an anion vacancy, $\nu_{\mathrm{c}}=$ corresponding frequency for a cation, and $f_{\mathrm{a}}=f_{\mathrm{c}}=f_{\mathrm{v}}=0.653=$ correlation factor for diffusion via nn vacancy jumps on a sc lattice [15]. Then the *microscopic* diffusion coefficient and mobility are, with the microscopic Nernst-Einstein relation,

$$d_{\mathrm{a}}=\tfrac{1}{6}\nu_{\mathrm{a}}\,a_0^2, \qquad \mu_{\mathrm{a}}=(e/k\,T)\;d_{\mathrm{a}}\,. \tag{8}$$

The *macroscopic* diffusion coefficient and conductivity,

$$D_{\mathrm{v}}^{*}(\mathrm{Cl})=f_{\mathrm{v}}\,x_0\,d_{\mathrm{a}}\,, \quad \sigma_{\mathrm{v}}(\mathrm{Cl})=N\,e\,x_0\,\mu_{\mathrm{a}}\,, \tag{9}$$

are connected by the macroscopic Einstein relation,

$$D_{\mathrm{v}}^{*}(\mathrm{Cl})=f_{\mathrm{v}}\,D_\sigma(\mathrm{Cl})=f_{\mathrm{v}}(k\,T/N\,e^2)\;\sigma_{\mathrm{v}}(\mathrm{Cl}), \tag{10}$$

as used in Eq. (6). The relative amounts of anion and cation motion are determined by the mobility ratio

$$\varphi=\frac{\mu_{\mathrm{a}}}{\mu_{\mathrm{c}}}=\frac{\mathrm{d_a}}{\mathrm{d_c}}=\frac{\nu_{\mathrm{a}}}{\nu_{\mathrm{c}}}=\frac{\sigma_{\mathrm{v}}(\mathrm{Cl})}{\sigma_{\mathrm{v}}(\mathrm{Tl})}. \tag{11}$$

If only Schottky defects are present and if only nn jumps into a vacancy occur, then all of the ionic conductivity and tracer diffusion is due to the motion of single vacancies.

$$\begin{aligned} D_\sigma \quad &= D_\sigma(\mathrm{Cl})+D_\sigma(\mathrm{Tl}),\\ D^{*}(\mathrm{Cl}) &= D_{\mathrm{v}}^{*}\;(\mathrm{Cl})=f_{\mathrm{v}}\,D_\sigma(\mathrm{Cl}),\\ D^{*}(\mathrm{Tl}) &= D_{\mathrm{v}}^{*}\;(\mathrm{Tl})=f_{\mathrm{v}}\,D_\sigma(\mathrm{Tl}). \end{aligned} \tag{12}$$

The diffusion ratios defined in Eq. (7) are found to be

$$R_{\mathrm{Cl}}=t_{\mathrm{a}}\,f_{\mathrm{v}}\,, \qquad R_{\mathrm{Tl}}=t_{\mathrm{c}}\,f_{\mathrm{v}}\,, \tag{13}$$

where $t_{\mathrm{a}}=\sigma_{\mathrm{v}}(\mathrm{Cl})/\sigma$ and $t_{\mathrm{c}}=1-t_{\mathrm{a}}$ are the transport numbers, and an overall check of this model is provided by

$$D^{*}(\mathrm{Cl})\;+D^{*}(\mathrm{Tl})\;=f_{\mathrm{v}}\,D_\sigma\,, \tag{14}$$

or

$$R_{\mathrm{Cl}}\quad +R_{\mathrm{Tl}}\quad =f_{\mathrm{v}}\,. \tag{15}$$

Since Fig. 3 shows that this check is satisfied within 10 to 15% of the total conductivity, we conclude that Schottky defects are, in fact, predominant in TlCl.

There is considerable other evidence that gives general support to this conclusion. Addition of Pb^{2+} should increase x_{c} and decrease x_{a} according to the mass action law [1] $x_{\mathrm{c}}\,x_{\mathrm{a}}=x_0^2$; with Cl much more mobile than Tl this should lead to a decrease of total conductivity and Cl diffusion, but to an increase of Tl diffusion. HAUFFE and GRIESSBACH-VIERK [12] did find an appreciable decrease in conductivity between 150° and 250 °C on adding up to 0.25 mole-% Pb, and they also obtained a qualitative result for a TUBANDT [18] type of mass transport experiment showing primarily transport of chlorine. BEUTHE [14] added 0.04 and 0.15 mole-% Pb and found a similar decrease in conductivity between 200° and 350 °C. He also observed a decrease of Cl diffusion by factors of 1.7 to 5 and an increase of Tl diffusion by factors of 2 to 6 over the same temperature range. Additional indirect evidence is afforded by the work of CHRISTY and DOBBS [19], who were able to obtain fairly good agreement with their data for thermoelectric power in TlCl : Pb by assuming Schottky defects with no association.

At first thought it may seem surprising that the mobility of the anion is so much larger than that of the cation since the Goldschmidt radii are 1.81 Å for Cl^- compared to 1.49 Å for Tl^+. Actually the repulsive energy at the saddle point for the jump of an ion into a vacancy is the same to first order, no matter which ion is jumping, and the anion is also found to be more mobile in CsCl [5], CsBr [6], and CsI [6], where the ionic radii are Cs^+ 1.65 Å, Br^- 1.965 Å, and I^+ 2.20 Å, although the ratio of mobilities is not so large as for TlCl. The most important factor in determining the relative activation energies for motion of anions and cations is probably the polarizability of the ion [16]. The polarization energy contributes a positive term to the jump activation energy, for the ion in the ground state is appreciably polarized by the electric field of the neighboring vacancy, giving a negative energy, whereas

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[17] J. GRACEY and R. J. FRIAUF, J. Phys. Chem. Solids **30**, 421 [1969].

[18] C. TUBANDT, in: Handbuch der Experimentalphysik (ed. by W. WIEN, F. HARMS, and H. LENZ), Akademische Verlags-GmbH, Leipzig 1932, Vol. **12**, Part 1, p. 383.

[19] R. W. CHRISTY and H. S. DOBBS, J. Chem. Phys. **46**, 722 [1967].

there is no polarization at the saddle point since the field is zero. Hence ions of small polarizability are favored by this term, and the polarizabilities[20] are Cl^- 3.0, Tl^+ 5.2 Å^3 (but Br^- 4.2, I^- 6.4, Cs^+ 3.3 Å^3). Thus the explanation is qualitatively correct for the extreme case of TlCl, but more detailed calculations would clearly be required to furnish a satisfactory explanation in all cases.

At one time it was thought that the very small values of the diffusion ratio for Tl might be explained by a special kind of one-dimensional interstitialcy motion[13], for which the correlation factor f would be zero[21, 22]! In an actual crystal a small contribution would be expected for occasional jumps off the original line of motion, but very small values of f would still be probable. With the larger diffusion ratios for Cl now known, it is necessary to postulate at least coexistence of Schottky defects. (Cl Frenkel defects seem unlikely because of the larger size of Cl, which would adversely influence the formation energy.) Then the combined diffusion ratio would be

$$R_{\mathrm{Cl}}+R_{\mathrm{Tl}}=f_{\mathrm{v}}(t_{\mathrm{a}}+t_{\mathrm{c}})+f_{\mathrm{i}}\,t_{\mathrm{i}}\,. \tag{16}$$

Since f_{i} is less than f_{v} for all likely interstitialcy mechanisms[22], the discrepancy in Fig. 3 would only be increased ($t_{\mathrm{a}}+t_{\mathrm{c}}+t_{\mathrm{i}}=1$ in any case). Hence the present experimental results seem to rule out consideration of any Frenkel defects.

It is nonetheless clear in Fig. 3 that there is some excess diffusion, which is not accounted for solely by considering jumps of nn ions into single vacancies. The two conceivable explanations for this excess, namely, contributions of neutral vacancy pairs to diffusion or the presence of nnn jumps into single vacancies, are discussed in the next two sections.

B) Vacancy Pairs

The first possibility to consider is that in addition to single vacancies there are a certain number of bound vacancy pairs, which make an additional contribution to diffusion but do not contribute to conductivity since they are electrically neutral. In the CsCl type structure shown in Fig. 4 each vacancy pair has 8 equivalent orientations, and there are 3 jumps of each kind that leave the vacancy pair bound but cause a rotation of it. The jump distance is the unit cell edge a_0, and there are jump frequencies into the vacancy pair of ν_{a}' and ν_{c}', which are not necessarily equal. The microscopic diffusion coefficient for Cl is defined as

$$d_{\mathrm{a}}'=\tfrac{1}{6}\,\nu_{\mathrm{a}}'\,a_0^2\,, \tag{17}$$

and the contribution of vacancy pairs to the macroscopic diffusion of Cl is

$$D_{\mathrm{pr}}^*\,(\mathrm{Cl})=f_{\mathrm{a}}'\,x_{\mathrm{pr}}\,d_{\mathrm{a}}'\,, \tag{18}$$

where x_{pr} is the mole fraction of vacancy pairs and f_{a}' is the correlation factor for diffusion of anions via vacancy pairs.

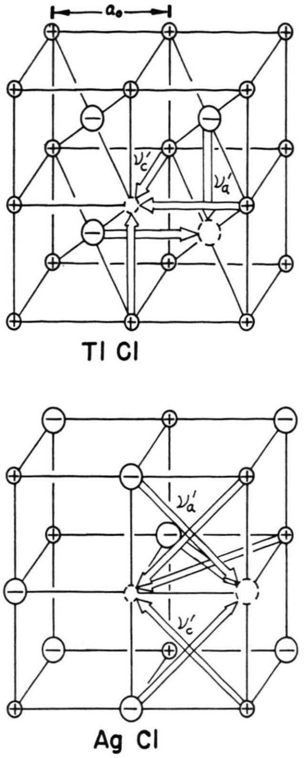

Fig. 4. Jumps into vacancy pairs in TlCl (sc) and AgCl (fcc). Ionic radii are not drawn to scale.

The vacancy pair can move through the lattice by a sequence of the two kinds of jumps given by ν_{a}' and ν_{c}' and can thereby make a contribution to the macroscopic diffusion coefficient as given by Eq. (18). The correlation factors f_{a}' and f_{c}' are functions of the frequency ratio $\varphi'=\nu_{\mathrm{a}}'/\nu_{\mathrm{c}}'$.

$$f_{\mathrm{c}}'=f_{\mathrm{pr}}(\varphi')\,,\quad f_{\mathrm{a}}'=f_{\mathrm{pr}}(1/\varphi')\,. \tag{19}$$

The general behavior of $f_{\mathrm{pr}}(\varphi')$ is shown in Fig. 5,

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[20] J. R. TESSMAN, A. H. KAHN, and W. SHOCKLEY, Phys. Rev. **92**, 890 [1953].

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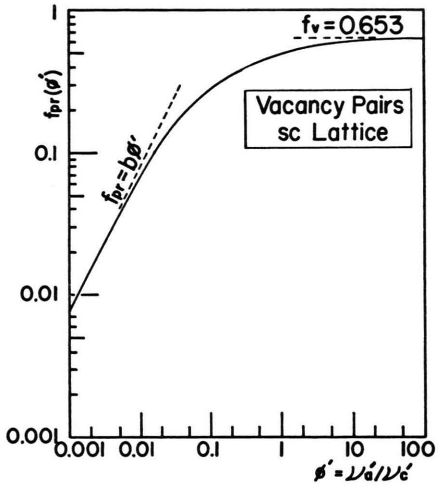

Fig. 5. Correlation function for diffusion by vacancy pairs on a simple cubic lattice. Numerical values are from HOWARD [23] reduced uniformly by 6.7% for all φ'.

and the limiting forms are given by [15]

$$\lim_{\varphi' \to 0} f_{pr}(\varphi') = b\,\varphi', \quad \lim_{\varphi' \to \infty} f_{pr}(\varphi') = f_v . \qquad (20)$$

Numerical values calculated by HOWARD [23] have been generally confirmed by this author [24], but all of Howard's values have been uniformly reduced by 6.7% in order to bring them into accord with the accurately established limiting value of $f_v = 0.653$ at large φ' [15]. For later purposes it is convenient to define another function $F(\varphi')$ that gives the ratio of anion to cation diffusion via vacancy pairs [3].

$$F(\varphi') = \frac{D^*_{pr}\,(\mathrm{Cl})}{D^*_{pr}\,(\mathrm{Tl})} = \frac{\varphi'\,f_{pr}(1/\varphi')}{f_{pr}(\varphi')} . \qquad (21)$$

This function is shown in Fig. 6 and has the following properties:

$$F(1/\varphi') = 1/F(\varphi'), \qquad \lim_{\varphi' \to \infty} F(\varphi') = b/f_v = 12.0 . \qquad (22)$$

If we assume for the moment that both Schottky defects and vacancy pairs are present and that all of the excess diffusion may be attributed to vacancy

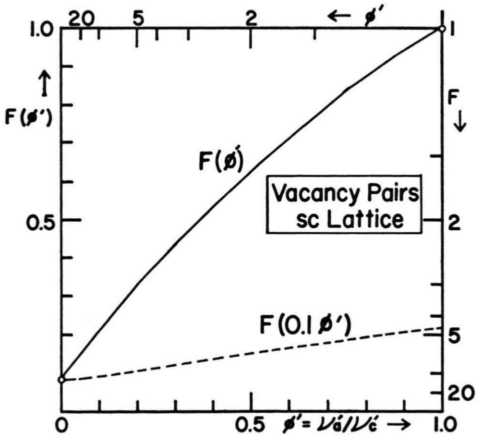

Fig. 6. Ratio of anion to cation diffusion via vacancy pairs on a simple cubic lattice, $F(\varphi') = D^*_{pr}\,(\mathrm{Cl})/D^*_{pr}\,(\mathrm{Tl})$. For $\varphi' > 1$ the scales on the top and right should be used. The dashed curve shows values of F for an expanded scale of φ' between 0 and 0.1.

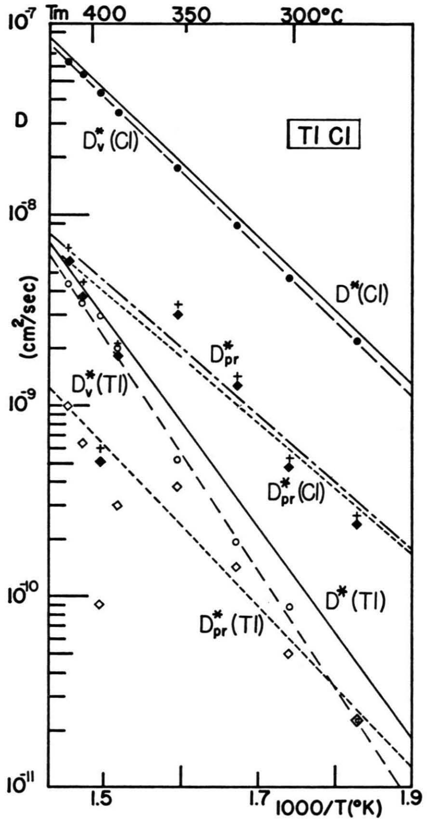

Fig. 7. Possible results for diffusion via vacancy pairs in TlCl. ——— D^*(Cl) and D^*(Tl), tracer diffusion coefficients from Fig. 2; ——— – ——— + D^*_{pr} total vacancy pair diffusion; - - - - - - - - ◆ D^*_{pr} (Cl) and ◇ D^*_{pr} (Tl), vacancy pair contribution for each ion by partition of D^*_{pr} with $\varphi' = \varphi$; ——— ——— ——— ● D^*_v(Cl) and ○ D^*_v(Tl), single vacancy contribution for each ion by subtraction of the appropriate vacancy pair contribution. The straight lines are least squares fits, with the point at 395.5 °C omitted for D^*_{pr}, D^*_{pr}(Cl), and D^*_{pr} (Tl).

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[23] R. E. HOWARD, Phys. Rev. **144**, 650 [1966].

[24] R. J. FRIAUF, to be published.

pairs, the counterparts of Eqs. (12) are

$$\begin{aligned} D_\sigma &= D_\sigma(\mathrm{Cl}) + D_\sigma(\mathrm{Tl}), \\ D^*(\mathrm{Cl}) &= D^*_\mathrm{v}(\mathrm{Cl}) + D^*_\mathrm{pr}(\mathrm{Cl}), \\ D^*(\mathrm{Tl}) &= D^*_\mathrm{v}(\mathrm{Tl}) + D^*_\mathrm{pr}(\mathrm{Tl}). \end{aligned} \tag{23}$$

By adding the last two equations and defining

$$D^*_\mathrm{pr} = D^*_\mathrm{pr}(\mathrm{Cl}) + D^*_\mathrm{pr}(\mathrm{Tl}), \tag{24}$$

we find the total diffusion from vacancy pairs to be

$$D^*_\mathrm{pr} = D^*(\mathrm{Cl}) + D^*(\mathrm{Tl}) - f_\mathrm{v} D_\sigma . \tag{25}$$

D^*_pr is calculated by using the directly measured values of $D^*(\mathrm{Cl})$ and D_σ at the eight temperatures for Cl diffusion along with interpolated values of $D^*(\mathrm{Tl})$ at these temperatures from the least squares fit of Fig. 2. The result is shown in Fig. 7, where we see that D^*_pr is approximately 10% of $D^*(\mathrm{Cl})$ but 1.3 to 7 times $D^*(\mathrm{Tl})$.

An unambiguous separation of $D^*_\mathrm{pr}(\mathrm{Cl})$ and $D^*_\mathrm{pr}(\mathrm{Tl})$ is not possible without at least one additional piece of experimental evidence, such as diffusion of one of the tracers in an electric field (or a doped crystal) or an independent determination of φ by conductivity measurements on doped crystals. Unfortunately no such experiments are presently available for TlCl with the required accuracy of much better than 10%. Hence in order to proceed with a tentative analysis, we introduce the additional assumption that $\varphi' = \varphi$, guided in part by the general observation that Cl diffusion is much larger than Tl diffusion in all respects. A further consideration is that an apreciable fraction of $D^*(\mathrm{Tl})$ must be attributed to $D^*_\mathrm{v}(\mathrm{Tl})$ so that $D_\sigma(\mathrm{Tl})$ will remain large enough to account for the increase in slope of σ at high temperatures. This precludes the possibility, for instance, that nearly all of $D^*(\mathrm{Tl})$ might be due to diffusion via vacancy pairs; it will be seen below that $D^*_\mathrm{pr}(\mathrm{Tl})$ is always less than 50% of $D^*(\mathrm{Tl})$ on the basis of the assumption used here.

The analysis starts with an estimate of φ at each temperature, initially from $\varphi = D^*(\mathrm{Cl})/D^*(\mathrm{Tl})$. Then with $\varphi' = \varphi$ the value of $F(\varphi')$ is read from Fig. 6, allowing D^*_pr to be partitioned according to

$$\begin{aligned} D^*_\mathrm{pr}(\mathrm{Cl}) &= F(1+F)^{-1} D^*_\mathrm{pr}, \\ D^*_\mathrm{pr}(\mathrm{Tl}) &= (1+F)^{-1} D^*_\mathrm{pr} . \end{aligned} \tag{26}$$

These values of $D^*_\mathrm{pr}(\mathrm{Cl})$, $D^*_\mathrm{pr}(\mathrm{Tl})$ are subtracted from $D^*(\mathrm{Cl})$, $D^*(\mathrm{Tl})$ in Eqs. (23) to give $D^*_\mathrm{v}(\mathrm{Cl})$, $D^*_\mathrm{v}(\mathrm{Tl})$. Finally a new value of $\varphi = D^*_\mathrm{v}(\mathrm{Cl})/D^*_\mathrm{v}(\mathrm{Tl})$ is calculated, and the process is repeated until self-consistency is attained. The results after five itera-

Table 3. Parameters for defect properties in TlCl.

Quantity	Pre-exponential	W (eV)
Vacancy pair model[a]		
D^*_pr	1.0×10^{-3} cm²/s	0.71 ± 0.09
$D^*_\mathrm{pr}(\mathrm{Cl})$	6.5×10^{-4}	0.69 ± 0.09
$D^*_\mathrm{pr}(\mathrm{Tl})$	1.4×10^{-3}	0.84 ± 0.08
$D^*_\mathrm{v}(\mathrm{Cl})$	3.5×10^{-2} cm²/s	0.783 ∓ 0.005
$D^*_\mathrm{v}(\mathrm{Tl})$	3.7	1.22 ± 0.04
$\varphi = D^*_\mathrm{v}(\mathrm{Cl})/D^*_\mathrm{v}(\mathrm{Tl})$	6.4×10^{-3}	-0.46 ∓ 0.04
d_a	9.8×10^{-4} cm²/s	0.104 ± 0.005
d_c	1.6×10^{-1}	0.56 ± 0.04
Jumps by nn and nnn[a]		
$\varkappa = \nu_2/\nu_1$	2.2×10^{-2}	-0.10 ± 0.13
$\varphi = D^*(\mathrm{Cl})/D^*(\mathrm{Tl})$	4.5×10^{-2}	-0.335 ± 0.014
d_a	9.9×10^{-4} cm²/s	0.105 ± 0.006
$\mathrm{d_c}$	2.2×10^{-2}	0.44 ± 0.02
Schottky defects		
$x_0(\mathrm{JY}^\mathrm{b})$	5.5×10 ———	$h_\mathrm{s} = 1.36 \pm 0.03$
$x_0(\mathrm{CD}^\mathrm{c})$	1.7×10^2	1.34 ± 0.1

[a] The temperature range for all quantities except x_0 is 275° to 415 °C.

[b] Jackson and Young [9]. Temperature range 200—325 °C.

[c] Christy and Dobbs [19]. Temperature range 275—400 °C.

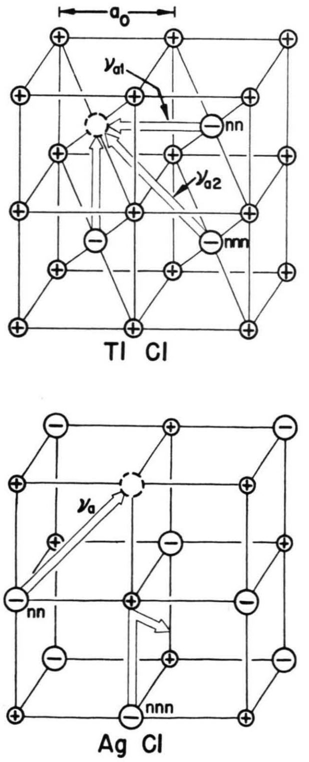

Fig. 8. Nearest neighbor (nn) and next nearest neighbor (nnn) jumps into single vacancies in TlCl (sc) and AgCl (fcc). Notice that the nnn jump is apparently impossible in the fcc structure. Ionic radii are not drawn to scale.

tions are included in Fig. 7. The general trends show that $\varphi = \varphi'$ ranges from 15 to 100 (Fig. 10), $F(\varphi')$ from 6 to 11, $D^*_{\mathrm{pr}}(\mathrm{Cl})$ from 8 to 12% of $D^*(\mathrm{Cl})$, and $D^*_{\mathrm{pr}}(\mathrm{Tl})$ from 20 to 50% of $D^*(\mathrm{Tl})$. The enthalpies of 0.69 eV for $D^{\mathrm{S}}_{\mathrm{pr}}(\mathrm{Cl})$ and 0.84 eV for $D^*_{\mathrm{pr}}(\mathrm{Tl})$ in Table 3 appear slightly small compared to 0.78 eV for $D^*_{\mathrm{v}}(\mathrm{Cl})$ and 1.22 eV for $D^*_{\mathrm{v}}(\mathrm{Tl})$, but there is nothing patently unreasonable about the results of this analysis.

C) Next Nearest Neighbor Jumps

An alternative explanation for the excess diffusion is offered by the possibility that jumps into a single vacancy may occur for ions not only in nn but also in nnn positions in the rather open sc structure of TlCl as illustrated in Fig. 8[25]. For a given anion vacancy there are 6nn, with jump distance $a_1 = a_0$ and jump frequency $\nu_{\mathrm{a}1}$, and 12 nnn, with $a_2 = \sqrt{2}\, a_0$ and $\nu_{\mathrm{a}2}$. The direct path for $\nu_{\mathrm{a}2}$ does place the jumping anion rather close to *two* cations at the saddle point position at the midpoint of a cube edge, but the saddle point for $\nu_{\mathrm{a}1}$ places the anion between *four* cations at the center of a cube face; without a detailed calculation it is not obvious that either activation enthalpy should be appreciably larger. In the more closely packed fcc structure, on the other hand, the nnn jump seems to be strongly forbidden because of the presence of a cation directly between a nnn anion and the vacancy.

For a mixture of nn and nnn jumps the *microscopic* diffusion coefficient and mobility are given by

$$d_{\mathrm{a}} = \tfrac{1}{6}\,(\nu_{\mathrm{a}1}\, a_1^2 + \nu_{\mathrm{a}2}\, a_2^2), \quad \mu_{\mathrm{a}} = (e/k\,T)\, d_{\mathrm{a}}\,. \qquad (27)$$

The *macroscopic* diffusion coefficient and conductivity are

$$D^*_{\mathrm{v}}\,(\mathrm{Cl}) = f_{\mathrm{a}}\, x_0\, d_{\mathrm{a}}, \; \sigma_{\mathrm{v}}(\mathrm{Cl}) = e\, N\, x_0\, \mu_{\mathrm{a}}\,. \qquad (28)$$

The correlation factor f_{a} is a function of the frequency ratio $\varkappa_{\mathrm{a}} = \nu_{\mathrm{a}2}/\nu_{\mathrm{a}1}$ that gives the relative fraction of nnn to nn jumps into anion vacancies. The value of f for different values of $\varkappa$ has been calculated by using a computer to follow the diffusion of probability for the random walk motion of a vacancy on the appropriate lattice[24], and the results are shown in Fig. 9, where one calculation suffices for the identical anion and cation sublattices. The correlation factor has the value 0.653 for a sc lattice when $\varkappa = 0$ (nn jumps only), rises to a flat maximum of 0.849 for $\varkappa = 1.67$, and falls slightly to the value 0.781 for a fcc lattice when $\varkappa = \infty$ (nnn jumps only). Thus the expected increase of f towards unity is seen when the average number of ions jumping into a vacancy increases because of the admixture of some proportion of nnn jumps[16].

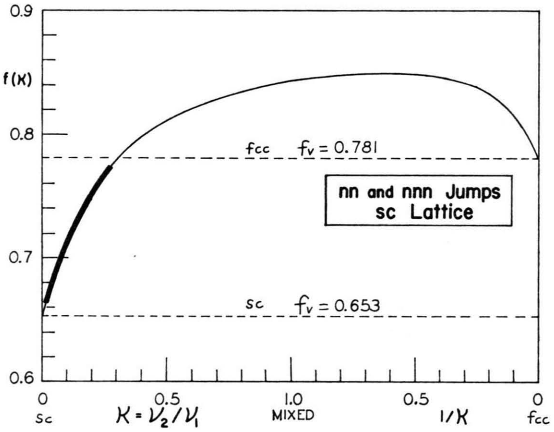

Fig. 9. Correlation function for diffusion by mixed nn (ν_1) and nnn (ν_2) jumps on a simple cubic lattice. Numerical values are from a computer calculation by FRIAUF[24]. The heavy section of the curve shows the range covered by experimental values of $R_{\mathrm{Cl}} + R_{\mathrm{Tl}}$ in TlCl. For $\varkappa > 1$ the abscissa represents $1/\varkappa$ instead of $\varkappa$.

If we assume that all of the excess diffusion comes from nnn jumps, i. e., if we neglect vacancy pairs for the moment, the counterparts of Eqs. (12) become

$$\begin{aligned} D_\sigma &= D_\sigma(\mathrm{Cl}) + D_\sigma(\mathrm{Tl}), \\ D^*(\mathrm{Cl}) &= D^*_{\mathrm{v}}\,(\mathrm{Cl}) = f_{\mathrm{a}}(\varkappa_{\mathrm{a}})\; D_\sigma(\mathrm{Cl}), \\ D^*(\mathrm{Tl}) &= D^*_{\mathrm{v}}\,(\mathrm{Tl}) = f_{\mathrm{c}}(\varkappa_{\mathrm{c}})\; D_\sigma(\mathrm{Tl}). \end{aligned} \qquad (29)$$

The diffusion ratios are now

$$R_{\mathrm{Cl}} = t_{\mathrm{a}}\, f_{\mathrm{a}}\,, \qquad R_{\mathrm{Tl}} = t_{\mathrm{c}}\, f_{\mathrm{c}}\,, \qquad (30)$$

and the sum of anion and cation diffusion becomes

$$D^*(\mathrm{Cl}) + D^*(\mathrm{Tl}) = (t_{\mathrm{a}}\, f_{\mathrm{a}} + t_{\mathrm{c}}\, f_{\mathrm{c}})\; D_\sigma\,. \qquad (31)$$

The excess diffusion, compared to what would be expected from nn jumps only, occurs because both f_{a} and f_{c} are larger than f_{v} when some nnn jumps are also present.

Since no accurate independent values of t_{a} and t_{c} are known, we now assume that $\varkappa_{\mathrm{c}} = \varkappa_{\mathrm{a}}$ (a similar analysis with $\varkappa_{\mathrm{c}} = 0$ gives very similar results). This

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[25] R. J. FRIAUF, Bull. Amer. Phys. Soc. **6**, 132 [1961].

choice makes $f_c = f_a$ and causes Eq. (31) to reduce to

$$R_{\mathrm{Cl}} + R_{\mathrm{Tl}} = f_a \qquad (32)$$

when expressed in terms of diffusion ratios. We can thus find f_a directly from the observed diffusion ratios, using experimental values of R_{Cl} and interpolated values of R_{Tl} as before, and can then proceed to obtain $\varkappa_a$ from f_a by means of the graph in Fig. 9. The general picture in Fig. 10 is a nearly constant value of $\varkappa$ between 0.1 and 0.2, giving only a modest fraction of nnn jumps. The temperature dependence of $\varkappa$ has doubtful significance according to Table 3, but would seem to give

$$\Delta h_2 = \Delta h_1 - 0.1 \text{ eV},$$

i. e., a slightly *lower* activation enthalpy for the nnn jump. This result may seem unexpected at first thought, but is not necessarily ruled out on further contemplation of Fig. 8, The pre-exponential factor for $\varkappa$ gives $\Delta s_2 - \Delta s_1 = -4.5$ e. u., which is perhaps rather large. A further consequence of the assumption that $\varkappa_c = \varkappa_a$ is that the mobilitiy ratio becomes

$$\varphi = \mu_a/\mu_c = D^*(\mathrm{Cl})/D^*(\mathrm{Tl}). \qquad (33)$$

Thus φ can be obtained directly from the experimental results in this case and is also shown in Fig. 10.

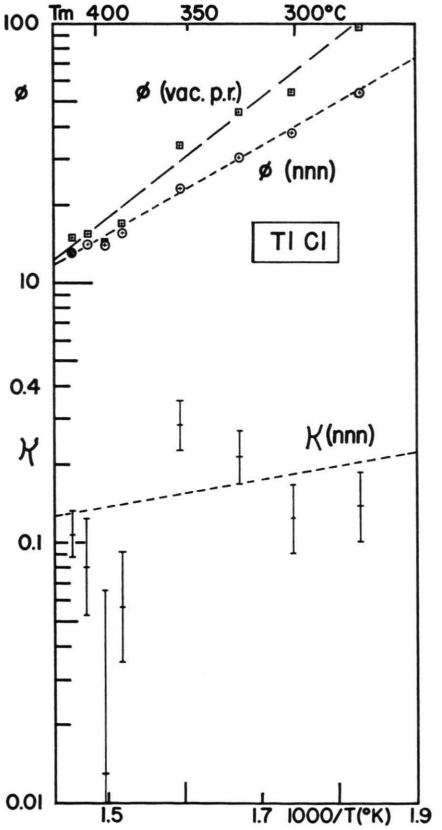

Fig. 10. Frequency and mobility ratios for several models of diffusion in TlCl. For the model with nn (ν_1) and nnn (ν_2) jumps $\varkappa$(nnn) $= \nu_2/\nu_1$ is obtained from Fig. 9 with the assumption $\varkappa_c = \varkappa_a$, and then φ(nnn) $= D^*(\mathrm{Cl})/D^*(\mathrm{Tl})$. For the vacancy pair model φ (vac. pr.) is obtained from $D_v^*(\mathrm{Cl})/D_v^*(\mathrm{Tl})$ after assuming $\varphi' = \varphi$ as in Fig. 7. The straight lines are least squares fits.

D) Calculation of Microscopic Diffusion Coefficients

Two independent experiments have given results for the concentration of Schottky defects in TlCl: CHRISTY and DOBBS[19] (CD) measured the thermoelectric power in pure and lead-doped crystals, and JACKSON and YOUNG[9] (JY) observed the polarization capacitance with blocking electrodes at audio frequencies. The formation enthalpies in Table 3 agree within experimental error, but the concentration at the melting point is 0.3% for CD, compared to 0.07% for JY, whose results we use here. By taking the mobility ratio from the analysis of the diffusion results, we can then calculate the microscopic mobilities from the total conductivity.

$$\sigma = N\,e\,(x_0\,\mu_a + x_0\,\mu_c) = Ne\;x_0\,\mu_a\,(1+\varphi^{-1}). \quad (34)$$

We prefer to express the results in terms of the corresponding microscopic diffusion coefficients by introducing the Nernst-Einstein relation from Eqs. (6) and (8).

$$d_a = D_\sigma/[x_0(1+\varphi^{-1})], \qquad d_c = d_a/\varphi. \quad (35)$$

The results are shown in Fig. 11 and summarized in Table 3. There is essentially no difference between the vacancy pair and nnn jumps models so far as d_a is concerned because the influence of φ on d_a is small when $\varphi \gg 1$. There is some discernible difference for d_c, but in either case $d_c \ll d_a$. With increasing temperature the cation transport number rises from 1 to 6% for the vacancy pair model and from 2 to 7% for the nnn jump model.

For subsequent discussion we shall use the results for d_c from the nnn model, since in that case φ in Eq. (33) is obtained directly from measured values, as was done by both JY and CD without reference to any specific model. The value of $\Delta h_a = 0.105$ eV is much smaller than corresponding values for alkali halides; the only comparable values are 0.008 and 0.058 eV for collinear interstitialcy mo-

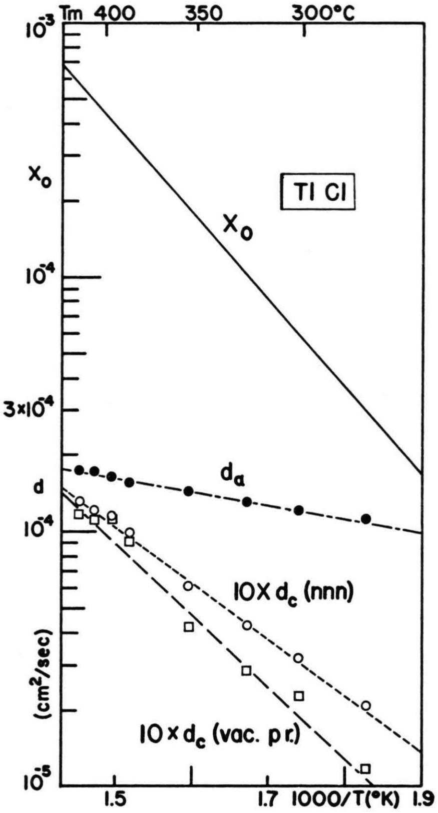

Fig. 11. Microscopic properties of Schottky defects in TlCl. The mole fraction x_0 is taken from Jackson and Young [9]. The microscopic diffusion coefficients are related to the mobilities by the microscopic Einstein relation, e. g., $d_a = (k\,T/e)\,\mu_a$. For d_a the difference between the results for the two models is too small to be shown on the graph. The straight lines are least squares fits.

tion in AgCl and AgBr, respectively [4], and perhaps 0.12 eV for Cl vacancies in $PbCl_2$ [26]. $\Delta h_c = 0.44$ eV is also rather small compared to other crystals, but is noticeably larger than Δh_a. The pre-exponential factors in d_a and d_c can be used to calculate an attempt frequency according to Eq. (8), giving

$$\nu_a = 4.0 \times 10^{12} \quad \text{and} \quad \nu_c = 90 \times 10^{12}\ \text{Hz}.$$

With an estimated Debye frequency of 3.6×10^{12} Hz (l. c. [27]) the corresponding entropies are

$$\Delta s_a/k = 0.10 \quad \text{and} \quad \Delta s_c/k = 3.2\ \text{e. u.},$$

which are small but not unreasonable.

V. Discussion

A) Low Temperature Results

A survey of all measurements of diffusion and ionic conductivity for TlCl is provided in Fig. 2. The diffusion results for 0° to 110 °C come from the NMR measurement of relaxation times for ^{35}Cl by Ailion and Samuelson [28]. They obtain an activation energy of 0.75 ± 0.03 eV, and furthermore the dependence on angle between the magnetic field and the crystal axes at 74 °C agrees very well with a treatment based on nn jumps into anion vacancies. Hence the line for D_{NMR} has been adjusted to fit smoothly into the extrapolation of D from higher temperatures (the NMR technique does not give a good estimate of the magnitude of the diffusion coefficient).

It seems remarkable that the same activation enthalpy should be found for the diffusion of Cl from 415 °C down to 0 °C, for the value of 0.75 eV presumably contains contributions from both formation and jumping. The conductivity results of JY [9] offer further experimental confirmation, however, since there is reproducible and reversible behavior for times of 1 or 2 days down to 80 °C, with again the same enthalpy (see Fig. 2 and Table 1). It is perhaps not unreasonable for thermodynamic equilibrium to occur since extrapolation of the anion jump frequency from higher temperatures gives $\nu_a = 10^{11}$ Hz and $d_a = 2 \times 10^{-5}\ \text{cm}^2/\text{s}$ at 50 °C, allowing in 1 day 10^{16} jumps and $x_{rms} = \sqrt{2\,d_a\,t} = 2$ cm(!) for an anion vacancy. But extrapolation of x_0 gives only 0.001 ppm at 50°, whereas it is unlikely that the impurity content of the crystals is less than 0.1 to 10 ppm. (At 200 °C both Beuthe [14] and Griessbach-Vierk [12] find a solubility for Pb in excess of 1000 ppm, but this will certainly decrease at lower temperatures.) Since the results above nonetheless show the lack of influence of impurities down to extremely small intrinsic defect concentrations [9], it seems likely that the charge of any aliovalent impurities is neutralized by the tight binding of oppositely charged impurities or vacancies.

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B) Ionic Transport Processes in the Melt

Several measurements have been made of ionic conductivity and tracer diffusion in liquid TlCl [29, 30] as shown in Fig. 2. The increase of conductivity and Cl diffusion by a factor of 300 corresponds to an increase in defect concentration from 0.07% in the crystal [9] to 20% in the liquid. The diffusion coefficients for Tl and Cl are much more nearly equal for the liquid than for the crystal ($t_{\mathrm{Tl}} = 48\%$) [30], and the activation enthalpies are also nearly equal ($W_{\mathrm{Cl}} = 0.198 \pm 0.020$ and $W_{\mathrm{Tl}} = 0.196 \pm 0.010$ eV) (l. c. [30]).

The combined diffusion ratio $R = R_{\mathrm{Cl}} + R_{\mathrm{Tl}}$ for liquid TlCl is 1.88 [30], which is noticeably larger than the results for the crystal (Fig. 3) and for other ionic crystals [31]. Perhaps the Nernst-Einstein relation does not apply to the non-dilute components in molten salts [32], but if it does a value of $R > 1$ must indicate some sort of coupling of the transport processes. A simple hole theory of liquid structure has described the coupling as the existence of vacancy pairs in the liquid [33], in analogy to the crystal; other theories suggest a coupling through short range frictional forces between ions [30]. According to the latter theory, for instance, the anomalously large value of R in liquid TlCl is ascribed to the unusually large polarizability of the Tl^+ ion (see Sec. IV A). But there does not seem to be any simple, direct correspondence between transport processes in the crystal and in the liquid. For NaCl the vacancy pair contribution to diffusion in the crystal at T_{melt} is 40% of the total [3], but R is only 1.12 in the liquid [34], whereas for TlCl the maximum contribution of vacancy pairs in the crystal is 10% (Fig. 7), even though $R = 1.88$ in the liquid [30].

C) Defect Structure and Transport Processes in the Crystal

All of the foregoing results and analyses establish that Schottky defects are predominant in crystalline TlCl. In particular there is no evidence for any electronic contribution to the conductivity or for the presence of any cation Frenkel defects. The two independent determinations of the concentration [9, 19] give essentially the same formation energy (Table 3), which also agrees well with a theoretical value of 1.27 eV calculated by MURTHY and MURTI [35] by an extension of the Mott-Littleton procedure with explicit consideration of van der Waals' interactions. The anion mobility parametres are well established since there is essentially no difference between the results for the two different models considered in Sec. IV. The cation mobility parameters are still subject to some possible variation, but the order of magnitude of d_{c} is fairly well delimited in Fig. 11 and is clearly much smaller than d_{a} for either model. The anion mobility parameters are well established after the conductivity is considered by means of the Einstein relation and the correlation factor for nn jumps can be accounted for by allowing a contribution of up to 20% from either vacancy pairs or nnn jumps into single vacancies. The analysis in Sec. IV shows that either model by itself can give an internally consistent explanation, or there could just as well be some combination of the two additional processes. One noteworthy feature is that all experimental values of $R_{\mathrm{Cl}} + R_{\mathrm{Tl}}$ do lie within the rather narrow range allowed by nnn jumps (Fig. 9), thereby providing a natural explanation for the nearly constant amount of excess diffusion (Fig. 3). The vacancy pair model, on the other hand, requires a partly fortuitous near equality of the formation and jump enthalpies to account for the same feature, but otherwise seems to show slightly less scatter (Fig. 7). The temperature dependence of the excess diffusion is slight and perhaps not statistically significant (see $R_{\mathrm{Cl}} + R_{\mathrm{Tl}}$ in Table 1 and $\varkappa$ in Table 3), but if anything, suggests a slight decrease near the melting point.

Even a diffusion experiment in an electric field would not allow a complete distinction between contributions from vacancy pairs and nnn jumps. The measurement of the tracer drift mobility for Cl, say, would allow a separate calculation of the amount of excess Cl diffusion [3], but there would still be no way

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[34] C. A. ANGELL, J. Phys. Chem. **69**, 399 [1965].

[35] C. S. N. MURTHY and Y. V. G. S. MURTI, private communication.

to tell, from the diffusion experiments alone, how much of the excess was due to an addition from vacancy pairs and how much was due to an increase of f_a over f_v by the presence of nnn as well as nn jumps. Some rather different type of experiment would be required that could provide a more direct look at either the vacancy pair or the nnn jump. Possibilities might be dielectric relaxation measurements to observe resonant rotation of vacancy pairs or high temperature NMR observations of jumps into the vacancy, but both of these are rather difficult experiments.

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