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Pressure and temperature dependences of the ionic conductivities of the thallous halides TlCl, TlBr, and TlI

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Detailed studies of the pressure and temperature dependences of the ionic conductivities of TlCl and TlBr have allowed determination of the lattice volume relaxations and energies associated with the formation and motion of Schottky defects in these crystals. The volume relaxations deduced from the conductivity are found to be comparable in magnitude with values calculated from the strain energy model and a dynamical model. The association energy of Tl^+ vacancies and divalent impurities was also determined for TlBr. A particularly important result is the finding that for these CsCl-type crystals the relaxation of the lattice associated with vacancy formation is *outward*. Earlier studies on ionic crystals having the NaCl structure have yielded a similar result. This outward relaxation thus appears to be a general result for ionic crystals of both the NaCl and CsCl types (and possibly other ionic lattice types), in disagreement with earlier theoretical calculations which show that the relaxation should be *inward* for all models of ionic vacancies investigated. The conductivity of TlI was studied in both the (low temperature and pressure) orthorhombic phase as well as in the cubic CsCl-type phase. There is a large electronic contribution to the conductivity in the orthorhombic phase. An interesting result for all three materials is the observation in the cubic phase of a pressure-induced transition from ionic to electronic conduction. This is in qualitative agreement with what is known about the pressure dependences of the electronic structure of these materials.

I. INTRODUCTION

This work deals with the effects of temperature and hydrostatic pressure on the ionic conductivities of the thallous halides (TlCl, TlBr, and TlI). The results on TlCl and TlBr have allowed determination of the lattice volume relaxations and energies associated with the formation and motion of Schottky defects in these crystals. The association energy of Tl^+ vacancies and divalent impurities was also determined for TlBr. These are the first such determinations of these properties from conductivity measurements for the thallous halides, and they are made possible by the large pressure-induced suppression of the intrinsic conductivities of these materials, which results in observation of extrinsic conduction regimes. A particularly important result is the finding that for these CsCl-type crystals the relaxation of the lattice associated with vacancy formation is *outward* (i.e., the formation volume is larger than the molar volume). Earlier studies on ionic crystals having the NaCl structure have yielded a similar result.[1] Both findings are in disagreement with earlier theoretical calculations, which show that the relaxation should be *inward* (i.e., the formation volume is smaller than the molar volume) for all models of ionic vacancies investigated.[2] Another result is the observation of a pressure-induced transition from ionic to electronic conduction in these crystals.

The present work was motivated by a variety of considerations. The thallous halides have low melting temperatures (700–730 K) and relatively high ionic conductivities. They also have relatively large dielectric constants.[3] This is important to ionic transport because the larger the dielectric constant of an ionic crystal, the lower is the energy of formation of lattice defects.[4] Also of interest is the fact that earlier studies have shown the existence in these crystals of weakly soft optic[3,5] and acoustic[6,7] phonons. Physically ionic transport occurs by hopping motion across an energy barrier, and this barrier can be expected to be smaller the "softer," or more anharmonic, the lattice. An additional consideration is that TlCl and TlBr have the cubic CsCl structure, and TlI transforms from an orthorhombic phase (D_{2h}^{17}) to the CsCl structure with increasing temperature and/or pressure.[3,8] There has been relatively little ionic transport work on ionic crystals having this structure compared to the NaCl structure, and, in particular, we are not aware of any earlier pressure studies on CsCl-type crystals. In the study of ionic transport, there is considerable interest in the investigation of the relaxation of ions around defects. The determination of the activation volume for the formation and motion of lattice defects from pressure studies of diffusion and/or ionic conductivity is one of the most direct means for studying this relaxation. For the NaCl structure, all model calculations predict an inward lattice relaxation for vacancies, whereas pressure results yield a relatively large outward relaxation.[1,2]

This disagreement is not understood. It is of much interest to examine the situation for the CsCl structure and other ionic-type lattices. Finally, the pressure dependence of the electronic structures of these crystals is known. Earlier studies have shown that these materials become good electronic conductors at sufficiently high pressure due to a gradual decrease in the band gap with increasing pressure.[9–11] Thus, a pressure-induced transition from ionic to electronic conduction can be expected.

Earlier, diffusion and/or ionic conductivity studies at atmospheric pressure on TlCl[12] and TlBr[13] have led to the following conclusions: (1) The conductivity is strictly ionic at 1 bar. (2) Schottky defects are predominant. (3) Diffusive jumps are predominantly nearest neighbor jumps. [A relatively small amount of excess diffusion ($\leq 10\%$) is present, at least for TlCl,[12] and this can be accounted for by rather modest contributions from either (i) bound jumps into vacancy pairs or (ii) next nearest neighbor jumps into single vacancies.] (4) The mobility of the anion vacancy is much larger than that of the Tl^+ vacancy. For TlCl the ratio of the mobilities of the two ions is 30–100 depending on the temperature.[12] (5) The intrinsic conductivity is high and polyvalent dopants are not sufficiently soluble in both crystals to give separable extrinsic regimes in the conductivity. Thus, there is no information from conductivity data on the formation and motion energies of the individual defects.

Some earlier atmospheric pressure studies have also been reported on the transport processes in TlI.[14,15] A particularly high electronic conductivity is observed in the orthorhombic phase, while in the cubic phase the conductivity is predominantly ionic with both the Tl^+ and I^- ions contributing to the transport process.[14]

The paper is organized as follows. In Sec. II we give a brief account of the experimental details and in Sec. III we recall some theoretical background necessary for the interpretation of the results. Section IV presents the results and their interpretation.

II. EXPERIMENTAL DETAILS

The ac conductivity was measured at frequencies of 10^2–10^4 Hz on samples in the form of thin rectangular plates typically 0.2–0.6 cm^2 in area by 0.06–0.12 cm thick. Electrodes consisting of platinum foil pasted to the large faces of the samples with a thin layer of colloidal graphite (Aquadag) were used. The apparatus and experimental techniques have been described elsewhere.[16]

The TlCl and TlBr samples were cut from several single crystals obtained from the Harshaw Chemical Company (Solon, Ohio, U.S.A.). Measurements were made along one of the cubic axes. The TlI samples were cut from a boule grown at this laboratory by the Bridgman-Stockbarger technique. As grown, the boule was a single crystal having the CsCl structure; however, upon cooling it transformed from this cubic structure to the orthohombic phase resulting in a polycrystalline mass with some preferred orientation.

All three materials were nominally pure. However, semiquantitative chemical analyses revealed a variety of impurities (some up to several 10 ppm) including Li, Al, Ca, Cu, Mg, Si, O, and Te.

III. THEORETICAL BACKGROUND

Before presenting and discussing the results it is helpful to recall some basic considerations. The ionic conductivity σ is given by the expression[16,17]

$$\sigma T = \left(\frac{ANq^2\nu r^2}{k}\right)\exp\left(\frac{\Delta G_f}{2kT}-\frac{\Delta G_m}{kT}\right) \tag{1a}$$

$$= \left(\frac{ANq^2\nu r^2}{k}\right)\exp\left(\frac{\Delta S_f}{2k}+\frac{\Delta S_m}{k}\right)\exp\left(-\frac{\Delta H_f}{2kT}-\frac{\Delta H_m}{kT}\right), \tag{1b}$$

where A is a constant which depends on the lattice type, N is the number of ions (sites) per unit volume, q is the ionic charge, ν is the vibrational (or attempt) frequency of the mobile species in the direction which carries it over the energy barrier, and r is the jump distance. The ΔG's are the Gibbs free energies associated with the formation (f) and motion (m) of the defects; they can be written in terms of the corresponding entropies, ΔS, and enthalpies, ΔH, as shown. Equation (1) is generally written in terms of a pre-exponential σ_0 and an activation energy E, i.e.,

$$\sigma T = \sigma_0 \exp(-E/kT). \tag{2}$$

Comparing Eqs. (1) and (2) we note that in the intrinsic regime E is equal to one-half of the formation energy for the defect (Schottky pairs in the present case) plus the mobility enthalpy (where one mobile species dominates), i.e., $E=\frac{1}{2}\Delta H_f+\Delta H_m$. In the extrinsic regime, on the other hand, E is simply the motional enthalpy of the dominant species, i.e., $E=\Delta H_m$.

The effect of pressure on the conductivity arises from the pressure dependences of ΔG_f, ΔG_m and the quantities N, ν, and r in the pre-exponential in Eq. (1a). It is helpful to define an activation volume ΔV, which may be viewed as the contribution of the defects and mobile species to the volume of the crystal.[18] ΔV is given by the thermodynamic identity

$$\Delta V = \left(\frac{\partial \Delta G}{\partial P}\right)_T . \tag{3}$$

Reference to Eq. (1a) shows that ΔV is given by

$$\Delta V = -kT\left[\left(\frac{\partial \ln\sigma}{\partial P}\right)_T - \left(\frac{\partial \ln N}{\partial P}\right)_T - \left(\frac{\partial \ln\nu}{\partial P}\right)_T - 2\left(\frac{\partial \ln r}{\partial P}\right)_T\right] . \tag{4}$$

This equation can be rewritten in the form[16]

$$\Delta V = kT\left[\left(\frac{\partial \ln R}{\partial P}\right)_T + \left(\frac{\partial \ln\nu}{\partial P}\right)_T\right] , \tag{5}$$

where R is the directly measured sample resistance. The present results and earlier work[1,16] show that in Eqs. (4) and (5) the pressure dependence of σ or R is by far the dominant contribution to ΔV. We note that in the intrinsic regime $\Delta V = \frac{1}{2}\Delta V_f + \Delta V_m$, whereas in the extrinsic regime (where the mobility of one of the species dominates) $\Delta V = \Delta V_m$.

IV. RESULTS AND DISCUSSION

A. Temperature dependence of the conductivity

Figure 1 shows the temperature dependence of the ionic conductivities of TlCl and TlBr at atmospheric pressure ($P = 0$) presented as $\log_{10}\sigma T$ vs T^{-1}. The conduction is intrinsic and sample independent over the wide temperature ranges indicated. The activation energies and pre-exponentials in this regime (stage I) are $E_I = 0.78 \pm 0.01$ eV and $\sigma_{0,I} = 1.75 \times 10^6\ \Omega^{-1}\ \mathrm{cm}^{-1}\mathrm{K}$ for TlCl, and $E_I = 0.785 \pm 0.01$ eV and $\sigma_{0,I} = 9.34 \times 10^5\ \Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{K}$ for TlBr. Our results on E_I are generally in close agreement with earlier results [12,13,19] in this temperature regime. We note that the activation energies for the two crystals are essentially the same, but the conductivity of TlCl is a little higher than that of TlBr. We believe that this is due to the fact that in both cases the anion is the dominant charge carrier in stage I and the Cl^- ion is smaller, less polarizable, and, therefore, more mobile than the Br^- ion.

Figure 2 shows the temperature dependence of the conductives of both phases of TlI at $P = 0$. The data are from several samples cut from the same boule. There is evidence from the present results and from earlier work[14] that there is a large electronic contribution to the conductivity in the low-temperature orthorhombic phase, whereas the conductivity is predominantly ionic in the cubic phase. In the cubic phase two conduction stages are observed. In stage I E_I (0.68 ± 0.03) eV and $\sigma_{0,I} = 2.18 \times 10^5\ \Omega^{-1}\,\mathrm{cm}^{-1}\,\mathrm{K}$. This value of E_I is in close agreement with earlier results, [14,15] and we believe that conduction in stage I is intrinsic. Stage II, with $E_{II} = 0.40 \pm 0.04$ eV and $\sigma_{0,I} \approx 1.5 \times 10^2\ \Omega^{-1}\,\mathrm{cm}^{-1}\,\mathrm{K}$, was observed only on cooling for the samples used. It is interrupted by the onset of the cubic-to-orthorhombic transition, and thus it exists over a rela-

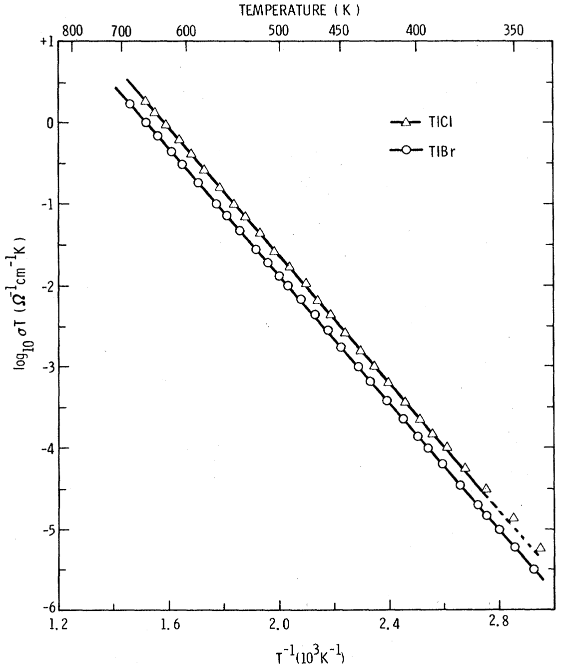

FIG. 1. Temperature dependences of the ionic conductivities of TlCl and TlBr in the intrinsic regime (stage I) at atmospheric pressure.

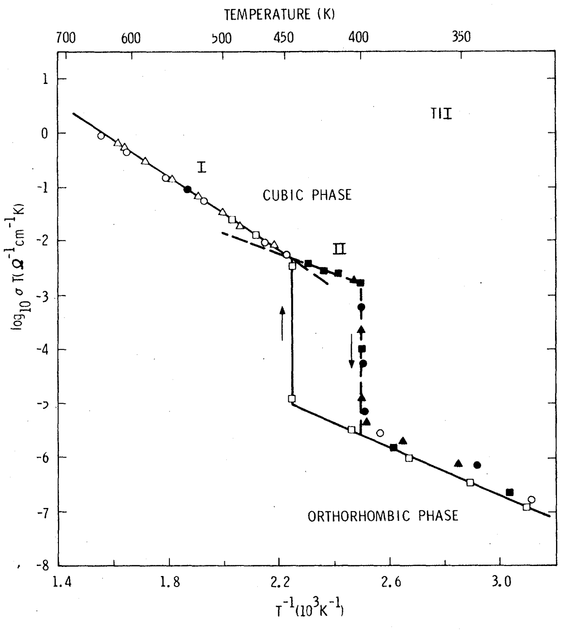

FIG. 2. Temperature dependences of the ionic conductivities of cubic and orthorhombic TlI at atmospheric pressure. Open (filled) symbols represent data taken on increasing (decreasing) temperature.

tivley short temperature range. Apparently it has not been seen before. There is substantial scatter in σ in the orthorhombic phase. This may be in part associated with the anisotropic nature of the conductivity in this phase and the fact that different samples acquire somewhat different crystalographic orientation on cooling from the isotropic cubic phase. In the orthorhombic phase $E \simeq 0.44$ eV (or $\simeq 0.41$ eV based on $\log_{10}\sigma$ vs T^{-1}). The conductivity increases by a factor of ~ 600 at the orthorhombic-to-cubic transition at 444 K. The transition is first order and its temperature decreases with increasing pressure, so that the transition can be induced by increasing pressure.[8] At 300 K the transition occurs at 0.46 GPa.[8]

B. Ionic-to-electronic conductivity transition

At pressures below ~ 0.5 GPa and at temperatures in the range 350–700 K the logarithm of the conductivities of TlCl and TlBr decrease linearly with pressure. Such results will be discussed in Sec. IV C. However, at higher pressures there is a marked change in the response and this is illustrated in Fig. 3, which shows some results at temperatures near 600 K. Specifically, there is a turnaround in the conductivity with pressure. This is a result of a pressure-induced transition from ionic conduction at low pressure to electronic conduction at high pressure. The electronic nature of the conduction at high pressure was confirmed by conductivity versus frequency measurements, by electrode polarization measurements, and by other considerations discussed below. The turnaround occurs sooner for TlBr than for TlCl, in agreement with our expectation on the basis of what is known about the pressure dependence of the electronic structure.[9,10] As will be discussed later, in the ionic regime, σ decreases with pressure as a result of a suppression of both the formation of defects and of their mobility. In the electronic regime, on the other hand, σ increases with pressure as a result of the decrease in the band gap.[9,10]

In TlI the ionic-to-electronic transition occurs at lower pressures and temperatures, as expected.[9–11] This is shown in Fig. 4. First, note that the 323-K and 373-K isotherms show the behavior in the low-pressure orthorhombic phase. A variety of measurements, including the indicated increase of σ with pressure, suggests that there is a large electronic contribution to the conductivity in this phase. This is in agreement with earlier studies of this phase at atmospheric pressure.[14] Figure 4 shows the jump in σ (whose magnitude depends on T) at the transition to the CsCl phase. In this latter phase, conduction is predominantly ionic at low pressure but becomes electronic at high pressure as indicated by the

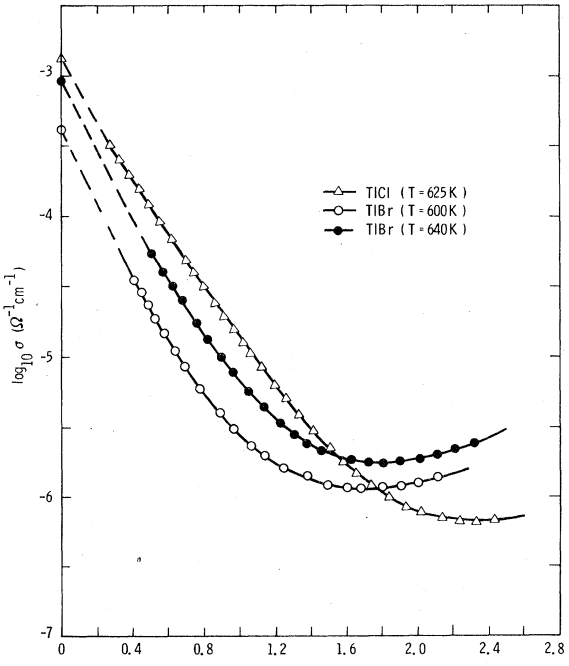

FIG. 3. Pressure dependences of the conductivities of TlCl and TlBr near 600 K showing the change (turnaround) in conductivity with pressure.

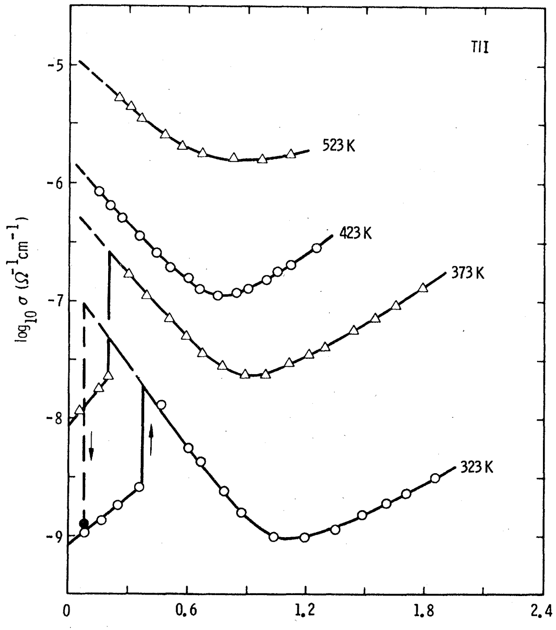

FIG. 4. Pressure dependence of the conductivity of TlI at different temperatures showing the change (turnaround) in conductivity with pressure in the cubic phase. The 323 and 373 K isotherms show the behavior at the orthorhombic-cubic transition at low pressures.

turnaround in σ. As one test of the electronic nature of the conduction at high pressure, we measured the temperature dependence of the conductivity in the high-pressure regime at different pressures. Some results are shown in Fig. 5. For electronic conduction, the conduction should be intrinsic at sufficiently high temperatures, and the activation energy determined from the $\sigma(T)$ data should be equal to one-half of the energy gap E_g. The three data points in the inset in Fig. 5 are values of E_g determined in this manner. The line in the inset represents E_g and its pressure dependence as determined directly from optical absorption edge measurements.[9] It is seen that the present results from conductivity data are in good agreement with the optical data, and this strongly confirms that the aforementioned observed turnaround in the conductivity versus pressure is associated with the transition from ionic to electronic conduction.

C. Pressure dependence of the conductivity

Figure 6 shows $\log_{10}\sigma T$ vs $1/T$ for TlBr at different pressures. There are many features in these data that are noteworthy. At high temperatures the conduction is ionic and intrinsic. There is a large suppression of σ with pressure. This is associated with a large increase in activation energy (see upper right inset), which we believe is largely due to the increase in Schottky-defect formation energy.

The upper left inset is a $\log_{10}\sigma$-versus-pressure plot showing where the $\log_{10}\sigma T$ vs $1/T$ isobars in the lower portion of the figure were taken. Data at the lower pressures are clearly in the ionic regime. However, the highest isobar (2.0 GPa) is clearly in the electronic conduction regime, and it can be seen that the activation energy at this pressure at high temperature is markedly different from those at lower pressures. In fact, $E = 0.4$ eV, as shown by the solid triangle in the upper right inset. This energy is believed to be associated with the ionization of an electronic impurity state within the band gap.[10]

The $\log_{10}\sigma T$ vs $1/T$ isobars in Fig. 6 show interesting features at low temperatures. Note that in the 0.4-GPa isobar there is a second conduction regime (stage II), following which σ again decreases faster with decreasing T (stage III). Stage II is further enhanced at 0.80 and 1.2 GPa (not shown). We believe that stage II is an extrinsic regime which becomes observable at high pressure because of the relatively large suppression of the intrinsic component of the conductivity. Stage II does not extend over a large temperature range, but, nevertheless, we are able to extract fairly accurate activation energies from the data.

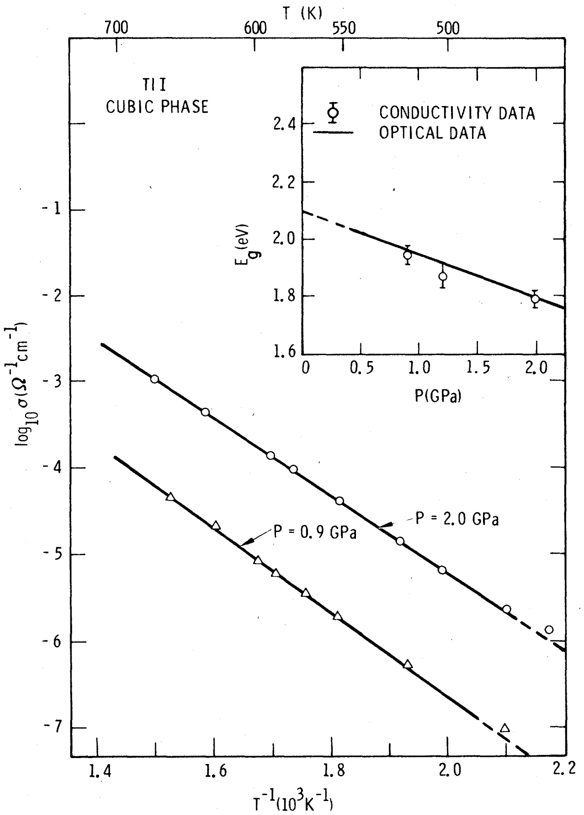

FIG. 5. Temperature dependence of the intrinsic, electronic conductivity of TlI at two high pressures. Inset compares the energy gap versus pressure deduced from the conductivity data with that determined from optical absorption data.

The results at 0.4, 0.8, and 1.2 GPa are shown in the upper right inset. Extrapolation of these $E_{\rm II}(P)$ data back to zero pressure yields $E_{\rm II} = 0.56 \pm 0.05$eV-- a value that compares with a value of ~ 0.5 eV, deduced from diffusion and thermoelectric power measurements for the mobility activation energy ΔH_m^+ of the Tl$^+$ in TlCl.[12,19] We believe that in the present case the 0.56-eV value also corresponds to the mobility activation energy of the Tl$^+$ ion in TlBr. This is consistent with the presence of divalent cation impurities (especially Ca^{++}) in our samples. The alternate choice of 0.56 eV for the mobility activation energy of the Br$^-$ vacancy would lead to an unacceptably low value (0.44 eV) for the formation energy of Schottky defects. Stage II has never been seen before in conductivity data. It is observed only at high pressure and this illustrates the usefulness of pressure as a complementary variable to temperature in the study of ionic transport processes.

Finally, the faster drop in σ with decreasing T in stage III is believed to be due to association

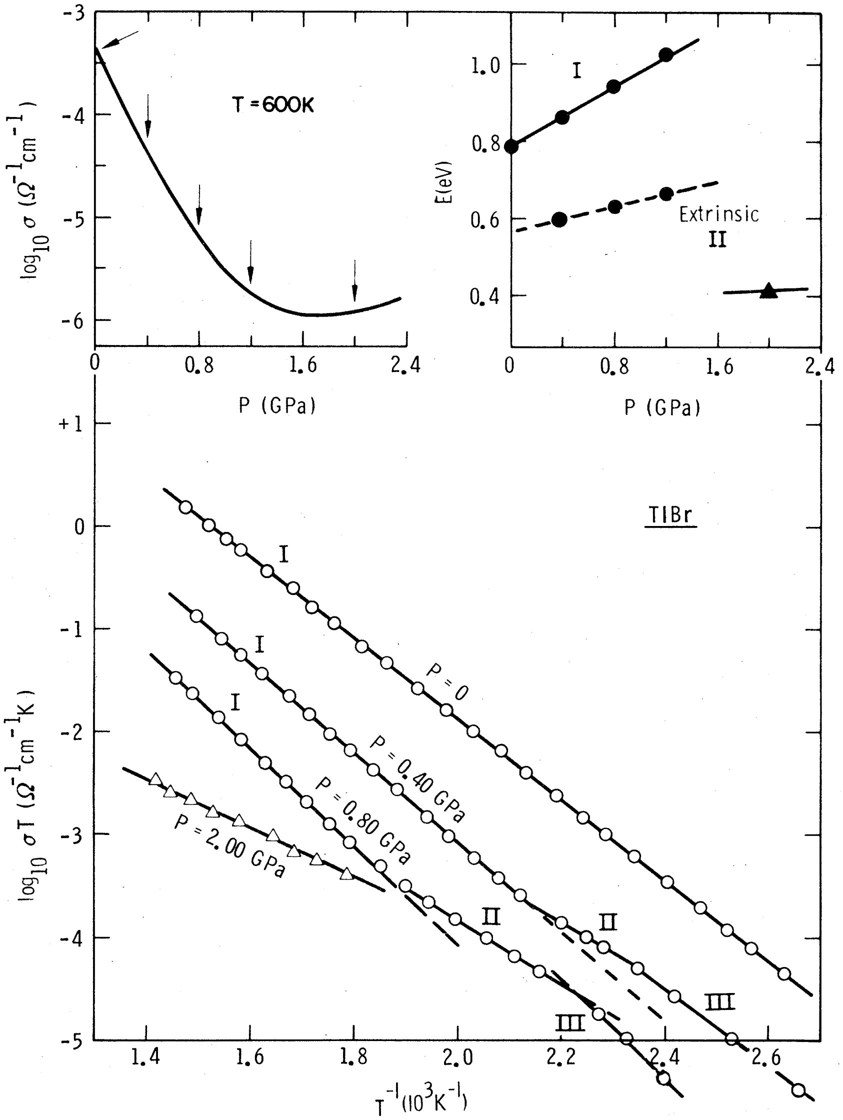

FIG. 6. Temperature dependence of the conductivity of a TlBr sample at different pressures. Also shown in the insets are the pressure dependence of σ at 600 K and of the activation energies in stages I and II. The data point at 2.0 GPa corresponds to electronic conduction.

(or binding) of the Tl^+ vacancies and divalent cation impurities to form neutral bound pairs which do not contribute to σ. On this basis, and from the activation energy is stage III ($E_{III} \simeq 0.74$ eV), we estimate this association energy, ΔH_a, to be $\simeq 0.36$ eV. ($E_{III} = \frac{1}{2}\Delta H_a + \Delta H_m^+ \rightarrow \frac{1}{2}\Delta H_a \approx 0.18$ eV.) To our knowledge, this is the first evaluation of this quantity. This, again, illustrates the usefulness of pressure in such studies.

Qualitatively similar results to the above were obtained on TlCl. Both stages I and II were studied. In one sample of this material a different stage was observed at high pressure. This is illustrated in Fig. 7. Again we note the large suppression of the conductivity with pressure in the intrinsic regime (stage I) and the associated increase in activation energy E_I. The new stage (labeled II′) is seen in the 1.0-GPa isobar and it has an activation energy of $\simeq 0.11$ eV.[20] Earlier atmospheric pressure thermoelectric power measurements,[21] space-charge polarization capacity and conductance measurements,[19] and diffusion measurements[12] have yielded 0.2, 0.09, and 0.104 eV, respectively, for the mobility enthalpy of the Cl^- ion in TlCl. The closeness of the activation energy in stage II′ to the latter two enthalpies suggests that the conductivity in stage II′ in Fig. 7 is dominated by the mobility of the Cl^- ion.

The pressure dependences of the conductivities of TlCl and TlBr in the various ionic conduction regimes are summarized in Fig. 8 as the initial (i.e., low pressure) logarithmic pressure derivatives of σ versus temperature. The results were obtained from both $\sigma(P)$ isotherms and $\sigma(T)$ isobars. In the intrinsic regime, $(\partial\ln\sigma/\partial P)_T$ is large and exhibits substantial temperature dependence, whereas in the extrinsic regimes this quantity is much smaller in magnitude. $\sigma(P)$ measurements on a TlBr sample at 316 K yielded $(\partial\ln\sigma/\partial P)_T = -2.5$ GPa^{-1} as shown. This value is quite different from those seen in stage II; however, its closeness to the value of $(\partial\ln\sigma/\partial P)_T$ of TlCl in stage II$'$ suggests that it may be associated with the same process, namely, the motion of Br$^-$ vacancies. This is speculative at this point (see also Sec. IV E).

A summary of the pressure results for the two phases of TlI is shown in Fig. 9. $(\partial\ln\sigma/\partial P)_T$ is positive for both the orthorhombic phase and for the cubic phase at $P \geq 1.4$ GPa, reflecting the electronic dominance in the conduction process. At lower pressures in the cubic phase, where the conduction is predominantly ionic, $(\partial\ln\sigma/\partial P)_T$ is negative and its temperature dependence is qualitatively similar to that observed for TlCl and TlBr (Fig. 8).

D. Motion and formation energies

Following the discussion of Sec. III, the above values of the activation energies allow determin-

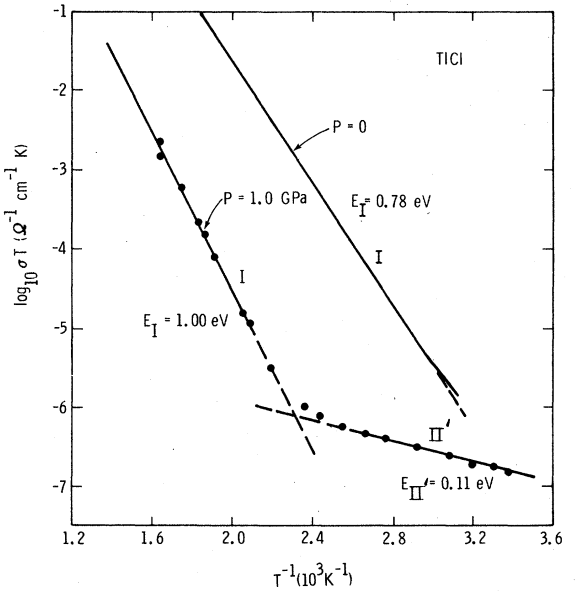

FIG. 7. Temperature dependence of the ionic conductivity of TlCl sample at atmospheric pressure and at 1.0 GPa. Emphasis is on the observation of stage II$'$ at high pressure.

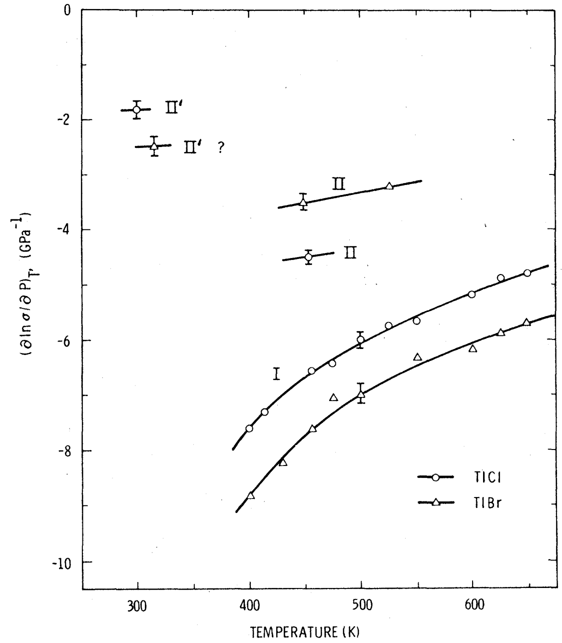

FIG. 8. Variation with temperature of the logarithmic pressure derivatives of the ionic conductivities of TlCl and TlBr in the various conduction stages. Typical error bars are shown.

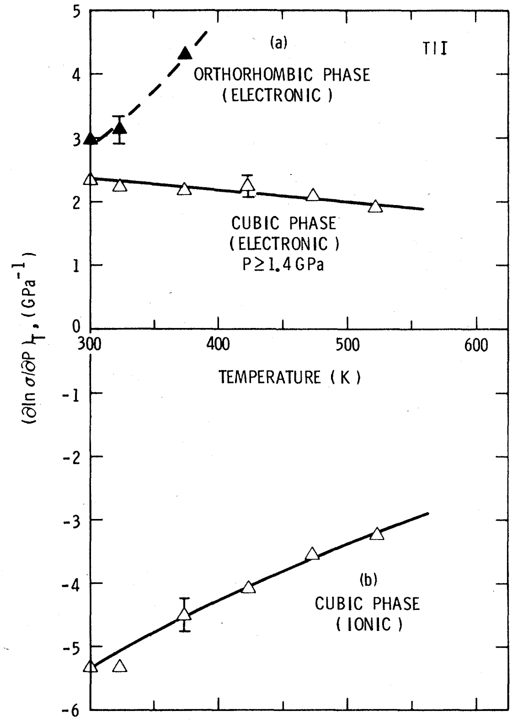

FIG. 9. Variation with temperature of the logarithmic pressure derivative of the conductivity of TlI in (a) the electronic regime and (b) the ionic regime (stage I). Typical error bars are shown.

ations of the motion and formation energies of the Schottky defects in TlCl and TlBr. The data in the ionic regime on cubic TlI did not allow such determinations. In this case, earlier results[14] have indicated that although the principal charge carrier in stage I is the I^- ion, the contribution of the Tl^+ ion is not negligible, being about 30%. This makes it difficult to separate E_I in this regime into its individual contributions. However, in stage II the conduction is extrinsic and $E_{II}=0.4\pm0.04$ eV is, by analogy with TlCl and TlBr (as discussed below), most likely associated with the motion enthalpy of the Tl^+ ion, ΔH_m^+.

Table I summarizes the motion and formation enthalpies for TlCl and TlBr and compares the present results with earlier data where such data are available. In the case of TlCl, our values of ΔH_m^+ and ΔH_m^- were determined directly from the $\sigma(T)$ data, as these quantities represent the activation energies in stages II and II′, respectively. It is seen that our values are comparable to earlier values. The activation energy in stage I ($E_I = 0.78$ eV) combined with $\Delta H_m^- = 0.11$ eV yields $\Delta H_f = 1.34$ eV, which is seen to compare very favorably with earlier results.

The ΔH results on TlBr require additional comments. Here we measured ΔH_m^+ directly from extrapolation of high-pressure data to zero, as ΔH_m^+ is simply E_{II}. The available samples did not allow us to determine ΔH_m^-; however, we evaluated this quantity as follows. In conductivity measurements on TlBr to high temperatures at atmospheric pressure, Hermann[13] observed two intrinsic activated regimes; in the lower-temperature regime the mobility of the Br^- vacancy dominates and $E = \frac{1}{2}\Delta H_f + \Delta H_m^-$, whereas in the higher-temperature regime the mobility of the Tl^+ ion apparently becomes dominant and E should be equal to $\frac{1}{2}\Delta H_f + \Delta H_m^+$. His two activation energies yield $\Delta H_m^+ - \Delta H_m^- = 0.31$ eV, which, when combined with our value of $\Delta H_m^+ = 0.56$, gives the $\Delta H_m^- = 0.25$ eV given in Table I. This ΔH_m^-, combined with our activation energy from $\sigma(T)$ data in stage I ($E_I = 0.785$ eV), finally yields $\Delta H_f = 1.1$ eV. There appear to be no earlier ΔH's for TlBr to compare with the present results in Table I.

Some general observations about the results in Table I should be made. The magnitudes of the ΔH_m's and ΔH_f's for both crystals are remarkably small compared with other ionic crystals (particularly the alkali halides) where Schottky defects are dominant.[22] For example, ΔH_f's for NaCl and CsCl are 2.2 and 2.3 eV, respectively.[22] The anomalously small values of ΔH_f for Schottky defects in TlCl and TlBr are most likely a manifestation of the large static dielectric constants ($\epsilon \simeq 30$, compared with $\epsilon \simeq 5$–6 for the alkali halides) and relatively soft phonons[3,5–7] in these materials. In a dielectric continuum model the formation energy for a vacancy is[4] of the order of $(Ze)^2/2\epsilon R$, where Ze is the defect charge and R is the defect radius. This result should be adequate for slowly varying fields far from the defect but cannot be expected to adequately describe the behavior very near the defect. To do so it is necessary to take into account both the details of the short-range interactions around the defect as well as the continuum energy away from it. In any case, however, the main point for the present consideration is that large ϵ's lead to low formation energies. The relatively low values of the ΔH_m's for both crystals may be a manifestation of the soft and strongly anharmonic nature of their lattices. We shall return to this point later (Sec. IV E). Finally, we note that ΔH_m^- is much smaller than ΔH_m^+ for both crystals and ΔH_m^- for the Cl^- ion is smaller than ΔH_m^- for the Br^- ion. A similar situation will be seen to be true for the motion volumes ΔV_m (as discussed below). These effects are undoubtedly due to the fact that the polarizability of the Tl^+ ion (5.2 A^3) is larger than that of the Br^- ion (4.2 A^3), which, in turn, is larger than that of the Cl^- ion

TABLE I. Values of the motional enthalpies for positive and negative ion vacancies as well as values of the formation enthalpy for Schottky defects in TlBr and TlCl.

	ΔH_m^+ (eV)	ΔH_m^- (eV)	ΔH_f (eV)	Reference
TlBr	0.56 ± 0.02	0.25 ± 0.05 [a]	1.1 ± 0.1	Present work
TlCl	0.54 ± 0.05	0.10 ± 0.02 [b]	1.36 ± 0.05	Present work
	0.4	0.09	1.36	Jackson & Young (Ref. 19)
	0.5	0.20	1.30	Christy & Dobbs (Ref. 21)
	(0.44 or 0.56) [c]	0.104	1.36 [c]	Friauf (Ref. 12)

[a] See text.

[b] This is the atmospheric pressure value estimated from $\Delta H_m^- = 0.11$ eV at 1.0 GPa.

[c] See Ref. 12.

(3.0 A^3).[23] It is known that the polarization energy contributes a positive term to ΔH_m.[4,12]

E. Motion and formation volumes for Schottky defects

1. Results

The activation volumes in the various conduction regimes of TlCl and TlBr were calculated using Eq. (5). In Eq. (5), $(\partial \ln R/\partial P)_T$ is the directly measured quantity and it is simply related to the values of $(\partial \ln \sigma/\partial P)_T$ in Fig. 8 since $\sigma = l/RA$, where l and A are the sample length and cross-sectional area, respectively. Since the linear compressibilities, i.e., $(-\partial \ln l/\partial P)_T$, of TlCl and TlBr are $\approx 1.5 \times 10^{-2}$/GPa,[3] reference to the magnitudes of $(\partial \ln \sigma/\partial P)_T$ in Fig. 8 shows that to a very good approximation $(\partial \ln R/\partial P)_T \simeq -(\partial \ln \sigma/\partial P)_T$. We make use of this approximation throughout the paper.

The pressure dependence of the attempt frequency $(\partial \ln \nu/\partial P)_T$ in Eq. (5) can be estimated in a number of ways. The pressure dependences of the elastic constants of TlCl and TlBr have been reported.[24,25] The results yield values of the various mode Grüneisen parameter γ_i ranging from ~0.5 to 3.3 at 300 K.[24] γ_i is given by

$$\gamma_i = -\left(\frac{\partial \ln \nu_i}{\partial \ln V}\right)_T = \frac{1}{\kappa}\left(\frac{\partial \ln \nu_i}{\partial P}\right)_T, \qquad (6)$$

where $\kappa = -(\partial \ln V/\partial P)_T$ is the volume compressibility. The elastic data also yield κ.

One can also calculate a macroscopic Grüneisen parameter γ given by

$$\gamma = \frac{\alpha}{\kappa}\left(\frac{V_m}{C_m}\right), \qquad (7)$$

where α, κ, V_m, and C_m are the volume thermal expansivity, compressibility, molar volume, and molar specific heat, respectively. Available values of the various parameters yield $\gamma \simeq 2.4$ at 300 K for both TlCl and TlBr,[25,26] a value nearly typical of macroscopic γ's for most ionic crystals. This γ decreases by ~25% between 300 and 700 K.[25]

The above γ's are characteristic of the acoustic phonons. However, optic phonons may be more relevant in ionic transport since the ionic displacements associated with such modes can be expected to move charge carriers towards saddle points. Information about the pressure dependences of the various optic-phonon branches in both TlCl and TlBr is available. The pressure dependences of the long-wavelength ($q = 0$) transverse-optic (TO) modes have been measured directly[5] and the Grüneisen parameters for all of the optic branches of TlBr have been calculated as a function of wave vector.[6] These combined results allow us to estimate that the optic-mode γ_i's fall in the range 1.5–4.3.

Although there is question as to how the attempt frequency ν in Eqs. (1) and (5) relates to particular vibrational modes (see also Sec. IV E 3), it seems reasonable that the above γ's and κ's put a bound on the quantity $(\partial \ln \nu/\partial P)_T$ in Eq. (5) and therby allow a good estimate of the contribution of this term to the activation volume in Eq. (5). Generally we find that this contribution is less than the experimental uncertainty in the term $(\partial \ln R/\partial P)_T$. The estimated ranges of the $(\partial \ln \nu/\partial P)_T$'s and the results in Fig. 8 lead to the results in Fig. 10, where the width of the shaded bands of ΔV values represents the estimated uncertainties in $(\partial \ln R/\partial P)_T$ and the ranges of values of $(\partial \ln \nu/\partial P)_T$. We note that the ΔV's are only weakly temperature dependent.

In the intrinsic regime the calculated ΔV in Fig. 10 represents $\frac{1}{2}\Delta V_f + \Delta V_m^-$, whereas in the extrinisic regimes ΔV represents the elastic volume relaxation associated with the motion of the individual species. As was true of the ΔH's, for TlCl the results yield both ΔV_m^+ and ΔV_m^- as shown. In the case of TlBr, the results yield ΔV_m^+, but, as noted earlier, it is questionable whether or not the one measured value of $(\partial \ln \sigma/\partial P)_T$ at 316K, and therefore the associated ΔV_m, does indeed represent the motion of the Br$^-$ ion vacancy. In

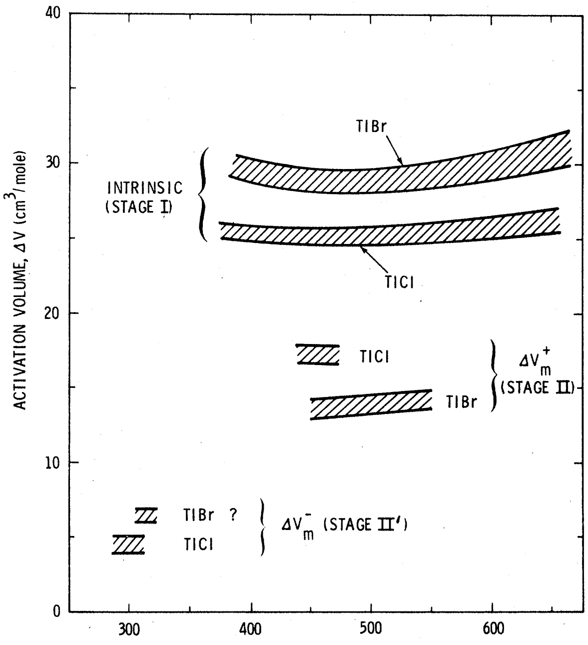

FIG. 10. Temperature dependence of the activation volumes of TlCl and TlBr in various conduction stages. The widths of the shaded bands represent the ranges of estimated uncertainties in the two logarithmic pressure derivatives in Eq. (5).

the absence of direct confirmation of this we can get an independent estimate of ΔV for this process. Flynn[4] has presented a dynamical theory of diffusion which leads to the prediction that

$$\Delta V_m^- / \Delta V_m^+ = \Delta G_m^- / \Delta G_m^+ . \qquad (8)$$

The known values of ΔV_m^+ and the $\Delta G_m^\pm$'s for TlBr lead to the conclusion that $\Delta V_m^- = 5.8-6.7$ cm^3/mole. This is in remarkably close agreement with the range of ΔV_m^- estimated from the measured $(\partial \ln \sigma / \partial P)_T$ at 316 K (see Fig. 10).

Table II summarizes the ΔV's for cation and anion motion as well as for the formation of Schottky defects in TlCl and TlBr. We note that despite the fact that the Tl$^+$ ion is smaller than the Cl$^-$ and Br$^-$ ions (ionic radii are 1.49, 1.81, and 1.97 Å, respectively, the volume relaxation associated with the motion of the Tl$^+$ ion is much larger than those associated with the motions of Cl$^-$ and Br$^-$ ions as is true of the ΔH_m's in Table I. Again this is undoubtedly due to the large ionic polarizability of the Tl$^+$ ion. In the energetics of the problem, the contribution of the polarization-energy term favors the motion of ions with small polarizability.[4,12]

One of the most important features of the results in Table II is the large value of the formation volume (ΔV_f) for Schottky defects in these crystals.[27] This value is ~ 15–20% larger than the molar volume V_M for both TlBr and TlCl, respectively. One can very readily confirm that this conclusion is not materially affected by any realistic uncertainties in the estimated value of ΔV_m^- for TlBr discussed above. We have recently found a similar result for CsCl,[28] where $\Delta V_f / V_M \approx 1.8-2.0$. Thus for the three crystals TlCl, TlBr, and CsCl, which have the CsCl structure, the relaxation of the lattice associated with vacancy formation is *outward* as is true of alkali halides having the NaCl structure.[1,2] For the NaCl structure, all earlier model calculations that have been done[2] predict an inward lattice relaxation for vacancies in qualitative disagreement with the conclusion deduced from the pressure results. The model calculations indicate that the inward relaxation is a general consequence of all models of ionic vacancies and is a manisfestation of the long range of the Coulomb field of the vacancy acting on the ions of the lattice coupled with the also slow decrease in induced moments with distance.[2] Thus the discrepancy between theory and experiment obtains for both the NaCl and CsCl structures and possibly for other ionic structure types. This is quite fundamental in that it relates to our understanding of the nature of forces in ionic crystals, and it deserves serious attention.[29] Faux and Lidiard[2] have raised the possibility that anharmonic lattice effects may be responsible for the discrepancy; specifically, the models calculate ΔV_f in the harmonic approximation, whereas experimentally ΔV_f is deduced from high-temperature data, where anharmonic effects may be important. However, as discussed elsewhere,[27] there is a variety of considerations which rule out this explanation.

Finally, it should be emphasized that Eq. (1), and thereby Eqs. (4) and (5), are based on the absolute rate theory.[18] Implicit in this theory is the assumption that the diffusive process can be described in terms of equilibrium statistical mechanics. Although there has been some criticism of this theory, it nevertheless has been very successful in treating diffusion and ionic conduction, and this success is generally taken as the strongest evidence for its validity.[17,18,22]

2. Strain energy model

It is of interest to compare the above values of ΔV with what can be calculated from a strain energy model of lattice imperfections. In this simple model[18] it is assumed that the work required to create or move a lattice defect goes into elastically straining the lattice and can be treated using ordinary elastic theory. Using this model it can be shown that[18]

$$\Delta V = \left[\left(\frac{\partial \ln C}{\partial P} \right)_T - \kappa \right] \Delta G , \qquad (9)$$

TABLE II. Values for the motional and formation volumes of Schottky defects in TlBr and TlCl. The ratios of the formation volumes to the molar volumes at 500 K are also given. All ΔV's are in units (cm^3/mole).

	Method	ΔV_m^+	ΔV_m^-	ΔV_f	$\Delta V_f / V_M$
TlBr	$\sigma(P)$ data	14.0 ± 1.0	6.3 ± 0.7	45.4 ± 3.0	1.17 ± 0.07
	Strain energy model	18.0	8.0	35.0	
	Dynamic model	(10.5–17.0)	(4.6–7.5)		
TlCl	$\sigma(P)$ data	17.0 ± 1.0	4.5 ± 0.08	41.6 ± 3.0	1.19 ± 0.07
	Strain energy model	15.3	3.1	38.0	
	Dynamic model	(9.0–14.6)	(1.9–3.0)		

where C is an effective shear modulus. For cubic crystal a suitable choice of C is[1]

$$C = \tfrac{3}{5}C_{44} + \tfrac{1}{5}(C_{11} - C_{12}). \tag{10}$$

Making use of some thermodynamic relations, Eq. (9) can be rewitten as[16]

$$\Delta V = \frac{[(\partial \ln C/\partial P)_T - \kappa]\Delta H}{1 + [(1/\kappa)(\partial \ln C/\partial P)_T - 1]\alpha T}, \tag{11}$$

where $\alpha \equiv (\partial \ln V/\partial T)_P$ is the volume expansivity. Known values[24–26] of the various quantities in Eq. (11) allow us to calculate the ΔV's in Table II. It is seen that these values are in reasonably close agreement with those deduced from the $\sigma(P)$ data. This agreement can be regarded as quite satisfactory in view of the simplicity of the model and the approximation[18] leading to Eq. (9). This suggests that the strain energy model provides a fair approximate description of the physics involved in the formation and motion of defects in TlCl and TlBr.

It has been customary, in the absence of direct data on $(\partial \ln C/\partial P)_T$, to resort to the Grüneisen approximation $(\partial \ln C/\partial \ln V)_T \approx -(2\gamma + \frac{1}{3})$ to estimate this quantity. Here γ is the macroscopic Grüneisen parameter which has values of 2.3 and 2.4 for TlBr and TlCl, respectively.[26] Using this approximation in Eq. (11) yields ΔV's which are ~40% smaller than those in Table II. Thus, use of the directly measured pressure dependence of C results in closer agreement with experimentally deduced ΔV's. A similar finding has been noted earlier for NaCl-type alkali halides.[1]

3. *Dynamical model*

The strain energy model is a static model. In principle, a more realistic view of the motion of lattice defects should reflect the dynamical nature of the problem. The dynamical approach treats the atomic displacements causing diffusion as a superposition of phonons. Phonons (especially short-wavelength TO phonons in ionic crystals) should be effective in moving mobile species towards saddle points. A diffusive jump occurs when the normally random phases of the displacement of the phonons coincide. Detailed dynamical theories of diffusion are quite complicated, but several approximate treatments have been given.[4] Following Flynn[4] we can write

$$\Delta V_m = \left(\frac{\partial \ln \nu_i^2}{\partial P}\right)_T \Delta G_m \tag{12a}$$

$$= 2\gamma_i \kappa \Delta G_m, \tag{12b}$$

where ν_i is the frequency of the appropriate phonon mode and γ_i is this mode's Grüneisen parameter [Eq. (6)]. Making use of some thermodynamic relations, Eq. (12b) can be rewritten as[16]

$$\Delta V_m = \frac{2\gamma_i \kappa \Delta H_m}{1 + 2\gamma_i \alpha T}. \tag{13}$$

All quantities on the right-hand side of Eq. (13), except γ_i, are accurately known.

In this model the value of ΔV_m calculated from Eq. (13) depends on the choice of the appropriate mode and γ_i. Optic-mode γ_i's have been measured directly for only the long-wavelength TO phonon and the values are 4.3 and 4.0 for TlBr and TlCl, respectively.[5] Cowley and Okazaki[6] calculated all of the mode γ_i's for TlBr using a shell model. Their γ_i's show considerable dispersion across the Brillouin zone and range from 2 to 5 for the transverse-optic (TO) modes. It is these TO modes which should be effective in moving mobile species toward saddle points. Assuming comparable γ_i's are valid for TlCl, this range of γ_i's leads to the range of ΔV_m's shown in Table II. These ΔV_m's range from 0.25 to 1.2 times those deduced from the $\sigma(P)$ data. Intuitively, we would expect that short-wavelength TO modes should be most effective in moving ions toward saddle points; however, the calculated γ_i's for these modes are in the range 2–3 and they are responsible for the low end of the range of the calculated ΔV_m's in Table II.

An interesting feature of the results in Table II is that the experimentally determined values of the γ_i's for the long-wavelength TO phonons in both crystals yield $\Delta V_m^+ = 17.0$ (14.6) cm^3/mole and $\Delta V_m^- = 7.5$ (3.0) cm^3/mole for TlBr (TlCl), respectively, and these values are in rather close agreement with those deduced from the $\sigma(p)$ data. The interesting point is that this TO mode is the soft optic mode of the system, which suggests a possible relationship between soft phonons and ionic transport. In this soft mode, the ionic displacements correspond to the vibration of the Tl$^+$ ions against the negative halogen ions. Reference to the CsCl crystal structure indicates that near-neighbor diffusive jumps in this lattice can be affected by the degree of anharmonicity (or softness) of this mode.

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