

HIGH PRESSURE STUDIES OF IONIC CONDUCTIVITY IN SOLIDS

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ABSTRACT

The pressure dependence of the ionic conductivity provides information about the volume relaxation associated with the formation of lattice defects as well as with the diffusive motion of these defects, and thereby helps elucidate the conduction process. Pressure results on a variety of crystals will be discussed with emphasis on recent results on crystals with large lattice polarizabilities and soft phonon modes. Pressure is shown to be an important--sometimes essential, variable in the study of ionic transport processes.

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INTRODUCTION

There has been a great deal of renewed interest in the past few years in the study of ionic charge transport in solids. This interest derives not only from the need to develop advanced solid state batteries, but also from the challenging physics involved. Ionic charge transport, and more generally ionic diffusion in solids, results from the existence and motion of crystalline defects. These defects can be either extrinsic or intrinsic.

Ionic conductivity and diffusion have been studied extensively at atmospheric pressure in a variety ionic crystals, and in many cases the mechanisms for the transport processes in terms of point defects have been established [1]. There have been some studies of the effects of hydrostatic pressure on ionic conductivity. Most of these studies have been on NaCl and the silver halides. In the earlier as well as in our present work pressure is found to be a complementary variable to temperature in trying to understand the mechanisms of ionic conduction. In some cases, as we shall see later, pressure turns out to be an essential variable. In ionic conductivity and other defect-dominated properties in general, it is important to know the elastic volume relaxation associated with the formation of lattice defects and the lattice relaxation accompanying the diffusive motion of these defects. Measurements of the hydrostatic pressure dependence of the ionic conductivity give direct information about these volume relaxations, and this information can in turn be used to better understand the mechanisms of ionic transport and to test the validity of proposed models.

The limited space available to us here does not allow a detailed treatment of the field. Consequently we shall comment only briefly on earlier work and devote the bulk of the paper to our recent results on the thallous halides and PbF₂. These materials are especially interesting because, among other properties, they possess large dielectric constants and also exhibit soft, relatively low-lying

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phonon modes. These factors are important in relation to ionic conduction because the larger the dielectric constant of an ionic crystal, the lower the energy of formation of lattice defects. Also, physically, ionic transport occurs by hopping motion across an energy barrier, and this barrier can be expected to become smaller the "softer," or more anharmonic, the lattice. Before going into the results, it is useful to review some well-known theoretical concepts and results necessary for the analysis and interpretation of experimental results.

THEORETICAL BACKGROUND

The simplest, and, for our present consideration, the most important lattice imperfections are vacancies and interstitials. A lattice vacancy is known as a Schottky defect. It is formed in a perfect crystal by transferring an atom from a lattice site in the interior to a site on the surface of the crystal. Another type of lattice defect is the Frenkel defect whereby an atom is transferred from a lattice site to an interstitial position, a normally unoccupied lattice position. In addition to the equilibrium concentration of defects present at any given temperature, controlled concentrations of vacancies and interstitials can often be introduced by doping an ionic crystal with aliovalent impurities.

The production of Schottky defects lowers the density of the crystal because the volume is increased without an increase in mass. The production of Frenkel defects, on the other hand, does not, to first order, change the volume of the crystal, and thus the density remains nearly unchanged. On this basis pressure can be expected to cause a relatively large suppression of the formation of Schottky defects. We shall show evidence for this later.

The conductivity σ in the intrinsic regime where one mobile species dominates can be written as [1]:

$$\begin{aligned} \sigma T &= \left(\frac{ANq^2 \nu r^2}{k} \right) \exp \left(- \frac{\Delta G_f}{2kT} - \frac{\Delta G_m}{kT} \right) \\ &= \left(\frac{ANq^2 \nu r^2}{k} \right) \exp \left(\frac{\Delta S_f}{2k} + \frac{\Delta S_m}{k} \right) \exp \left(- \frac{\Delta H_f}{2kT} - \frac{\Delta H_m}{kT} \right) \quad (1) \end{aligned}$$

where A is a geometrical factor, N is the number of ions per unit volume, ν is an attempt frequency, r is the jump distance, and ΔG , ΔS and ΔH are the Gibbs free energy, entropy and enthalpy associated with the formation (f) and motion (m) of lattice defects.

In dealing with experimental data Eq. (1) is more commonly written as

$$\sigma T = \sigma_0 \exp(-E/k_B T) \quad , \quad (2)$$

where it is seen that the measured activation energy E is $\frac{1}{2} \Delta H_f + \Delta H_m$.

In the extrinsic regime where the change in carrier concentration with T is negligible, the measured activation energy is simply associated with the motion of the mobile species (assuming the mobility of this species dominates), and $E = \Delta H_m$.

The pressure dependence of σ arises from the pressure dependences of ΔG_f and ΔG_m as well as from the change in the pre-exponential factors N, ν and \bar{r} .

It is instructive in the study of ionic transport to define an activation volume, ΔV , associated with defect formation or the motion of mobile species. In the absolute reaction-rate theory this quantity, which represents the

contribution of the defect or the mobile species to the volume of the crystal, is defined via the familiar expression $\Delta V = (\partial \Delta G / \partial P)_T$. Reference to Eq. (1) shows that ΔV is related to the pressure dependence of the conductivity by

$$\Delta V = -kT \left[\left(\frac{\partial \ln \sigma}{\partial P} \right)_T - \left(\frac{\partial \ln N}{\partial P} \right)_T - \left(\frac{\partial \ln v}{\partial P} \right)_T - 2 \left(\frac{\partial \ln r}{\partial P} \right)_T \right] \quad (3)$$

Generally, to a very good approximation, and within the accuracy of $\sigma(P)$ data, $\Delta V \approx -kT(\partial \ln \sigma / \partial P)_T$, so that the measured pressure dependence of σ gives a direct measure of ΔV [2-4]. This approximation can be seriously in error in the super-ionic regime [5], however.

In the intrinsic regime the deduced ΔV is $(\Delta V_m + \frac{1}{2}\Delta V_f)$, where ΔV_m and ΔV_f are the motional and formation activation volumes, respectively. In the extrinsic regime, on the other hand, ΔV is simply ΔV_m , in cases where the mobility of one mobile species dominates.

It has been common to compare experimentally deduced values of ΔV with values calculated from a strain-energy model of lattice imperfections [6]. In this rather simple continuum model 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 [6]

$$\Delta V / \Delta G = -\kappa + (\partial \ln C / \partial P)_T = -\kappa [1 + (\partial \ln C / \partial \ln v)_T] \quad (4)$$

where C is an effective elastic shear modulus and $\kappa \equiv -(\partial \ln v / \partial P)_T$ is the isothermal compressibility. For a cubic crystal a suitable choice of C is $C = \frac{3}{5} C_{44} + \frac{1}{5}(C_{11} - C_{12})$ [6]. $(\partial \ln C / \partial P)_T$ can be evaluated from the pressure dependences of the C_{ij} 's, where such data are available. In the absence of such data $(\partial \ln C / \partial \ln v)_T$ can be estimated using the Grüneisen approximation leading to the result [6]

$$\Delta V = 2(\gamma - \frac{1}{3})\kappa \Delta G \quad (5)$$

where γ is the elastic Grüneisen parameter.

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. In one dynamical approach the parameters which determine diffusive motion are defined in terms of the normal coordinates of the crystal. The atomic displacements causing diffusion are treated as a superposition of phonons. Phonons (especially short wavelength transverse optic modes in ionic crystals) should be effective in moving mobile species towards saddle points. A diffusive jump occurs when the normally random phases of the displacements of the phonons coincide. Detailed dynamical theories of diffusion are quite complicated, but several approximate treatments have been given [7,8]. In the context of these treatments it can be shown that the activation volume for diffusive motion is related to the pressure dependence of the relevant phonon frequency ν_1 by [8]

$$\Delta V_m = (\partial \ln \nu_1^2 / \partial P)_T \Delta G_m = 2\gamma_1 \kappa \Delta G_m \quad (6)$$

RESULTS AND DISCUSSION

Earlier Work

Table I summarizes some of the earlier as well as our present results on the pressure dependence of the ionic conductivity of a number of materials expressed in terms of the motional and formation activation volumes. Reference to earlier

work is restricted to the most studied and/or understood cases and to the most recent results. We now comment briefly on the entries in Table I.

TABLE I Summary of the activation volumes associated with the motion (ΔV_m) and formation (ΔV_f) of the indicated lattice defects in a variety of ionic crystals. Also given is the ratio of ΔV_f to the molar volume V_M .

Material	Crystal Structure	Dominant Disorder	Mobile Species	ΔV_m (cm^3/mole)	ΔV_f (cm^3/mole)	$\Delta V_f/V_M$	Ref.
NaCl	NaCl	Schottky	Na^+ Vac.	7	55	1.9	3
KCl	NaCl	Schottky	K^+ Vac.	8	61	1.5	3
NaBr	NaCl	Schottky	Na^+ Vac.	8	44	1.2	3
KBr	NaCl	Schottky	K^+ Vac.	11	54	1.1	3
AgCl	NaCl	Frenkel	Ag_+^+ Inter. Ag_+^- Vac.	3.3 4.7	16.7		11 11
AgBr	NaCl	Frenkel	Ag_+^+ Inter. Ag_+^- Vac.	2.6 7.4	16.0		12 12
α -AgI	bcc	Superionic	Ag_+^+	0.6-0.8			5
α -RbAg ₄ I ₅	cubic	Superionic	Ag	- 0.4			5
β -RbAg ₄ I ₅	rhomb.	Superionic	Ag^+	- 0.2			5
TlCl	CsCl	Schottky	Cl_-^- Vac. Tl Vac.	4.5 15.9	41.0	1.16	22 22
TlBr	CsCl	Schottky	Br_-^- Vac. Tl Vac.	6.5 13.5	44.4	1.14	22 22
β -PbF ₂	CaF ₂	Frenkel	F_-^- Vac. F_-^- Inter.	1.9 3.5	4	0.13	
α -PbF ₂	Ortho.	Frenkel	F_-^- Vac. F_-^- Inter.	3.5 3.2	7	0.25	

NaCl has been by far the most widely studied solid ionic conductor at high pressure. The work is primarily due to Lazarus and coworkers [2,3,9] who also investigated the isomorphous crystals NaBr, KCl, KBr and RbCl. Schottky defects are dominant in these crystals with charge transport primarily by cation vacancies. The ΔV_m 's in Table I agree quite well (generally smaller by < 30%) with predictions ΔV_m of the strain-energy model when experimentally-determined values of $(\partial \ln C / \partial P)_T$ are used in Eq. (4); however, the dynamical model [see Eq. (6)] yields values of ΔV_m which are ~ 3-4 times larger than the experimental ΔV_m 's (for KCl and KBr for ΔV_m which $\partial \ln v / \partial P$ for only the long wavelength TO mode is known). An important result of this work is the finding that the Schottky defect formation volumes are substantially larger than the molar volumes, especially for NaCl and KCl. This result is in disagreement with model calculations which predict an inward relaxation (i.e. $\Delta V_f/V_M < 1.0$) of the lattice upon vacancy formation [10]. We shall come back to a discussion of this point.

In AgCl and AgBr Frenkel disorder in the cation sublattice is the dominant lattice defect. Charge transport occurs by the motion of both Ag^+ vacancies and interstitials. The effect of hydrostatic pressure on the ionic conductivities of

AgCl and AgBr have been investigated by Abey and Tomizuka [11] and by Kurnick [12], respectively. The results yield the activation volumes for Ag⁺ vacancy and Ag⁺ interstitial motion as well as the formation for Ag⁺ Frenkel defects. It is seen from Table I that the ΔV 's for Ag⁺ interstitial motion are considerably smaller than the corresponding values for Ag⁺ vacancy motion. The ΔV_f 's for Ag⁺ Frenkel pairs are much smaller than the molar volumes, as is expected for Frenkel disorder. The strain-energy model yields values of ΔV_m and ΔV_f which are of the correct magnitude but generally 30-60% smaller than the experimental values.

α -AgI and α - and β -RbAg₄I₅ are grouped together in Table I because in these phases these materials are superionic conductors having $\sigma \approx 1-10 \Omega^{-1} \text{cm}^{-1}$. Conduction in the so-called superionic regime is characterized by very large scale disorder in the mobile ion sublattice, and the magnitude σ implies that in each case essentially all of the mobile ions must contribute to the conductivity. For such widespread disorder to occur the mobile species must be able to diffuse from one site to another without any appreciable perturbation of neighboring ions. This requires that the lattice structure be open and usually that there be more than one site per ion so that the mobile ion always has an empty site next to it making diffusion easy--conditions that are met in the AgI and RbAg₄I₅ lattices. The activation volumes for these phases are very small (Table I) as are the activation energies (0.1-0.2 eV). The magnitudes of these properties are not as present understood in terms of specific models, but qualitatively they reflect the nature of the superionic state, i.e. large disorder and the presence of a large number of unoccupied sites. The negative sign of ΔV (i.e. increase in σ with pressure) for both α - and β -RbAg₄I₅ is not understood, although possible explanations have been advanced [5].

Finally, an important ionic conductor not listed in Table I is sodium β -alumina (Na₂O·11 Al₂O₃). This crystal is the prototype of a group of alkali metal β -aluminas having a layered hexagonal crystal structure. The structure consists of close-packed oxygen layers which are perpendicular to the hexagonal c-axis and held apart by Al-O-Al bridges. Ionic transport in these materials results from the two-dimensional diffusion of the alkali metal ions between the layers. The effects of pressure on σ of Na⁺ β -alumina and its Li⁺ and K⁺ substituted analogs were investigated by Rdzilowski and Kummer [13]. The results show that σ decreases (increases) with pressure for the K⁺ (Li⁺) compound but is independent of pressure (up to 0.4 GPa) for the Na⁺ compound. The corresponding activation volumes are positive, 0 and negative for the K⁺ Na⁺ and Li⁺ β -aluminas. This is consistent with expectations based on detailed knowledge of the structure [13]. The Na⁺ ion size is such that Na⁺ moves from site to site without serious steric hindrance, whereas the motion of K⁺, which is larger, requires lattice expansion. In the case of Li⁺, the negative ΔV is believed to be due to the notion that in its motion from site to site the small Li⁺ moves some distance out of its potential well toward the midplane of the channel causing a local contraction of the lattice [13].

The Thallous Halides

In the present work we investigated the effects of temperature and hydrostatic pressure on the ionic conductivities of the thallous halides TlCl and TlBr. The work was motivated by a variety of considerations. These crystals have low melting temperatures (700-730 K) and relatively high ionic conductivities. They also have relatively large dielectric constants [14] and weakly soft optic [14,15] and acoustic [16] phonons. They crystallize in CsCl structure. There has been relatively little ionic transport work on 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. There is considerable interest in the investigation of the relaxation of ions around defects. The determination of the activation volume is one of the most direct means for studying this relaxation. For the NaCl structure all model calculations predict an inward lattice relaxation (i.e. a volume contraction) for vacancies, whereas pressure results yield a relatively large outward relaxation (i.e., volume expansion) [10]. This disagreement is not understood. It is of much interest to examine the situation for the CsCl structure. Finally, earlier studies have shown that these materials become good electronic conductors at sufficiently high pressure due to a gradual decrease in the bandgap with increasing pressure [17-19]. Thus a pressure-induced transition from ionic to electronic conduction can be expected.

Earlier diffusion and/or ionic conductivity studies at 1 bar on TlCl [20] and TlBr [21] 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 near neighbor jumps. (4) The mobility of the anion vacancy is much larger than the Tl^+ vacancy, and (5) the intrinsic conductivity is high and polyvalent dopants are insufficiently soluble in both crystals to give a separable extrinsic regime. Thus there is no information from conductivity data on the formation and motion energies of the individual defects.

Space limitations do not allow us to go into any details here and we restrict the presentation to some of the important results. A more detailed account will be published elsewhere [22].

At low pressures and over a wide temperature range (325-700 K) $\log \sigma$ decreases linearly with pressure. Figure 1 shows the pressure dependence of $\log \sigma$ for TlCl and TlBr around 600K. The purpose of this figure is not to emphasize the linear low pressure response, but rather to draw attention to the turnaround in the conductivity at higher pressures. This turnaround is a result of a pressure-induced transition from ionic conduction at low pressure to electronic conduction at high pressure. The turnaround occurs at lower pressures for TlBr (and even lower still for TlI [22]) than for TlCl as is expected from the known pressure dependence of the electronic structure [17-19]. In the ionic regime σ decreases with increasing pressure as a result of the suppression of both the formation of defects and of their mobility (see below). In the electronic regime, on the other hand, σ increases with increasing pressure as a result of the decrease in the bandgap [18].

Figure 2 shows isobars of $\log \sigma T$ vs. $1/T$ for TlBr. There are many features in these data that are noteworthy. At high T 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 $\log \sigma$ vs. pressure plot showing where the $\log \sigma T$ vs. $1/T$ isobars in the lower portion of the graph 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 (≈ 0.4 eV) at this pressure at high T is markedly different than those at lower pressures. This energy is believed to be associated with the ionization of an impurity state within the bandgap [18]. Measurements of σ vs. T on TlI [22] (which has a smaller bandgap than TlCl and TlBr) at pressures beyond the turnaround in σ vs. P yielded values of the bandgap and its pressure derivative that are in excellent agreement with optical data. This provides evidence that the conduction is electronic in this high pressure regime.

The log σ vs. $1/T$ isobars in Fig. 2 show interesting features at low temperatures. Note that in the 0.4 GPa isobar there is a second conduction stage (II) following which σ again decreases faster with decreasing T (stage III). Stage II is further enhanced at 0.80 GPa 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. The results at 0.4, 0.8 and 1.2 GPa are shown in the upper right inset. Extrapolation of these $E_{II}(P)$ data back to zero pressure yields $E_{II} = 0.56 \pm 0.05$ eV--a value that compares with a value of ~ 0.5 eV deduced from diffusion and thermoelectric power measurements for the mobility activation energy of the Tl^+ in $TlCl$ [20]. 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 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. Regime II has never been seen before in the conductivity data. It is observed only at high pressure.

Finally, the faster drop in σ with decreasing T in stage III is believed to be due to association 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 in stage III ($E_{III} = 0.74$ eV) we estimate this association energy to be ~ 0.35 eV. To our knowledge this is the first evaluation of this quantity. This again illustrates the usefulness of pressure as a complementary variable to temperature in studying ionic transport processes.

Qualitatively similar results to the above were obtained on $TlCl$. Furthermore, measurements on different samples with different trace impurities have allowed a determination of both the cation and anion motional enthalpies (ΔH_m^+ and ΔH_m^-) as well as the formation enthalpies (ΔH_f) for Schottky pairs in both crystals. The results in eV for $TlCl$ ($TlBr$) are $\Delta H_m^+ = 0.60$ (0.56), $\Delta H_m^- = 0.10$ (0.25), and $\Delta H_f = 1.36$ (1.1). The $TlCl$ results are in generally good agreement with ΔH values determined from diffusion and thermoelectric power measurements [20]. Apparently there are no earlier data on $TlBr$ to compare the present results with. As noted earlier, it is not possible to obtain these results from σ data at 1 bar because of the absence of extrinsic regimes in $\sigma(T)$.

Table I shows the activation volumes for cation and anion motion and for the formation of Schottky pairs in $TlBr$ and $TlCl$. These ΔV 's were evaluated from $\sigma(P)$ data via Eq. (3). We note that the motional volumes for the Tl^+ ion are considerably larger than those for the Br^- and Cl^- ions as is true of the motional enthalpies. This is most likely due to the large polarizability of the Tl^+ ion. One of the most important features of the results in Table I is the large value of the formation volume, ΔV_f , for Schottky defects. This value is $\sim 15\%$ larger than the molar volume, V_M , for both $TlBr$ and $TlCl$. Thus for these crystals, which have the $CsCl$ structure, the relaxation of the lattice associated with vacancy formation is outward as is true of ionic crystals having the $NaCl$ structure [3,10]. As noted earlier, detailed model calculations on the $NaCl$ structure [10] yield inward (or negative) volume relaxation, 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 manifestation 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 [10]. Thus the discrepancy between theory and experiment extends to $TlCl$ and $TlBr$ and most

likely to other crystals having the CsCl structure. This discrepancy is quite fundamental in that it relates to our understanding of the nature of forces in ionic solids, and it deserves attention.

Use of the known elastic properties of TlBr and TlCl in the strain-energy model yields ΔV_m 's in reasonably good agreement with those deduced from $\sigma(P)$ data [22]. In terms of the dynamical model the value of ΔV_m calculated from Eq. (6) depends on the choice of the appropriate mode and γ_1 . Optic mode γ_1 's have been measured directly for only the long wavelength TO phonon and the values are 4.0 and 4.4 for TlBr and TlCl, respectively [15]. Cowley and Okazaki [23] calculated all of the mode γ_1 's for TlBr using a shell model. Their γ_1 's show considerable dispersion across the Brillouin zone and range from ~ 1.5 -5 for the optic modes. Assuming comparable γ_1 's are valid for TlCl, this range of γ_1 's leads to a range of ΔV_m 's which are generally smaller than those deduced from the $\sigma(P)$ data. An interesting feature of these results is that the experimentally determined values of the γ_1 's for the long wavelength TO phonon in both crystals yield ΔV_m 's which are in very 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-- thus the possible connection between soft phonons and ionic transport. This mode appears to have the correct symmetry to move ions across saddle points.

Lead Fluoride

Lead fluoride, PbF_2 , can exist at normal conditions in either the cubic fluorite structure ($Fm\bar{3}m$, often referred to as the β -phase) or in an orthorhombic structure ($Fmnb$, often referred to as the α phase). The α phase has $\sim 10\%$ higher density than the β phase, and it transforms to the latter phase at ~ 610 K at atmospheric pressure [4]. The β phase, on the other hand, transforms to the α modification at high pressure, the transition pressure being ~ 0.4 GPa at 300 K [4]. Both phases exhibit relatively high ionic conductivity, and the β phase becomes a "superionic" conductor at high temperature where its conductivity attains at ≥ 800 K what appears to be one of the highest values for any known solid ionic conductor [4].

Much of the current interest in PbF_2 has centered around its high ionic conductivity. Like most ionic crystals having the fluorite structure, PbF_2 is known to be a fluorine ion conductor and Frenkel defects are the dominant defects [4]. We have performed a detailed investigation of the effects of temperature and hydrostatic pressure on the conductivity in both phases with some emphasis on the behavior near the phase transitions. Details will appear elsewhere [4]. The work was motivated in part by the large dielectric constants and the soft, low lying phonon modes of the crystal [4]. As a function of temperature, the conductivity of each phase exhibits a number of activated stages as shown in Fig. 3. Measurements on a variety of samples with different impurities along with earlier published data have allowed a determination of the conduction mechanisms in the various stages as well as the mobility and formation energies and volumes for each process [4]. Briefly, the conduction processes in the various stages are as follows: (a) β - PbF_2 . In stage I conduction is extrinsic, the mobile charge carrier being a F ion vacancy (V_F^+) or interstitial (F_i^-) depending on the dopant. In stage II conduction is intrinsic by F ion vacancies. In stage III conduction is intrinsic by F ion interstitials, and in stage IV the F ion sublattice exhibits liquid-like character, the F ions being disordered and in continuous motion and thus accounting for the very high conductivity. This is the phenomenon referred to as sublattice melting. (b) α - PbF_2 . In stage II conduction is extrinsic by either F ion vacancies or interstitials depending on the dopant, and in stage III conduction is intrinsic by F ion vacancies.

An important result of the work is that the formation and mobility enthalpies of β - PbF_2 (0.94 eV and ≤ 0.52 eV, respectively) are considerably (\lesssim a factor of 2) smaller than those observed for other fluorites, such as CaF_2 , SrF_2 and BaF_2 [4]. We believe that the smaller values of these enthalpies in the case of PbF_2 are to be expected and are a manifestation of the large static dielectric constant, ϵ (≈ 30 compared with $\epsilon \approx 7$ for the alkaline earth fluorides), and the soft phonons in this material. In a dielectric continuum model [8] the formation energy for a vacancy is $\propto Ze^2/2\epsilon R$, where Ze is the defect charge and R is the defect radius. This expression 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 important point for our present consideration is that large ϵ 's can be expected to lead to low formation energies. The TO mode in PbF_2 causes opposite displacements of the F and Pb sublattices and can be expected to be quite efficient in moving ions towards saddle points. The fact that this mode is relatively soft and the lattice strongly anharmonic provides a tempting explanation for the relatively small mobility enthalpies for F vacancies and interstitials in PbF_2 .

Table I summarizes the calculated ΔV 's based on Eq. (3). Several features of these results should be noted. The ΔV_f 's are quite small in both phases consistent with Frenkel defects as the dominant disorder in these crystals. ΔV_f for β - PbF_2 is considerably smaller than that for α - PbF_2 , and this can be understood on the basis of the more open structure of the cubic β phase [4]. The ΔV_m 's are small for both phases. A hard sphere model suggests that $\Delta V_m \approx$ the volume of the diffusing species for vacancy and interstitial motion. In the present case the ΔV_m 's are \ll the molar volume of the F ion. The relatively small ΔV_m 's reflect partly the fact that real ions are not hard spheres and more importantly the relatively open and highly anharmonic (and soft) nature of the lattice vibrations of the PbF_2 lattices. In β - PbF_2 ΔV_m associated with F vacancy motion is about one-half that associated with F interstitial motion whereas in the α phase these two ΔV_m 's are more nearly equal. All of these features can be qualitatively understood from consideration of the details of the two crystal structures [4].

The strain-energy model, based on the use of macroscopic Grüneisen parameters, yields ΔV 's which are ~ 10 -60% smaller than those deduced from $\sigma(P)$ data [4]. This agreement can be viewed as satisfactory considering the approximations and assumptions in the model and parameters used. In terms of the dynamical model, the only known optic mode γ known is that associated with the long wavelength TO mode. Use of this mode γ in Eq. (6) yields ΔV_m 's in remarkably close agreement with the experimental ΔV_m 's [4]. Although this agreement may be somewhat fortuitous, it is interesting to note that this mode is the soft mode of the system [24].

CONCLUDING REMARKS

In this paper we have given a brief overview of the effects of pressure on the ionic conductivities of a variety of crystals. This overview was presented largely in terms of the activation volumes associated with the formation and motion of lattice defects as these are properties that are uniquely determined from pressure experiments. One of the most important results of the present work is the finding that for the thallose halides, which have the CsCl structure, the formation volume for Schottky defects is larger than the molar volume (i.e., there is an outward lattice relaxation upon vacancy formation) as is true of alkali halides having the NaCl structure. Very recently

we found a similar result for CsCl. All of these results are in disagreement with detailed model calculations which yield inward volume relaxation. This discrepancy deserves attention in that it relates in a fundamental manner to our understanding of the nature of forces in ionic solids.

Pressure studies can also provide a better understanding of the nature of the energy barriers associated with ionic transport and are, in addition, important to the understanding of the phase transitions observed in many ionic conductors. Space limitations precluded the treatment of these aspects in this paper.

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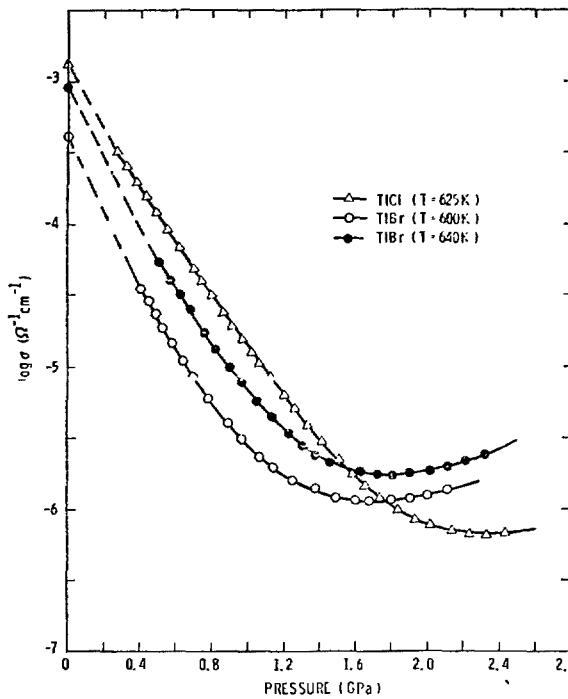


Fig. 1

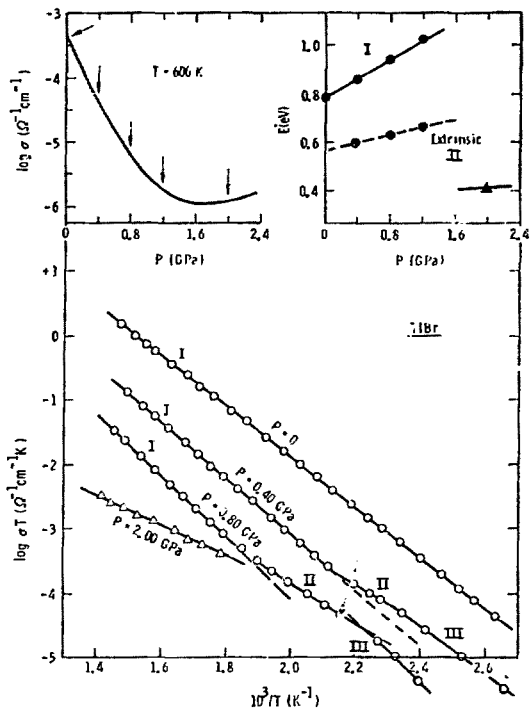


Fig. 2

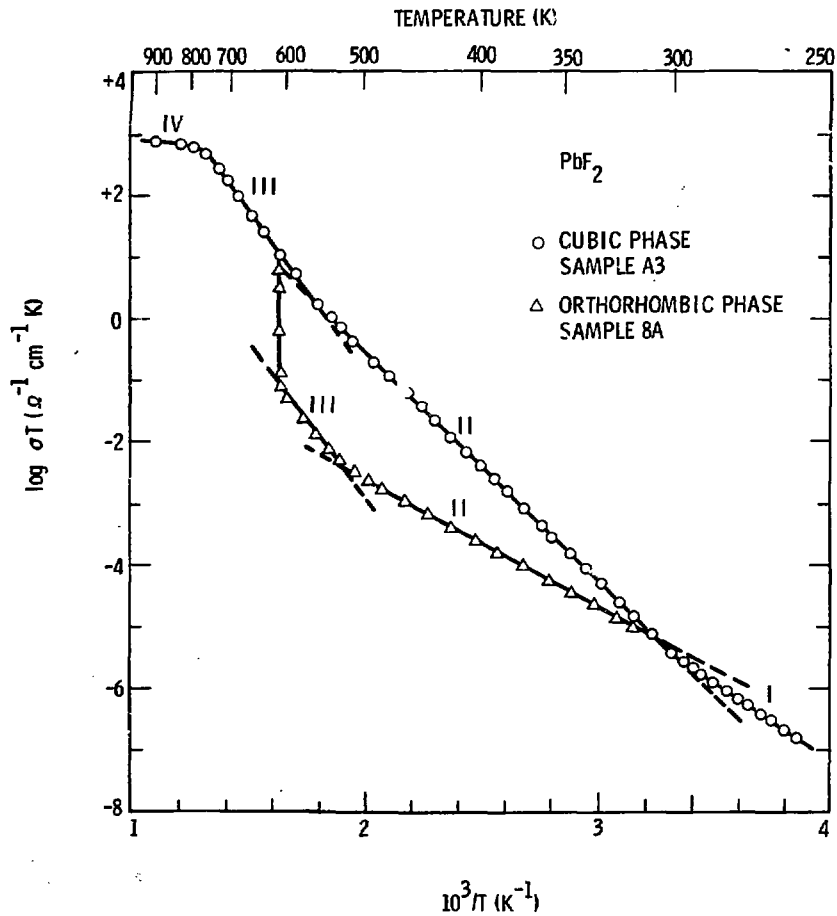


Fig. 3