Ionic conductivity and activation volumes in the lead halides PbCl$_2$, PbBr$_2$, and PbI$_2$

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The effect of hydrostatic pressure on the ionic conductivities of PbCl$_2$, PbBr$_2$, and PbI$_2$ has been investigated. Activation volumes for vacancy motion in PbCl$_2$ and PbBr$_2$ are found to be 4.7 and 4.4 cm^3/mole, respectively. Defect-formation volumes are found to be large in PbCl$_2$ and PbBr$_2$, and consistent with the dominance of Schottky defects in those materials. The activation volumes for PbI$_2$ are all found to be small and consistent with the dominance of Frenkel defects in both the low-pressure layered hexagonal phase and in the high-pressure phase. Transition temperatures and pressures are given for the high-pressure phase transition in PbI$_2$ and are found to agree with values reported elsewhere.

I. INTRODUCTION

The present work on the lead halides was undertaken to compare the conduction mechanisms of these materials with the mechanisms in the fluorite-structured materials, which we have already reported.[1,2] As in the earlier studies, the effect of hydrostatic pressure on the ionic conductivity was examined.

The ionic conductivity can be written as

$$\sigma = \frac{ne^2}{kT}\alpha \nu a^2 \exp\left(-\frac{\Delta G_m}{kT}\right) , \qquad (1)$$

where n is the density of charge carriers (defects), e is their charge, k is Boltzmann's constant, T is the absolute temperature, α is a geometrical factor of order unity, ν is the attempt frequency of the ion to hop over the Gibb's-free-energy barrier ΔG_m, and a is the jump distance. The validity of the Nernst-Einstein relation and of the reaction-rate theory of diffusion is presumed in writing Eq. (1). At low temperature n is nearly constant, with its magnitude determined by the density of aliovalent impurities. In this region Eq. (1) describes extrinsic conduction. At higher temperatures n is given by[3]

$$n = (N_a N')^{1/2}\exp[-\Delta G_f(F)/2kT] , \qquad (2)$$

where N_a is the density of anion lattice sites, N' is the density of anion interstitial sites, and $\Delta G_f(F)$ is the Gibb's free energy of formation of a Frenkel defect. The dominance of Frenkel defects is presumed in the derivation of Eq. (2). If Schottky defects are presumed to dominate then it is not difficult to show that

$$n = N_c \exp[-\Delta G_f(S)/3kT] , \qquad (3)$$

where N_c is the density of cation lattice sites and

$\Delta G_f(S)$ is the Gibb's free energy of formation of a Schottky defect.

Substitution of Eq. (2) into Eq. (1) and using the relation $\Delta G = \Delta H - T\Delta S$ yields

$$\sigma = \frac{\sigma_0}{T}\exp\left(-\frac{\frac{1}{2}\Delta H_f + \Delta H_m}{kT}\right) , \qquad (4)$$

where

$$\sigma_0 = \frac{(N_a N')^{1/2}e^2\alpha \nu a^2}{k}\exp\left(\frac{\frac{1}{2}\Delta S_f + \Delta S_m}{k}\right) . \qquad (5)$$

Equation (4) describes the conductivity in the intrinsic region where defects are both formed and moved and there is a single mobile charged defect species. If Eq. (3) were substituted into Eq. (1), then the 2 in the exponentials in Eqs. (4) and (5) becomes a 3 and the factor $(N_a N')^{1/2}$ is replaced by N_c. In the case where more than one species is mobile, the right-hand side of Eq. (4) should be replaced by a sum of such terms with the relevant exponents and prefactors.

The pressure dependence of the conductivity is contained in the enthalpy: $\Delta H = \Delta E + P\Delta V$. By using the definition $dG = V\,dP - S\,dT$,

$$\Delta V = (\partial \Delta G/\partial P)_T . \qquad (6)$$

From Eq. (4), then,

$$\frac{1}{2}\Delta V_f + \Delta V_m = -kT\left[\left(\frac{\partial \ln\sigma}{\partial P}\right)_T - 2\left(\frac{\partial \ln a}{\partial P}\right)_T - \left(\frac{\partial \ln\nu}{\partial P}\right)_T\right.$$
$$\left. -1/2\left(\frac{\partial \ln NN'}{\partial P}\right)_T\right] , \qquad (7)$$

where ΔV_f is the Frenkel-defect formation volume

and ΔV_m is the activation volume of motion for the mobile species (vacancy or interstitial). This can be simplified to[4]

$$\frac{1}{2}\Delta V_f + \Delta V_m = kT\left[\left(\frac{\partial \ln R}{\partial P}\right)_T + \gamma K_T\right] , \qquad (8)$$

where R is the sample resistance, γ is the Grüneisen parameter for the phonon mode relevant to the diffusion, and K_T is the isothermal compressibility of the material. If Schottky defects are presumed to dominate then the 2 in Eq. (8) is replaced by 3. The second term on the right side of Eq. (8) is generally on the order of 10% or less of the first term.

While Eq. (8) was derived for the intrinsic region of the conductivity, the same equation holds for the extrinsic region, except that the left side of Eq. (8) would just contain the motion parameter, ΔV_m. In the case of more than one mobile charged species, the resulting equations would include similar terms for each of the charge carriers.

An order-of-magnitude estimate of the formation volume of a Schottky defect can be made by imagining the removal of one doubly charged cation and two singly charged anions from the crystal interior and placing them on the crystal surface. In first approximation, this would increase the crystal volume by one molecular volume. If the crystal relaxes about the vacancies, then the relaxation should be outward since charged atoms have been removed to the surface. Thus the formation volume of a Schottky defect would be expected to be on the order of magnitude of the molar volume of the crystal or larger. This expectation is confirmed in the alkali halides.[5]

The estimation of the formation volume of anion Frenkel defects can be done similarly. An anion taken from the crystal interior and placed on the surface increases the volume by one atomic volume. The removal of an anion from the crystal surface and placed in an interstitial position forms the Frenkel defect and decreases the crystal volume by one atomic volume. The net result (to first order) is a formation volume of zero. If the relaxation of the lattice is considered about the vacancy and interstitial, then the formation volume is still expected to be small compared to the molar volume, and it may be negative. The interpretation of data is then fairly clear: small formation volumes indicate Frenkel defects and large formation volumes, comparable to the molar volume or larger, indicate Schottky defects.

The interpretation of the motion volume, ΔV_m, is more obscure. The motion volume is normally interpreted as a lattice dilatation associated with a diffusional jump in the reaction-rate model of diffusion,[6,7] or as the pressure derivative of appropriate normal modes in the dynamical diffusion model.[8]

II. EXPERIMENTAL

The samples used in the atmospheric-pressure measurements were single crystals. All of the crystals were kindly provided by J. Schoonman. Typical aliovalent impurities in the $PbCl_2$ were (in ppm) Si,100; Al,30; Ta,10; Fe,110; Ti,30; and S,10. Impurities in the $PbBr_2$ were (in ppm) Si,300; Al,40; Se,30; Ta,20; Na,10; Cr,20; Fe,20; and Tl,10. Since the samples did not cleave readily, they were broken into usable sizes, and two sides were sanded roughly parallel on fine-grit carborundum paper. Typical sample lengths varied from about 1 to 3 mm with cross sections around 3.5 by 3.5 mm.

The electrodes were platinum buttons with a layer of graphite painted on them for the actual contact with the sample. These electrodes gave reproducible results on thermal cycling and were found to yield frequency-independent resistances for frequencies in the range of 1 to 10 kHz. The resistances were measured with a Hewlett-Packard model 4262A digital LCR meter and control unit as described earlier.[1,2] The atmospheric-pressure data were taken at preset time intervals while the samples were being heated or cooled. For heating rates from 0.05 to 6 K/min, no effect of the rate could be seen. The high-pressure system used for determination of activation volumes was the same as described earlier.[1,2]

III. RESULTS AND DISCUSSION

A. High-pressure phase transition in PbI_2

A high-pressure phase transition was observed in PbI_2 by the change in sample resistance across the transition. This is a rather unusual transition in two respects. First, the resistance of the sample in the high-pressure phase was lower at high temperature than the resistance in the low-pressure phase; second, the entropy change across the transition is apparently near zero. The transition temperatures and pressures are shown in Fig. 1. The data show a slight hysteresis in the transition, but generally the transition seems to be essentially independent of temperature with a critical pressure of about 0.39 GPa. Using the Clausius-Clapeyron equation,

$$\frac{dP_c}{dT_c} = \frac{\Delta S_c}{\Delta V_c} , \qquad (9)$$

where ΔS_c is the entropy change across the transition and ΔV_c is the volume change, results in $\Delta S_c \approx 0$, since $dP_c/dT_c \approx 0$.

The observation of this transition has apparently been reported twice previously. The first report was by Bridgman[9] who measured a transition pressure of about 0.4 GPa at room temperature. He also noted another transition at higher pressure. A more recent
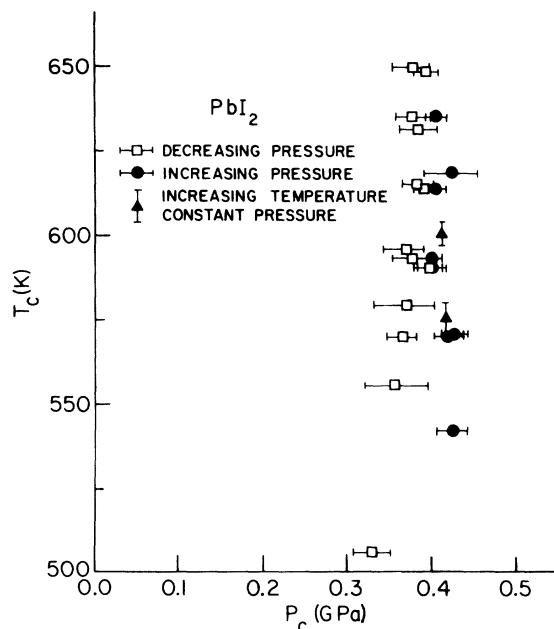
FIG. 1. Transition temperatures and pressures for the high-pressure phase transition in PbI_2.

FIG. 2. Temperature dependence of the conductivity of $PbCl_2$.

study[10] showed results similar to the present work, but indicated a slightly higher-transition pressure of ~ 0.5 GPa. In that work they also observed the higher-pressure transition at about 1.5 GPa at 625 K. Both of these authors noted a very small temperature dependence of the 0.4-GPa transition.

The crystal structures of the high-pressure phases of PbI_2 are apparently unknown, but the low-pressure phase is described as layered hexagonal,[11] with a ratio $c/a = 1.51 (c/a = 1.63$ represents close packing).

B. Ionic conductivity

The temperature dependence of the conductivity of $PbCl_2$ is shown in Fig. 2. The data exhibit two activated regions, labeled I and II, as well as anomalous rise at about 765 K. This rise in the conductivity was recently observed by other authors,[12] who attribute the effect to a "diffuse" transition similar to those observed in the fluorites. It may actually be a first-order phase transition to the less dense cubic (fluorite) structure, since the size of the increase is similar to that observed in PbF_2 and $SrCl_2$.[1] The possibility that it is due to melting of the crystal seems possible, but unlikely, since the effect occurs at about 10 K below the reported melting point.[13] The narrow temperature range between the melting point and this 765-K transition does not allow the region to be studied easily.

The dominant defects in $PbCl_2$ are believed to be Schottky type, i.e., one cation vacancy and two anion vacancies.[12,14-17] The anion vacancies are apparently
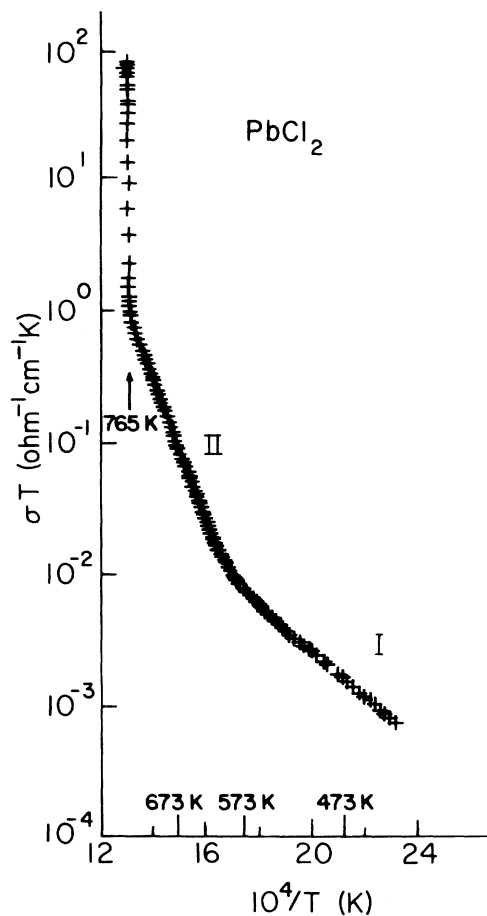
the only mobile defects.[14-16,18,19] The identification of Schottky-defect domination comes from doping experiments[14-17] which indicate that only anion vacancies are mobile. This is consistent with the notion that the available interstitial sites are too small to accommodate chlorine ions. Figure 3 shows the orthorhombic crystal structure of $PbBr_2$ (and $PbCl_2$). Barsis and Taylor,[20] however, pointed out that the results of the doping experiments of Simkovich[15] could equally well be interpreted as dominance of anion Frenkel defects, with the anion interstitial being immobile. We shall see in Sec. III C that the high-pressure data tend to support the hypothesis of Schottky-defect domination. Transport-number measurements[18] indicate that the anion transport number increases from 0.90 to 0.96 in the temperature range 470–590 K. The cation transport number accounts for the remainder of the conductivity. The fact that at least some cation transport occurs also suggests the presence of Schottky defects.

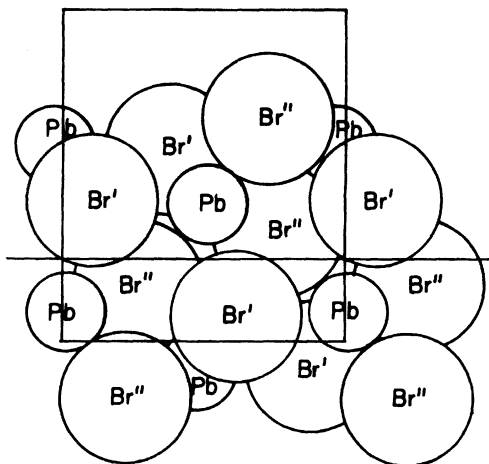The data shown in Fig. 4 for $PbBr_2$ are useful as an example of the differences that can be obtained by

FIG. 3. Orthorhombic crystal structure of $PbCl_2$ and $PbBr_2$. Taken from Ref. 21.

fitting $\ln \sigma T$ vs $1/T$ to a series of straight lines, rather than by fitting σT to a sum of exponentials. In the case of the data shown in Fig. 4, the data could be fitted easily to the sum of two exponentials for both the increasing temperature data and the decreasing temperature data. The activation energies used in the
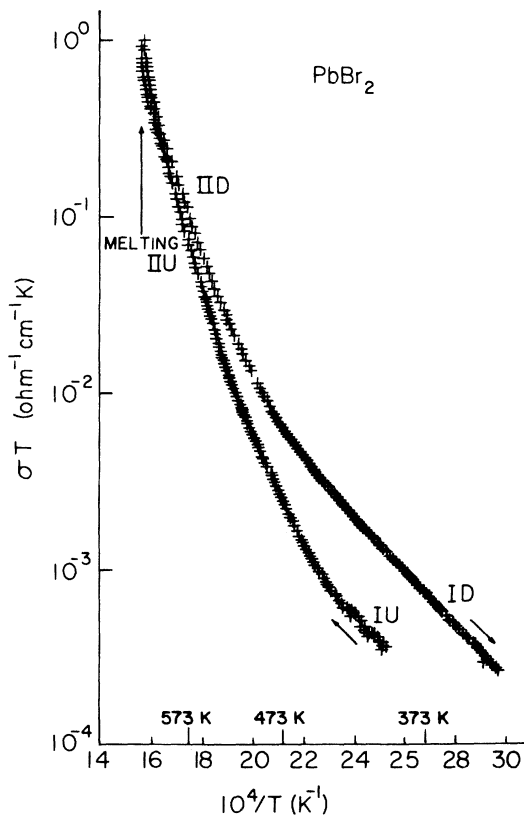

FIG. 4. Temperature dependence of the conductivity of $PbBr_2$ for both increasing and decreasing temperature.

exponents were the same on both increasing and decreasing temperature; only the prefactors needed to be altered to take account of the contamination that occurred when the sample melted. The values obtained for the activation energies and prefactors are given in Table I. If those same data were fitted to two straight lines for both increasing and decreasing temperatures, then activation energies of 0.26 and 0.30 eV were obtained for regions IU and ID, and activation energies of 1.0 and 0.88 eV were obtained for regions IIU and IID. It is clear that correct values can be obtained by fitting straight lines, but only if care is taken and the data are sufficiently accurate and consistent.

The extrinsic activation energy 0.30 ± 0.02 eV given in Table I for $PbBr_2$ is consistent with values obtained elsewhere for the energy of motion of vacancies.[17,22–24] The value 1.00 ± 0.03 eV obtained for the intrinsic region (II) is somewhat higher than previously published values.[22,24–26] It is worth noting that all of the conductivity measurements on $PbCl_2$, $PbBr_2$, and PbI_2 were made parallel to the c axis. This fact is apparently not important in $PbCl_2$ and $PbBr_2$ because the activation energy of motion is found to be essentially independent of the crystal orientation.[15] The dominant defects in $PbBr_2$ are believed to be Schottky type, for basically the same reasons as for $PbCl_2$ (Ref. 22): insufficient space for the anion interstitial, if Frenkel defects were to be present. The formation energy of a Schottky defect in $PbBr_2$ is then $3(1.00 - 0.30) = 2.10 \pm 0.08$ eV.

The temperature dependence of the conductivity of two unused samples of PbI_2 is shown in Fig. 5. The sharply inclined set of data (indicated by $+$) represents the conductivity of the high-pressure phase, while the other points represent the conductivity of the low-pressure phase. The two curves actually cross at about 605 K, as can be seen in Fig. 6 where data for a single sample are shown. The data for the high-pressure phase shown in Fig. 6 were taken during the first heat-up of that sample; then the pressure was released and the data for the low-pressure phase were taken both during heat-up and cool-down. These data indicate the effect of contamination in the low-pressure phase.

The data for the high-pressure phase exhibit at least two activated regions, labeled II and III. It is presumed that region II is intrinsic and an unobserved extrinsic region I exists at lower temperatures. The data in region II were fitted to a single exponential and exhibit an activation enthalpy of about 2.2 ± 0.2 eV and an unusually high-exponential prefactor of about 10^{15} ohm^{-1} cm^{-1} K. The data in region III appear to exhibit a lower activation enthalpy than found for region II, but the data do not extend over a sufficiently wide temperature range to be meaningful.

The data for the low-pressure phase of PbI_2 are more complex. Beginning with the uncontaminated

TABLE I. Activation energies and prefactors for anion motion in $PbCl_2$, $PbBr_2$, and PbI_2.

Region	Identification[a]	ΔE (eV)	Prefactor $(ohm^{-1}cm^{-1}K)$	Technique[b]	Ref.
$PbCl_2$					
I	extrinsic vac.	0.30 ± 0.01		cond.	12
II	intrinsic vac.	0.80 ± 0.05			
I	ext. vac.	0.20 ± 0.03		cond.	14
II	int. vac.	0.71 ± 0.06			
I	ext. vac.	0.38 ± 0.02		diffusion	16
II	int. vac.	0.79 ± 0.03			
I	ext. vac.	0.33 ± 0.02		cond.	16
II	int. vac.	0.78 ± 0.01			
I	ext. vac.	0.30 ± 0.02		cond.	17
II	int. vac.	0.55 ± 0.04			
I	ext. vac.	0.35 ± 0.02		cond.	22
I	ext. vac.	0.35 ± 0.02		dielectric relaxation	
I	ext. vac.	0.32 ± 0.02	1.7	cond.	Present
II	int. vac.	1.12 ± 0.04	1.57×10^7		work
$PbBr_2$					
I	ext. vac.	0.25 ± 0.01		cond.	22
I	ext. vac.	0.05 ± 0.02		dielectric relaxation	
I	ext. vac.	0.29 ± 0.04		cond.	23
II	int. vac.	0.77 ± 0.05			
I	ext. vac.	0.25 ± 0.01			25
II	intr. vac.	0.77 ± 0.04	1.69×10^5		
I	ext. vac.	0.23 ± 0.02			
II	intr. vac.	0.83 ± 0.04	5.0×10^5		26
I	ext. vac.	0.30 ± 0.02	2.15	cond.	Present
II	int. vac.	1.00 ± 0.02	4.5×10^7		work
IU	ext. vac.	0.30	2.2		Present
IIU	int. vac.	1.00	4.5×10^7		work
ID	ext. vac.	0.30	9.0		Fig. 4.
IID	int. vac.	1.00	5.5×10^7		
PbI_2 (low-pressure phase)					
I	ext. Pb	0.41		diff.	28,29
II	int. Pb	1.30			
I	ext.				
I	ext.				
I	ext. Iodine vac.	0.26 (parallel to c axis)		cond. and ionic thermocurrents	31
I	ext. Pb	0.6 (perpendicular) 0.6-0.7 (parallel) 0.3-0.4 (perpendicular)			
IA	ext. I	0.20 ± 0.06 unused		cond.	Present
IB	ext. Pb	0.40 ± 0.03 samples			work
II	intr. Pb	1.45 ± 0.05			
IB	contamination	4.1 ± 0.2			
IA	ext.	0.2 - 0.4 previously			
IB	ext.	0.35 - 0.65 used			
II	intr.	1.45 samples			
IV	contamination	4.1			
PbI_2 (high-pressure phase)					
II	intr.	2.2 ± 0.2		cond.	Present work

[a]vac. is vacancy, int. is interstitial, ext. is extrinsic, and intr. is intrinsic.
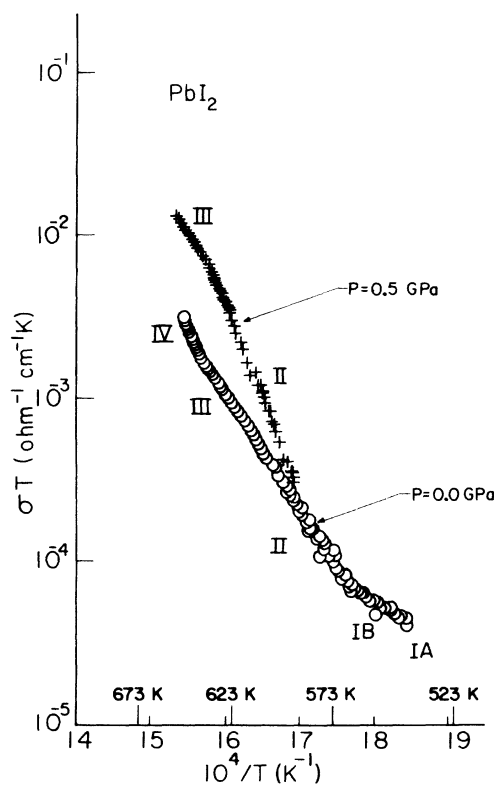[b]cond. is conductivity and diff. is diffusion.

FIG. 5. Temperature dependence of the conductivity of two unused samples of PbI_2. Steeper curve is for the high-pressure phase.
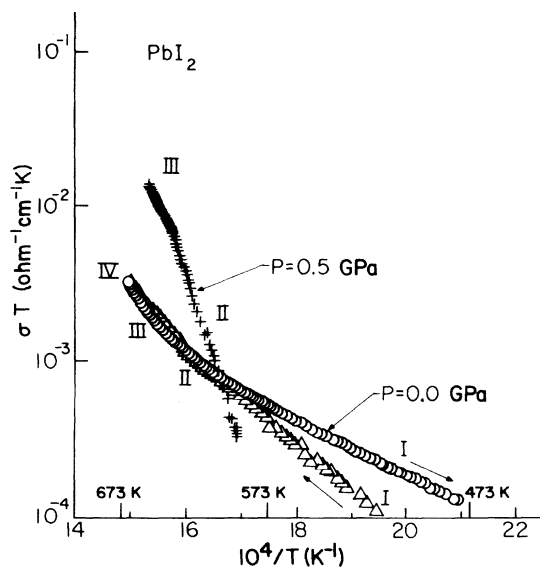

FIG. 6. Temperature dependence of the conductivity of a sample that was first heated to high temperatures in the high-pressure phase and then heated again in the low-pressure phase.

samples (Fig. 5), five activated regions were observed. Two regions were observed at low temperatures: one, labeled IB is shown in the figure and the other, which would be labeled IA, is not shown at even lower temperatures. The activation energy in region IA was 0.20 ± 0.06 eV and that in region IB was 0.40 ± 0.05 eV. Not all samples exhibited both regions IA and IB, most exhibited IA or IB, but not both. The relatively large uncertainties are given because of the considerable scatter of the data due to "pick up" by the high-resistance (10–20-Mohm) sample. All of the samples in the low-pressure phase exhibited region II with an activation energy of about 1.45 ± 0.05 eV. Region III, shown in Fig. 5 appears as a slight downward curvature from an extrapolation of region II. This behavior was only observed in one sample and is probably not an inherent property of the material (it may be due to the electrode breaking loose from the sample). It is interesting to note that the samples which were contaminated (Fig. 6), exhibited a large deviation from the behavior shown in Fig. 5, beginning at about the same temperature that region III appears. This may be a coincidence, or it may be that region III is related to the contamination process of the sample. The region labeled IV appears as an upward curvature of the conductivity curve at high temperatures. This region is almost certainly related to contamination of the sample, because any sample which had been heated to the temperatures where region IV appears was found to exhibit extrinsic conduction throughout most of the lower temperature ranges when the sample was cooled down. This behavior can be observed in Fig. 6. The activation energy for region IV was found to be ~ 4.1 eV.

How is the observed conductivity curve to be interpreted? The transport number measurements of Tubandt et al.[19] indicate that, for their samples, iodine motion was mainly responsible for the observed conductivity at about 530 K, but lead motion was mainly responsible at about 560 K. The fact that both types of ions are apparently mobile tends to imply that Schottky defects are dominant in PbI_2, with both the anion and cation vacancies being mobile (unlike $PbCl_2$ and $PbBr_2$, where only the anions contribute significantly to the conductivity). This possibility was also recently suggested by other work.[27] However, the high-pressure measurements, to be discussed in Sec. III C, indicate that Frenkel defects are dominant in both the high- and low-pressure phases of PbI_2. The conductivity curve for the low-pressure phase, shown in Fig. 5, indicates that 530 K occurs in region IA, while 560 K occurs in region IB. Thus, it seems reasonable to identify regions IA as extrinsic conduction by iodine and region IB as extrinsic conduction by lead. The identification of region IB is supported by data for lead diffusion in PbI_2, which indicated an activation energy for lead motion of 0.41 eV,[28,29] which agrees with the value 0.40 ± 0.03 eV found in

the present work in region IB.

The observation of two extrinsic regions is rather unusual, and the effect might be caused by the presence of impurities which would introduce either vacancies or interstitials (whichever is more mobile) on the cation sublattice to permit observation of region IB. In addition, there may be a small amount of PbI present in the PbI_2, which would tend to introduce vacancies on the anion sublattice and permit observation of region IA. Some recent work[30] on PbI_2 samples with excess lead or iodine indicated conductivity-activation energies of 0.24 and 0.41 eV for samples with excess iodine and lead, respectively. These activation energies are consistent with the values found in regions IA and IB in the present work, but if excess iodine or lead were responsible for the conduction observed in the other work, then interstitial conduction can be inferred, because excess ions would tend to combine with whatever vacancies were present, leaving only interstitials behind. However, the authors of that work[30] also point out that they cannot exclude the possibility of the presence of vacancies. The alternate explanation for regions IA and IB is that the identification made above should be reversed, with regions IA being extrinsic conduction by lead and IB conduction by iodine. This possibility is not favored, because of the diffusion results and also because of some additional recent results[31] on KI-doped PbI_2, where an activation energy for iodine vacancy motion was observed to be 0.26 eV along the c axis. Those authors[31] also report that the activation energy for motion of anion vacancies perpendicular to the c axis to be 0.6 eV and the activation energies for cation vacancy motion to be 0.6—0.7 eV, parallel to the c axis, and 0.3—0.4 eV, perpendicular to the c axis. The value obtained in the present work for lead motion parallel to the c axis (region IB) is rather smaller than the value given above, and it is more consistent with the value reported for the perpendicular direction.

Before considering the other observed regions of conductivity in the pure, unused sample (Fig. 5), it is useful to consider the behavior of the samples that had previously been heated to high temperatures (Fig. 6). These data exhibit three activated regions of conductivity and the hint of a fourth region. The high-temperature regions II and IV are apparently still present (region III may also be present, as will be discussed). The activation energies observed at lower temperatures were in the range 0.35 - 0.65 eV and were sample dependent. At the lower temperatures the activation energy appeared to be in the range 0.2—0.4 eV and was also sample dependent, but this region did not extend over a sufficiently wide temperature range to be investigated more carefully. It is expected that samples heated to high temperatures would tend to lose iodine (considering the volatile nature of that substance), and this would tend to in-

troduce excess vacancies on the anion sublattice, so that the regions observed at temperatures lower than $\sim 320\,°C$ are extrinsic, with conduction via anion vacancies (at least down to a temperature region where the extrinsic lead conduction might be dominant).

The activation energy observed for region II (Fig. 5) was 1.45 ±0.07 eV. This region is presumably intrinsic, with conduction by lead ions. The activation energy observed in the present work is similar to that reported for lead-tracer diffusion[28,29] (1.30 eV), although the agreement is not outstanding. Because the high-pressure measurements show that Frenkel defects are dominant in PbI_2, and the diffusion measurements show that lead motion accounts for most of the conductivity, it is clear that cation Frenkel disorder dominates in the low-pressure phase of PbI_2 at temperatures up to at least 520 K where it appears that the iodine must become mobile, in order that it escape and leave vacancies behind; this decomposition is presumably occurring in regions III and IV. The existence of region III is still not certain, but, as previously stated, it appears to be related to the decomposition or contamination. When a sample was cooled down from region IV, the conductivity curve first deviated from the curve taken on increasing temperature when region III was reached.

The most likely description of the observed conductivity of the low-pressure phase of PbI_2 can be summarized as follows. At low temperatures the conductivity is generally extrinsic and·by motion of lead ions, sometimes by iodine motion, possibly due to the presence of PbI, and sometimes by both iodine and lead. At higher temperatures (560—620 K) the conduction is probably by intrinsic cation defect motion. At still higher-temperatures decomposition and/or contamination occur, resulting in the presence of excess anion vacancies. The Frenkel-defect formation energy ΔE_f, is $2(1.45-0.40)=2.10 \pm 0.12$ eV. The data for PbI_2 are summarized in Table I.

C. Activation volumes

The activation volumes of $PbCl_2$ are shown in Fig. 7. These volumes were found from data such as those shown in Fig. 8. The data in Fig. 7 indicate that the activation volume at low temperatures is approximately 4.7 ± 0.2 cm^3/mole and at high temperatures is approximately 19.8 ± 0.5 cm^3/mole. These values are identified as the activation volume for motion of anion vacancies and the intrinsic activation volume, respectively. Compressibility and Grüneisen parameter data are apparently unavailable for $PbCl_2$, $PbBr_2$, and PbI_2; therefore, constant values of $K_T = 10^{-12}$ cm^2/dyn and $\gamma = 1.5$ were used in calculating the activation volumes of those materials (this choice results in an error of less than 2% in the activation volumes of $PbCl_2$ and $PbBr_2$ and an error as large as 30% for the tiny activation volumes to be
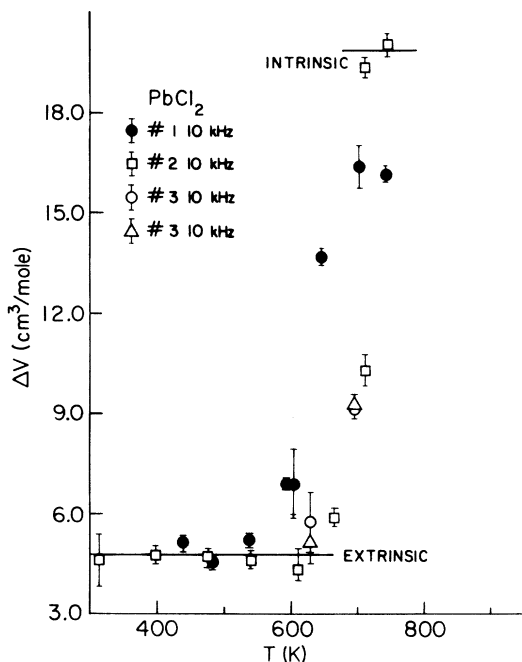
FIG. 7. Activation volumes for $PbCl_2$.

described for PbI_2).

If anion Frenkel defects were presumed to dominate in $PbCl_2$, the formation volume of a mole of defects would be $\Delta V_f(F) = 2(19.8 - 4.7)$ $= 30.2 \pm 1.1$ cm^3/mole. If Schottky defects are presumed to dominate (as has been done in the in-

terpretation of the conductivity data), the formation volume of a mole of Schottky defects would be $\Delta V_f(S) = 3(19.8 - 4.7) = 45.3 \pm 1.6$ cm^3/mole. These values should be compared to the molar volume of 47.5 cm^3/mole. The formation volume of Schottky defects is so close to the molar volume that one is forced to conclude that Schottky defects are dominant in $PbCl_2$. The fact that the measured formation volume is slightly smaller than the molar volume is probably not significant because the error made in determining ΔV_m or the intrinsic activation volume is multiplied by 3 in calculating ΔV_f. In fact, early measurements indicated an intrinsic activation volume of ~ 16 cm^3/mole, which would give $\Delta V_f(S)$ much too small. This kind of problem resulted from not being completely certain that the activation volume was measured for a sample well into the intrinsic region of the conductivity, so that no residue from the extrinsic region would cause the activation volume to indicate a value between extrinsic and intrinsic. The fact that it was necessary to go to a temperature only about 20 K below the melting point to obtain an activation volume truly indicative of the intrinsic region points out the need for caution in interpretation of data closer to the extrinsic region.

The activation volumes of $PbBr_2$ are shown in Fig. 9. The data shown are for two different samples which had different amounts of TlBr dopant. It is evident that sample No. 1 had a higher concentration of dopant, because the activation volume remained typical of the extrinsic region to higher temperatures
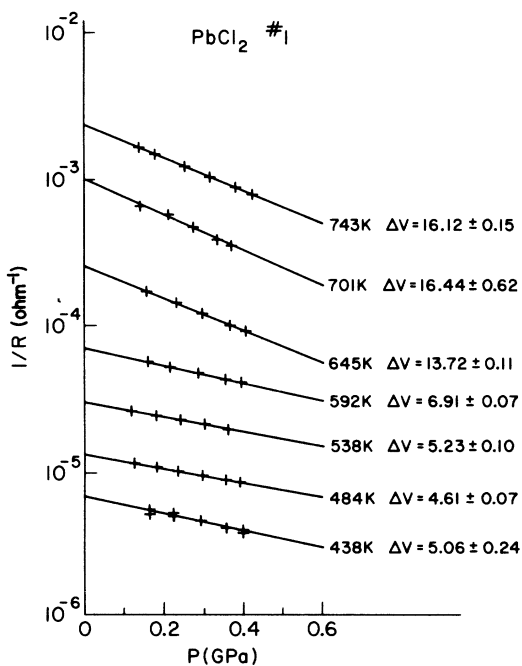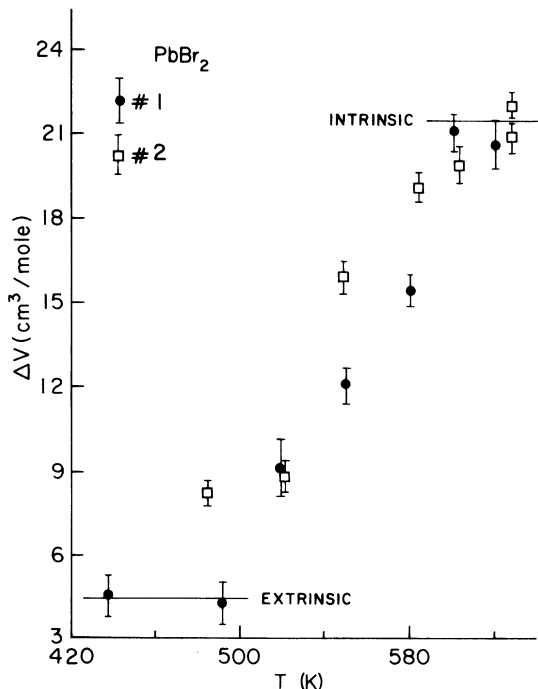

FIG. 8. Type of data from which the activation volumes were extracted.

FIG. 9. Activation volumes for $PbBr_2$.

than for sample No. 2. The activation volume for motion of anion vacancies is approximately 4.4 ±0.6 cm³/mole, while the intrinsic activation volume is approximately 21.6 ±0.6 cm³/mole. These values lead to the formation volume of a mole of Schottky defects, $\Delta V_f(S) = 3(21.6 - 4.4) = 51.6$ ±2.3 cm³/mole. This value is, again, so close to the molar volume of 55.1 cm³, that Schottky defects must be dominant in PbBr₂. It could be argued that Frenkel defects are dominant in both PbCl₂ and PbBr₂, but the anion interstitial is locked into its site by its neighbors and cannot move because the lattice is already very highly relaxed outward from the interstitial to accommodate its presence. This seems unlikely, but the presence of a small number of anion Frenkel defects could explain the difference between the molar volume and the Schottky-trio formation volume. Such a possibility was recently suggested by Acuña and Jacobs[32] to explain some results for the conductivity of doped KCl.

The activation volumes of PbI₂ are shown in Fig. 10. Values for the high-pressure phase (HPP) are found to be very small (1.4 ±0.6 cm³/mole), and they do not appear to vary in any consistent way with increasing temperature. The activation volumes of the low-pressure phase (LPP) are also quite small, and they appear to increase with temperature up to about 630 K, where a subsequent decrease is observed. The activation volume for motion in the LPP is about 2.2 ±0.5 cm³/mole and the intrinsic activation volume is approximately 6.8 cm³/mole. Regardless of whether Frenkel or Schottky defects are presumed to dominate, the formation volume will be tiny compared to the molar volume of 74.9 cm³/mole for PbI₂. Therefore, Frenkel defects are clearly dominant in PbI₂ in both the LPP and HPP. The Frenkel-defect formation volume in the LPP is $\Delta V_f(F) = 2(6.8 - 2.2) = 9.2$ ±1.6 cm³/mole.

The decrease in the activation volume of the LPP at high temperatures is rather odd. In the alkaline-earth fluorides the activation volume for the equivalent region was observed to increase,[2] apparently due to a contribution from mobile oxygen contaminant. In those materials the oxygen replaced smaller fluorine ions. In PbI₂ the oxygen would replace much larger iodine ions, and thus might be expected to be less affected by pressure in their movements about the lattice. This could explain the observed falloff, if the iodine were the more mobile ion at high temperatures. The falloff may also be caused
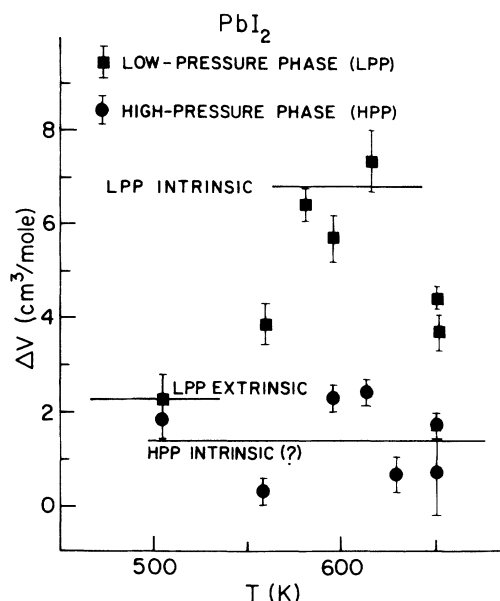

FIG. 10. Activation volumes for both the high-pressure phase and the low-pressure phase of PbI₂.

by an increased contribution to the conductivity by electrons, or more precisely, holes, which have been investigated[27] at lower temperatures in this material and found to be present, but not in sufficient quantity to affect the conductivity at those lower temperatures.

It is interesting to note that anion Frenkel defects are found to dominate in both the cubic and orthorhombic phases of PbF₂,[1] while Schottky defects dominate in PbCl₂ and PbBr₂, and then with the even larger anion in PbI₂, we find that cation Frenkel defects are dominant. It is also interesting that Schottky defects are dominant in PbCl₂ and PbBr₂, but in the corresponding orthorhombic phases of PbF₂ and SrCl₂,[1] Frenkel defects are dominant.

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[1]J. Oberschmidt and D. Lazarus, Phys. Rev. B 21, 2952 (1980).

[2]J. Oberschmidt and D. Lazarus, B 21, 5823 (1980) (following paper).

[3]N. N. Greenwood, in *Ionic Crystals, Lattice Defects and Nonstoichiometry.* (Chemical Publishing Company, Inc., New York, 1970).

[4]G. A. Samara, J. Phys. Chem. Solids 40, 509 (1979).

[5]D. N. Yoon and D. Lazarus, Phys. Rev. B 5, 4935 (1972).

[6]C. Zener, J. Appl. Phys. 22, 372 (1951).

[7]R. W. Keyes, in *Progress in Very High Pressure Research*, edited by F. P. Bundy, W. R. Hibbard, Jr., and H. M. Strong (Wiley, New York, 1961).

[8]C. P. Flynn, in *Point Defects and Diffusion* (Clarendon, Oxford, 1972).

[9]P. W. Bridgman, Proc. Am. Acad. Arts Sci. 72, 45 (1937).

[10]A. Kirfel, thesis (Mineralogisches Institut, Bonn, 1968) (unpublished); K. Seifert, Fortschr. Mineral. 45, 214 (1968).

[11]R.W.G. Wyckoff, *Crystal Structures* (Interscience, New York, 1948), Sec. I.

[12]F.E.A. Melo, K. W. Garrett, J. Mendos Filho, and J. E. Moreira, Solid State Commun. 31, 29 (1979).

[13]*CRC Handbook of Chemistry and Physics*, 60th ed., edited by R. C. Weast (CRC, Baton Rouge, 1979).

[14]H. Hoshino, M. Yamazaki, Y. Nakamura, and M. Shimoji, J. Phys. Soc. Jpn. 26, 1422 (1969).

[15]G. Simkovich, J. Phys. Chem. Solids 24, 213 (1963).

[16]A. K. Pansare and A. V. Patankar, Pramana 2, 282 (1974).

[17]K. J. DeVries and J. H. Van Santen, Physica (Utrecht) 29, 482 (1963).

[18]G. M. Schwab and G. Eulitz, Z. Phys. Chem. 55, 179 (1967).

[19]C. Tubandt, H. Reinhold, and G. Liebold, Z. Anorg. Allg. Chem. 197, 229 (1931).

[20]E. Barsis and A. Taylor, J. Chem. Phys. 45, 1154 (1966).

[21]W. Nieuwenkamp and J. M. Bijvoet, Z. Kristallogr. Kristallogeom. Kristallphys. Kristallchem. 84, 49 (1932).

[22]W. E. Van Den Brom, J. Schoonman, and J.H.W. De Wit, J. Solid State Chem. 4, 475 (1972).

[23]J. Schoonman and J. F. Verwey, Physica (Utrecht) 39, 244 (1968).

[24]J. F. Verney and J. Schoonman, Physica (Utrecht) 35, 386 (1967).

[25]J. Schoonman, J. Solid State Chem. 4, 466 (1972).

[26]H. Hoshino, S. Yokose, and M. Shimoji, J. Solid State Chem. 7, 1 (1973).

[27]A. P. Lingras and G. Simkovich, J. Phys. Chem. Solids 39, 1225 (1978).

[28]G. V. Von Hevsey and W. Seith, Z. Phys. 56, 790 (1929).

[29]W. Seith, Z. Phys. 56, 802 (1929); 57, 869 (1930).

[30]F. Adduci, L. Baldassarre, G. Maggipinto, A. Minafra, and F. Levy, Phys. Status Solidi (a) 52, K173 (1979).

[31]T. Hagihara, K. Iwamoto, K. Fukumoto, and N. Ayai, J. Phys. (Paris) Colloq. (in press).

[32]L. A. Acuna and P.W.M. Jacobs, J. Phys. (Paris) Colloq. (in press).