PHYSICAL REVIEW B VOLUME 21, NUMBER 7 1 APRIL 1980

Ionic conductivity, activation volumes, and high-pressure phase transitions in PbF_2 and $SrCl_2$

J. Oberschmidt* and D. Lazarus
Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

(Received 22 October 1979)

The effect of hydrostatic pressure on the ionic conductivities and phase transitions in PbF_2 and $SrCl_2$ has been investigated. The cubic to orthorhombic transition in PbF_2 was studied in the temperature range of 300 to 850 K for pressures up to 0.55 GPa; the similar transition in $SrCl_2$ was investigated in the range 500 to 1050 K for pressures to 0.45 GPa. The transition temperature was seen to increase linearly with increasing pressure at higher temperatures in both materials. There is considerable hysteresis in the transition at lower temperatures. The activation volumes were extracted from the effect of pressure on the conductivity. The volumes are small at all times, and are consistent with the dominance of Frenkel defects in these materials.

I. INTRODUCTION

Lead fluoride and strontium chloride have been the subjects of a large number of investigations in recent years. This interest has centered around their unusually high ionic conductivities at high temperatures, but they have other interesting physical properties as well. We sought to investigate the conduction mechanisms in these materials by the use of hydrostatic pressure—a technique which has been shown to be valuable in the past.[1,2]

The ionic conductivity can be written as

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

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 Gibbs-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 temperatures 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]

$$n = (NN')^{1/2} \exp(-\Delta G_f/2kT) , \tag{2}$$

where N is the density of anion lattice sites, N' is the density of anion interstitial sites, and ΔG_f is the Gibbs free energy of formation of a Frenkel defect. The existence of Frenkel defects is presumed in the derivation of Eq. (2). The applicability of the Frenkel model is implied from doping experiments,[4,5] and is also justified by the results of the present experiment.

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

$$\sigma = \frac{\sigma_0}{T} \exp \frac{-(\Delta H_f/2 + \Delta H_m)}{kT} , \tag{3}$$

where

$$\sigma_0 = \frac{(NN')^{1/2} e^2 \alpha \nu a^2}{k} \exp\left(\frac{\Delta S_f}{2k} + \frac{\Delta S_m}{k}\right) . \tag{4}$$

Equation (3) describes the conductivity in the intrinsic region where defects are both formed and moved and there is a single mobile charged defect species. In the case where more than one species is mobile, the right-hand side of Eq. (3) 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 $dG = VdP - SdT$

$$\Delta V = \left(\frac{\partial \Delta G}{\partial P}\right)_T . \tag{5}$$

From Eq. (3), then,

$$\frac{\Delta V_f}{2} + \Delta V_m = -kT\left[\left(\frac{\partial \ln \sigma}{\partial P}\right)_T - 2\left(\frac{\partial \ln a}{\partial P}\right)_T - \left(\frac{\partial \ln \nu}{\partial P}\right)_T - \frac{1}{2}\left(\frac{\partial \ln NN'}{\partial P}\right)_T\right] , \tag{6}$$

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[6]

$$\frac{\Delta V_f}{2}+\Delta V_m=kT\left[\left(\frac{\partial \ln R}{\partial P}\right)_T+\gamma K_T\right] , \qquad (7)$$

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.

The second term on the right-hand side of Eq. (7) is generally on the order of 10% or less of the first term. The values for the compressibility were found by linearly extrapolating the elastic constant data for $SrCl_2$ (Ref. 7) and PbF_2 (Ref. 8). The elastic constants give the adiabatic compressibility rather than the isothermal compressibility, but the difference is fairly small. There is some evidence[9] that the compressibility rises faster than linearly at high temperatures. This effect was not taken into account in Eq. (7), but, once again, the effect is fairly small. The Grüneisen parameter used is 1.5 for both materials.

While Eq. (7) was derived for the intrinsic region of the conductivity, the same equation holds for the extrinsic region, except that the left-hand side of Eq. (7) 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.[1]

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,[10] or as the pressure derivative of appropriate normal modes in the dynamical-diffusion model.[11]

II. EXPERIMENTAL

The samples used in the atmospheric-pressure measurements were single crystals. The PbF_2 was obtained from Harshaw, and the $SrCl_2$ was kindly provided by A. Chadwick. Typical aliovalent impurities in the $SrCl_2$ were Si, 1500; Al, 700; Na, 200; and Be, 150 ppm. Impurities in the PbF_2 were Si, 100; Al, 50; S, 50; Ta, 40; and Na, 20 ppm. Since the samples did not cleave readily, they were broken into usable sizes, and two sides were ground roughly parallel and then slightly polished on fine grit Carborundum paper. Typical sample lengths varied from about 2 to 12 mm with cross sections around $3.5 \times 3.5\ \text{mm}^2$.

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 2 to 20 kHz for sample conductivities up to approximately $10^{-3}\ \Omega^{-1}\text{cm}^{-1}$. At higher temperatures (conductivities) the frequency dependence was so large (even at 100 kHz) that accurate data could not be obtained. This effect will be discussed later. Other electrode materials such as silver paint or evaporated platinum were tried, but were not found to yield reproducible results on thermal cycling.

During preliminary measurements the conductance measurements were made with a General Radio model 1608-A impedance bridge. With this bridge it was possible to observe the frequency dependence of the conductance from 20 Hz to 20 kHz as well as the effect of the applied voltage from 50 mV to 1.5 V (peak to peak). These measurements made it clear that 10 kHz was a suitable measuring frequency, except at high temperatures. It was also found that the measured resistance was independent of applied voltage in the range mentioned. The bridge has some drawbacks which make it undesirable for the present experiments: First, it provides basically only for a two-wire measurement, so that the lead resistance is included in the measurement along with the sample and electrodes (fairly long leads are required to get into a remote pressure vessel); second, and more serious, the bridge takes a long time to null. This is a serious problem in a pressure vessel where the temperature may drift slowly away while the bridge is being nulled. These two problems were overcome by the use of a Hewlett-Packard model 4262A digital LCR meter. This instrument is a microprocessor-controlled meter which can make a four-wire resistance measurement, with a digitized output, in approximately 100 msec at 10 kHz. A separate control unit was built to provide for recording the temperature, pressure, and sample resistance on a teletype for later analysis. This unit allowed data to be taken automatically at preset time intervals as the sample was heated or cooled. The effect of heating rate was checked to see that the sample had sufficient time to equilibrate. For heating rates from 0.5 to 12 K/min no effect was observed on $SrCl_2$. The PbF_2 was rather sluggish in this respect and required the slower heating rates. Nearly all data were taken for heating rates less than 6 K/min. The measuring thermocouples also served as the resistance measurement leads, so that the temperature at each end of the sample could be monitored directly, and a precise mean temperature for the sample established. Details of the sample holder will appear elsewhere.[12]

The high-pressure measurements were done in an internally heated vessel made by the Tem-Pres Division of Leco Corporation. The vessel is designed to attain temperatures to 1673 K and hydrostatic pressures to 1 GPa (10 kbar) simultaneously. The pressure medium used in these measurements was argon gas, which was passed through two cold traps to eliminate any residual water or oil. The pressure was measured to ± 1% with a calibrated Harwood manganin gauge or a Heise Bourdon tube gauge. The vessel was flushed with argon to remove air by raising the pressure to 0.1 GPa (1 kbar) and releasing it. This procedure was fairly satisfactory, but clear evidence of oxygen contamination could be observed in various ways after samples had been heated to high temperatures. Some PbF_2 samples were gray on the surface after removal from the system, and Auger electron spectroscopy (AES) showed layers of PbO as thick as 2000 Å. (The argon itself has as much as 100 ppm of oxygen; at a few thousand atmospheres pressure there could be as much as a tenth of an atmosphere of oxygen in the "pure" gas.)

Internally heated pressure vessels are notorious for their temperature gradients. This one is no exception. Over a distance of 3 or 4 cm, there may be a temperature difference of as much as 500 K. With proper sample location, the temperature difference across the sample can be made small. Across a sample 8 mm long the temperature difference may still be as much as 10 K, and it may shift with pressure. The temperature differences in these measurements were normally around 3 to 5 K and could be monitored directly by the two thermocouples/electrodes at the sample ends.

For activation-volume determinations [cf. Eq. (7)] resistance was measured for various pressures at constant temperature. Normally, such measurements are done on decreasing pressure to save time waiting for sample equilibration. In the present case, measurements were made on both increasing and decreasing pressure to observe the first-order, cubic to orthorhombic phase transition. After a sample once goes through the phase transition, it is no longer a single crystal.

III. RESULTS AND DISCUSSION

A. Phase transitions

The phase transitions were normally observed by taking resistance readings at various pressures at constant temperature. Typical data for $SrCl_2$ are shown in Fig. 1 (the data for PbF_2 are similar). At low temperatures the conductivities of the two phases are similar, the conductivity of the β (cubic) phase being slightly higher. At higher temperatures the difference is more than two orders of magnitude.

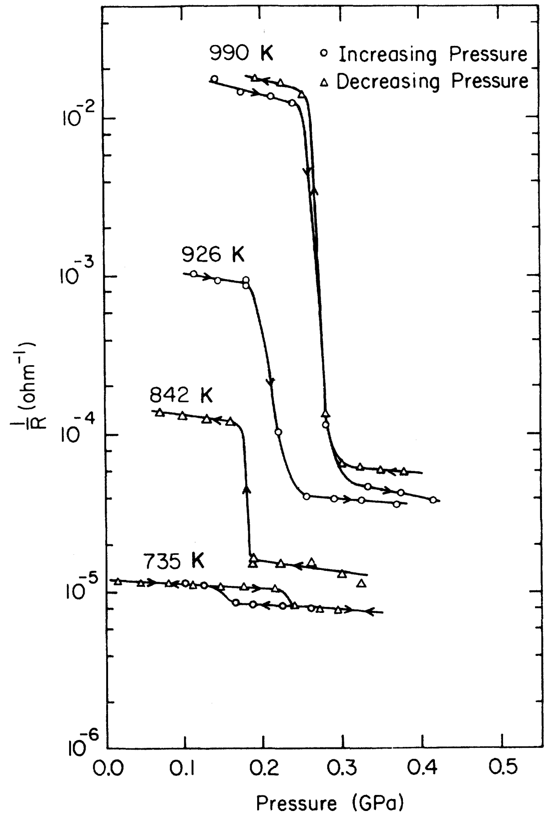

FIG. 1. The change in the sample conductance across the phase transition in $SrCl_2$. Data for PbF_2 are similar.

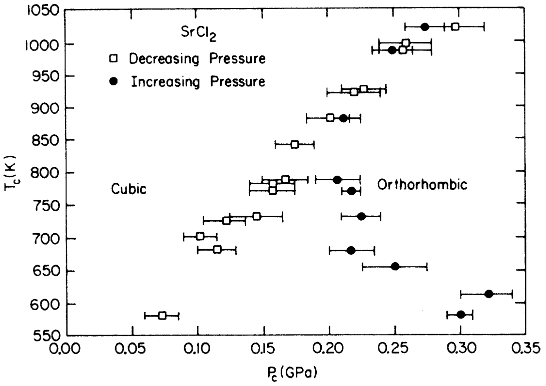

FIG. 2. The transition temperature vs transition pressure for $SrCl_2$. Note the hysteresis at lower temperatures.

Figures 2 and 3 show the transition temperature plotted against the transition pressure for $SrCl_2$ and PbF_2. The $SrCl_2$ data show a large hysteresis at low temperatures. This effect can also be seen in Fig. 1. As temperature increases, the hysteresis decreases until it is practically nonexistent. The critical temperature-pressure data for PbF_2 are remarkably similar, except that the α-PbF_2 does not convert back to the β phase on releasing pressure at low temperature. This behavior of PbF_2 is well known.[6] The conversion is finally attained by reheating the α-PbF_2 to around 610 K at atmospheric pressure. While taking the low-temperature data, we noted that the transition pressures observed were somewhat higher than those reported by Samara.[6] To check this, we annealed one sample at a lower pressure, close to Samara's value; after 10 min the sample was still in the β phase, but after 2 h it had transformed to the α phase. Undoubtedly, the other low-temperature data would fall into the lower range if the samples had been annealed long enough. This effect has also been noted previously.[8]

The phase transition in $SrCl_2$ has apparently been observed only once previously,[13] at ambient temperature and a very high pressure of 5.8 GPa (58 kbar). Our data indicate a much lower transition pressure (~0.1–0.2 GPa) at higher temperatures (~800 K). Observation of the transition in PbF_2 at temperatures above 450 K had not been reported until after our work had been completed. The recent results for the transition at higher temperatures[14] generally agree with ours.

The high-temperature data in Figs. 2 and 3 were fitted to straight lines. From this fit we obtain $P_c = -(1.49 \pm 0.09) \times 10^{10}$ dyn/cm^2 + $[(2.40 \pm 0.12) \times 10^7] T_c$ dyn/cm^2 for PbF_2 and $P_c = -(2.48 \pm 0.35) \times 10^9$ dyn/cm^2 + $[(5.19 \pm 0.40) \times 10^6] T_c$ dyn/cm^2 for $SrCl_2$. The entropy changes at the phase transition can be calculated from the Clausius-Clapeyron equation

$$\frac{dP_c}{dT_c} = \frac{\Delta S}{\Delta V} , \tag{8}$$

where ΔS is the entropy change and ΔV the volume change across the phase transition. Since $\Delta V = M/\rho_c - M/\rho_0$, where M is the molar mass, and ρ_c and ρ_0 are the known densities of the cubic and orthorhombic phases, the entropy change can be found using the measured densities of $SrCl_2$ (Ref. 13) and PbF_2 (Ref. 15). We find $\Delta S(SrCl_2) = 0.38k$ (0.76 cal/g mole K) and $\Delta S(PbF_2) = 0.88k$ (1.78 cal/g mole K).

B. Ionic conductivity

The conductivity data of PbF_2 at atmospheric pressure are shown in Fig. 4. These data support the description of the conduction mechanisms proposed by Bonne and Schoonman[16] and by Samara[6]: The conduction at low temperatures is by extrinsic vacan-

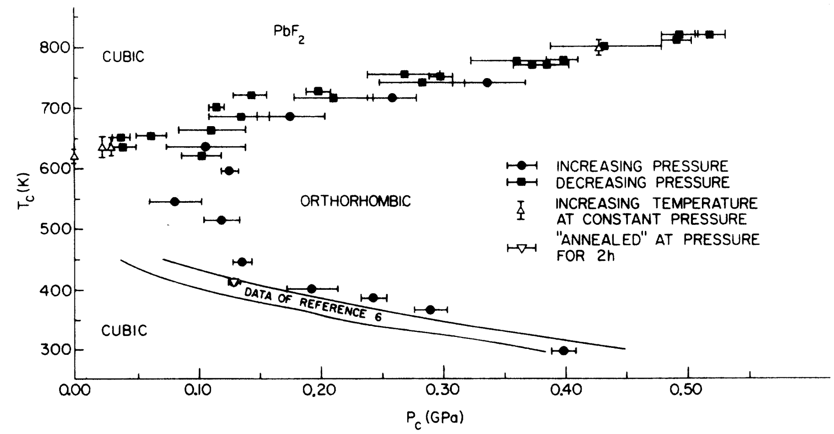

FIG. 3. The transition temperature vs transition pressure for PbF_2.

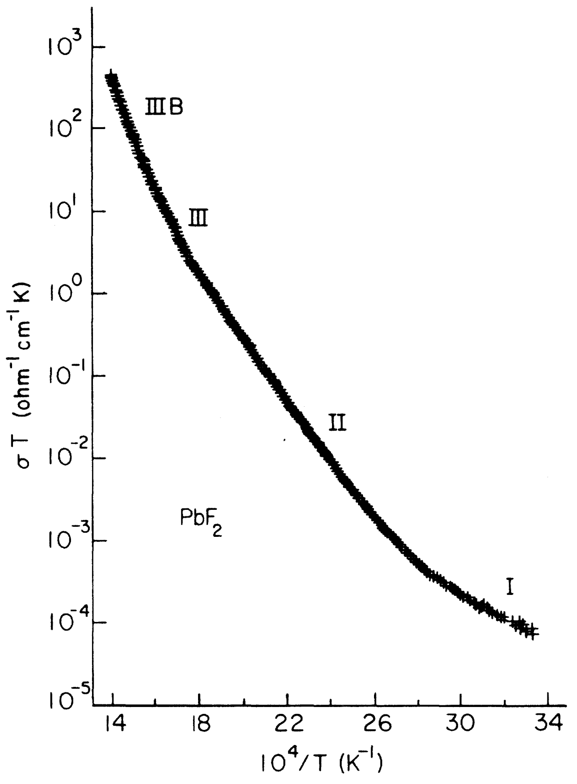

FIG. 4. The temperature dependence of the ionic conductivity of β-PbF_2. Roman numerals are explained in the text.

cies (region I in Fig. 4); in region II conduction is by intrinsic vacancies; in region III conduction is by intrinsic interstitials. In region IIIB, a new conduction mechanism appears. There is an upward curvature of the data here which may be explained in one of several ways. The most likely explanation is that it is due to contamination of the sample with oxygen. Another possibility is suggested by some recent neutron scattering results.[17,18] These results at least suggest that there is more than one type of interstitial site in PbF_2. This curvature may be due to the increasing use of the higher-energy interstitial site by the ions. A region which would be marked IV, at the highest temperatures, is not shown in Fig. 4. In region IV the conductivity data are observed to curve *downward* from an extrapolation of region III or IIIB.[19,20] As mentioned earlier, a very strong frequency dependence of the resistance was observed at high temperatures in these materials, as well as other fluorite-structured materials.[12] This frequency dependence results from the polarization of the sample at the electrode interface. The size of the effect was observed by measuring the sample resistance at 100 Hz, 1 kHz, and 10 kHz with the Hewlett-Packard meter. The sample resistance was seen to decrease by about a factor of 4 in going from 100 Hz to 1 kHz and by about a factor of 2 in going from 1 to 10 kHz. To check the possibility that the Hewlett-Packard measuring current might be too high (1 mA); a simple measuring circuit was set up using a Princeton Applied Research HR-8 lock-in amplifier. The current was set to 50 μA, and the voltage across the sample was measured using the same phase as measured across a metal film resistor in series with the sample. The sample resistance was then calculated presuming the validity of Ohm's law. (This "in-phase" component is not simply the sample resistance, but it is expected to be close at a sufficiently high frequency.) This was done for frequencies up to 150 kHz—the limit of the HR-8. The same approximate relation between the resistance and the measuring frequency was observed as with the Hewlett-Packard meter. The frequency dependence was present even at 150 kHz; so it was clear that even higher frequencies were necessary to obtain meaningful data in this high-conductivity region. Unfortunately, we do not have the proper equipment to conduct such a study. It appears that the conductivity does indeed tend to fall away at very high temperatures, but it is not clear that the effect is as large as reported previously since, as the frequency was increased, the conductivity also increased at high temperatures. The neutron scattering data[17,18] also indicate that the concentration of Frenkel defects, which is related to the conductivity via Eq. (1), reaches a saturation point at high temperatures.

The PbF_2 data show four fairly well-defined regions of conductivity, and could be fit to an equation of the form

$$Y = Ae^{-Bx} + Ce^{-Dx} + Ee^{-Fx} + Ge^{-Hx} \; . \tag{9}$$

By suitable choice of the eight parameters A, B, C, D, E, F, G, and H, a good fit to the data was obtained. The values of the parameters are given in Table I, each pair corresponding to one of the four regions I, II, III, and IIIB. The uncertainties given for the activation energies in Table I were obtained by varying the parameters in Eq. (9).

The internal consistency in the activation energies observed by Samara[6] is also observed here. Suppose that the conduction in region II is by intrinsic vacancies, then the activation energy would be $\Delta H_f/2 + \Delta H_m(\mathrm{vac})$, where ΔH_f is the formation energy of Frenkel defects, and $\Delta H_m(\mathrm{vac})$ is the motion energy of vacancies. Suppose also that the conduction in region III is by intrinsic interstitials (only), then the activation energy here would be $\Delta H_f/2 + \Delta H(\mathrm{int})$. If the appropriate motion energies are subtracted from the activation energies in these two regions [i.e., $\Delta H_m(\mathrm{vac}) \approx 0.25$ eV from region II and $\Delta H_m(\mathrm{int}) \approx 0.52$ eV[6] from region III], values of $\frac{1}{2}\Delta H_f$ of 0.52 ± 0.04 and 0.59 ± 0.04 eV are obtained for regions II and III, respectively. These give values

TABLE I. Activation energies and prefactors:

$$\sigma T = A_{\mathrm{I}} \exp\left(-\frac{\Delta E_{\mathrm{I}}}{kT}\right) + A_{\mathrm{II}} \exp\left(-\frac{\Delta E_{\mathrm{II}}}{kT}\right) + A_{\mathrm{III}} \exp\left(-\frac{\Delta E_{\mathrm{III}}}{kT}\right) + A_{\mathrm{IV}} \exp\left(-\frac{\Delta E_{\mathrm{IV}}}{kT}\right) .$$

A's are in $\Omega^{-1}\mathrm{cm}^{-1}\mathrm{K}$; ΔE's in eV .

Region	A	ΔE	A	ΔE
	β-PbF$_2$ (cubic)		β-SrCl$_2$ (cubic)	
I	1.0×10^{0}	0.25 ± 0.02	1.5×10^{1}	0.37 ± 0.03
II	9.6×10^{6}	0.75 ± 0.03	1.8×10^{9}	1.62 ± 0.03
III	2.4×10^{9}	1.12 ± 0.03	$\cdots$	$\cdots$
IIIB	1.65×10^{15}	1.80 ± 0.03	2.2×10^{19}	3.4 ± 0.2
	α-PbF$_2$ (orthorhombic)		α-SrCl$_2$ (orthorhombic)	
I	$\cdots$	0.33 ± 0.03	$\cdots$	0.44 ± 0.02
II	$\cdots$	$\cdots$	$\cdots$	1.08 ± 0.04

of $\Delta H_f \approx 1.1$ eV which are consistent within the uncertainty.

The activation energy for motion in the orthorhombic phase was obtained from data taken while heating a sample in that phase. A hint of an intrinsic region was observed, but it did not extend over a sufficiently large temperature region to obtain meaningful data before the sample converted to the cubic phase.

The exponential prefactors given in Table I are reasonable and agree with those found elsewhere.[6,16] The values found for region IIIB are perhaps too large, and they may imply the existence of more than one process.

The values of the parameters obtained for SrCl$_2$ are given in Table I, and some of the data are shown in Fig. 5, for both the cubic and orthorhombic phases. Since the orthorhombic phase is not stable at atmospheric pressure, the conductivity was measured at the pressure shown in the figure. The fact that the curve for the orthorhombic phase is not smooth is explained by the fact that the sample was polycrystalline after going through the phase transition, and the pressure varied as the temperature was raised. These data show an activation energy of 0.44 ±0.02 eV. This region is presumably extrinsic, with conduction via vacancies. This identification is based on the fact that the sample was contaminated with oxygen by the time this measurement was made, so we label this region I with $\Delta E_m(\mathrm{vac}) = 0.44$ eV. The intrinsic and extrinsic regions were observed for the orthorhombic phase in one other sample. The intrinsic activation energy observed was 1.08 eV; thus, the formation energy of Frenkel defects in the orthorhombic phase is 1.32 eV.

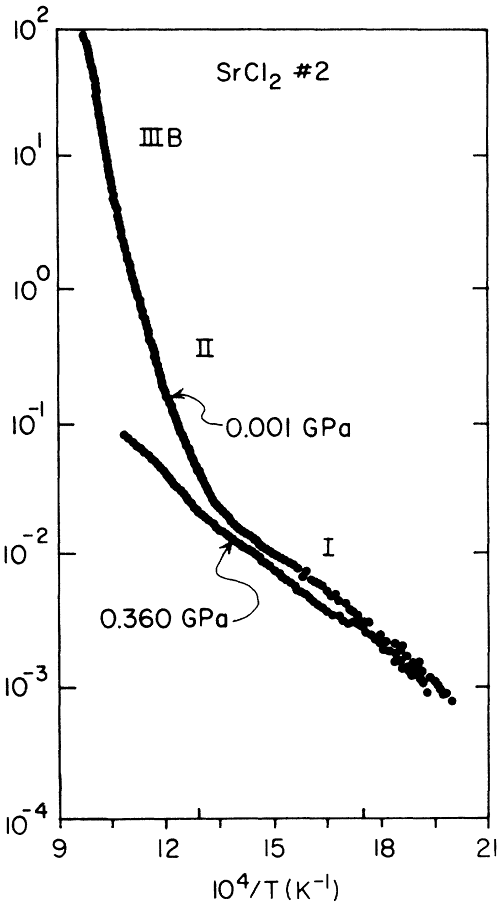

FIG. 5. The ionic conductivity of β-SrCl$_2$ and α-SrCl$_2$. The upper curve is for the cubic phase and the lower curve is for the orthorhombic phase. Roman numerals are explained in the text.

The data for the cubic phase of SrCl$_2$ are somewhat different from the data for cubic PbF$_2$. These data seem to fit reasonably well to three exponentials instead of the four required for PbF$_2$. While this does not rule out an interpretation of the data in terms of a change in conduction mechanism, or at least an increasing contribution by interstitials, it does make that possibility much less likely. In the lowest-temperature region (I) conduction is by extrinsic vacancies. The activation energies, found for three samples, were 0.33, 0.38, and 0.41 eV. These values agree reasonably well with those observed by others.[4,21,22] Region II is probably dominated by conduction by intrinsic vacancies. The average activation energy found for region II is 1.62 eV. This leads to a formation energy of Frenkel defects of 2.50 eV.

Comparable activation energies were found earlier in region II: 1.25,[21] 1.9,[4] and 1.8 eV.[22] In region IIIB we obtain an average activation energy of 3.4 eV, consistent with values previously reported,[21,23] and possibly due to oxygen contamination. The exponential prefactors in regions I and II are quite reasonable, but the exponential prefactor in region IIIB is unusually large, as is the activation energy. The large prefactor tends to imply the existence of more than one activated process in region IIIB. Association regions were observed in some samples but were not investigated. One $SrCl_2$ sample which had been highly contaminated showed three regions with activation energies of 0.13, 0.83, and 2.1 eV. These values are significantly lower than those given above, presumably due to the contamination.

C. Activation Volumes

Obtaining accurate values for the activation volume is difficult for PbF_2 and $SrCl_2$ because of the phase transition which limits the pressure range available. The fact that the samples are polycrystalline after the phase transition also limits the reliability of the data. However, since all values measured for activation volume are much smaller than molar volumes, it is clear that Frenkel disorder dominates throughout the temperature range investigated.

The activation volumes for PbF_2 and $SrCl_2$ are shown in Figs. 6 and 7. Clearly, the value measured for the activation volume at a given temperature depends on the history of the sample. If, for example, the activation volume is measured at some low temperature in the intrinsic region, and the sample is subsequently heated to high temperatures and becomes contaminated, then, when the activation volume is again measured at the low temperature, it may be an extrinsic value because of the contamination. Due to equipment limitations, sample resistances above 1 MΩ could not be measured accurately in the pressure vessel, and we could not measure the extrinsic region in nominally pure samples. In order to get any data for the extrinsic region, it was necessary to make measurements on deliberately contaminated samples.

The data in Fig. 6 for PbF_2 are typical and illustrate the history of two different samples. Beginning with the dashed curve and the open circles and squares at low temperatures at the lower left of the figure, the first point corresponds to the activation volume for motion of vacancies in the cubic phase. This point was obtained by raising the pressure and temperature carefully so that the crystal remained in the cubic phase. The pressure was then raised again along with the temperature until the crystal was well across the phase transition into the orthorhombic phase. Then the five activation volumes shown as open squares in the temperature range 475–675 K were measured, being careful not to get too close to the transition back to cubic. The lower-temperature points evidently correspond to the motion volume of vacancies in the orthorhombic phase, and the other points represent intermediate values between extrinsic and

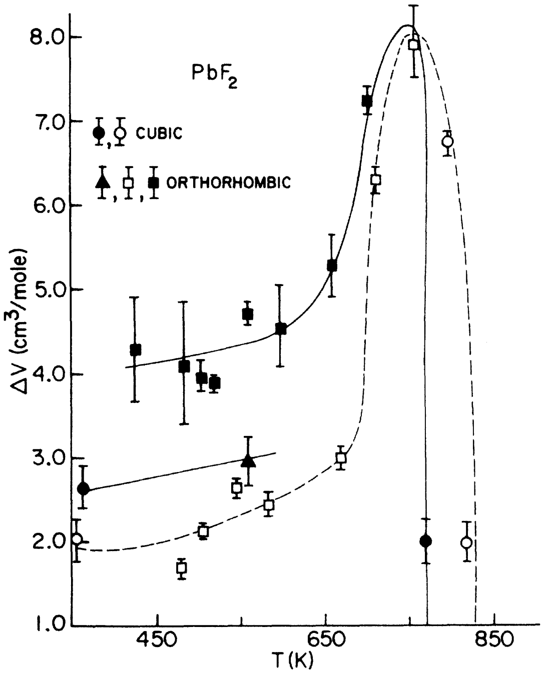

FIG. 6. The activation volumes of α- and β-PbF_2. The solid and dashed curves are explained in the text.

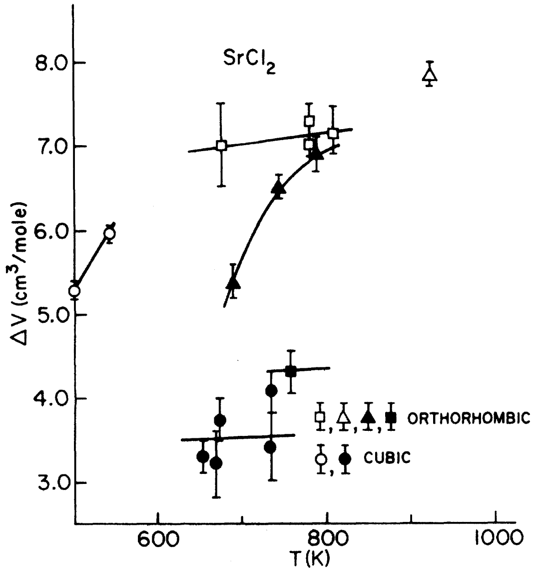

FIG. 7. The activation volumes of α- and β-$SrCl_2$. The curves are explained in the text.

intrinsic. (This was the only sample in which the extrinsic region was observed without prior contamination at high temperature.) The activation volume has a fairly sudden rise in the vicinity of 700 K in the orthorhombic phase, corresponding to entry into the intrinsic region of the conductivity, where the activation volume is equal to the sum of the motion volume and half the formation volume of the Frenkel defect. The problem for interpretation here is: Which of the two open squares at 6.3 and 7.9 cm^3/mole is the proper intrinsic value? We did not observe an intrinsic region in the atmospheric-pressure measurements in the orthorhombic phase, nor did it appear under pressure as in the $SrCl_2$ data shown in Fig. 5. It may be that the interpretation suggested for the cubic phase is also applicable to the orthorhombic phase: Then, the 6.3-cm^3 value would correspond to intrinsic vacancies and the 7.9 cm^3 to intrinsic interstitials. It may also be that the 7.9 cm^3 corresponds to the region of contamination, but this is not clear; so we take the average of these two values and subtract 2.1 cm^3 for the motion volume. This gives a formation volume of Frenkel defects for the orthorhombic phase of 10 cm^3/mole. This formation volume is small compared to the molar volume of 29.76 cm^3, indicating Frenkel disorder. Continuing to higher temperatures, the sample is allowed to convert to the cubic phase, represented by the open circles at around 800 and 820 K. The value of 6.75 cm^3/mole is typical of this region for the cubic phase, but the average of three samples is somewhat lower—around 6.5 cm^3. This value does not agree with the value of around 3.5 cm^3 reported by Samara[6] for the intrinsic vacancy; so it may be either the value for the *intrinsic* interstitial or it may be in the region where contamination of the sample occurred (region IIIB). It is probably a combination of the two, but the internal consistency of the data again shows in the interpretation of the data as a change in conduction mechanism. If we take the value of 6.5 cm^3 and subtract the value by Samara[6] of 3.5 cm^3 for the motion volume of interstitials, then we obtain the formation volume of Frenkel defects of $\Delta V_f = 6$ cm^3 for the cubic phase. If the motion volume of vacancies of 1.75 cm^3/mole (the average value) is subtracted from the activation volume obtained from the intrinsic vacancy region (4.25 cm^3, observed on other samples), we obtain a formation volume of 5 cm^3/mole, consistent, within errors (±0.8 cm^3/mole) with the first. These data are summarized in Table II.

The highest-temperature data point shown for the cubic phase is at 820 K. This point indicates a large drop in the activation volume down to values typical of the extrinsic region. This would seem to favor an interpretation for this high-temperature region (where the conductivity curve flattens) as a region where the concentration of intrinsic defects has reached a saturation level,[20] and the measured activation energy or activation volume should be similar to the corresponding motion parameters of whatever defect is the most mobile. This explanation may not be correct, since this high-conductivity region is where the large frequency dependence occurs. This systematic error (the small activation volumes observed are reproducible if the same frequency is used) prohibited us from obtaining accurate data in this region, just as for the atmospheric-pressure measurements.

TABLE II. Average activation volumes in cm^3/mole.

PbF_2			$SrCl_2$	
Cubic	Orthorhombic		Cubic	Orthorhombic
1.75 ±0.25	2.1 ±0.4	Extrinsic vacancy	3.5 ±0.3	4.3 ±0.3
4.25 ±0.35	7.1 ±0.4	Intrinsic vacancy	6.5(?)	7.1 ±0.4
6.5 ±0.4	· · ·	Intrinsic interstitial	· · ·	· · ·
6.8(?)	7.9 ±0.4	Oxygen contamination	· · ·	7.8 ±0.2
3.5	2.8(?)	Extrinsic interstitial[a]	· · ·	· · ·
5.0–6.0 ±0.8	10.0 ±1.0	Formation volume of Frenkel defect	6	5.6 ±0.9
32.0	28.9	Molar volume	51.1	45.0

[a] Reference 6.

When a higher measuring frequency is used,[12] the activation volumes tended to go to somewhat higher values in the high-temperature region, larger than the extrinsic values, but still consistent with the dominance of Frenkel defects. An alternative explanation for the behavior in region IV is that it is caused by saturation of the total density of both intrinsic and extrinsic defects. The extrinsic defects could be due to loss of fluorine and chlorine, either by replacement with oxygen or by decomposition of the material. This explanation is also consistent with the identifications of region III as due to intrinsic interstitials and region IIIB as contamination. When the contamination by oxygen is severe enough, the additional vacancies induced could combine with the intrinsic interstitials, suppressing the interstitial concentration, and effectively allowing the dominance of vacancy motion (again). It is not clear that this explanation will be satisfactory for those materials where conduction by intrinsic interstitials has not been identified, but the possibility of reaching a saturation level of defects, either intrinsic or extrinsic, could be argued to explain the data.

Another set of data are shown by the solid curve and solid symbols in Fig. 6. No data were obtainable at low temperatures on this sample, so it was heated until the resistance read on scale. The temperature was then high enough that the sample would convert to orthorhombic if the pressure were raised to obtain data over a reasonable pressure range. The pressure was then raised, and the sample converted to orthorhombic. The activation volumes shown by the solid squares were then obtained for the orthorhombic phase. As can be seen from the figure, the lower-temperature points fall in the range 3.75 cm^3 to 4.75 cm^3/mole. These values are evidently in the range between extrinsic and intrinsic. At higher temperatures, there is an increase in the activation volume corresponding to entry into the intrinsic region. The next value was taken at a still higher temperature, where the sample converted back to the cubic phase, and the low value of the activation volume shown by the solid circle at 770 K is associated with a frequency dependence of the resistance. The sample was then left in the cubic phase, and the temperature was lowered. The two points shown at the left side of the figure as a solid circle and solid triangle were then taken. The solid circle shows a value typical of the contaminated solid, close to the extrinsic value. The sample was then again converted to orthorhombic, and the solid-triangle value was taken. Again, this is near the extrinsic value for the orthorhombic phase, consistent with contamination occurring at high temperatures. If the sample is contaminated further, then these near-extrinsic values come down further.

The data for SrCl_2, shown in Fig. 7, are interpreted in a similar way. We observe a group of activation volumes in the range of 6.5 to 7.5 cm^3. By considering the evolution of the activation volume from lower temperatures, it is clear that the intrinsic activation volume $[\frac{1}{2}\Delta V_f + \Delta V_m(\text{vac})]$ is about 7.1 cm^3/mole for the orthorhombic phase. These data are shown by the open squares and the solid triangles for two cases. One case, shown by the open squares, is a sample which apparently showed intrinsic behavior (or nearly intrinsic) throughout the temperature range 650 to 820 K. The other sample, shown by solid triangles, exhibited activation volumes typical of the region between extrinsic and intrinsic, with values approaching the intrinsic value. One point, shown by an open triangle, appears at 925 K. This value of 7.8 cm^3/mole is somewhat higher than the intrinsic activation volume and also occurs in the temperature range where the oxygen contamination becomes significant. The increase in the activation volume is therefore presumably due to a contribution from mobile oxygen. After one sample had become significantly contaminated, the activation volumes for the extrinsic region of both the orthorhombic and cubic phases were measured. The value for the orthorhombic phase shown by the solid square and those for the cubic phase are shown by the solid circles. These values of 4.3 and 3.5 cm^3 are the activation volumes for motion of vacancies in the orthorhombic and cubic phases, respectively. The open circles at 500 and 545 K are activation volumes for the cubic phase. They are presumably in the region between the extrinsic and intrinsic conduction values, since there is a change between the two values. At higher temperatures and pressures, the phase transition interfered too much to obtain reasonably consistent activation volumes for the intrinsic region in cubic SrCl_2. It would appear that the intrinsic value is in the range 6–7 cm^3/mole. These data are summarized in Table II. It is clear that Frenkel defects are dominant in these two materials throughout the temperature range 300 to 950 K for PbF_2 and 400 to 1100 K for SrCl_2.

ACKNOWLEDGMENTS

We wish to express our sincere thanks to G. A. Samara and A. V. Chadwick for providing samples, and to L. E. McNeil for her invaluable assistance in the laboratory. This work was supported in part by the U.S. DOE under Contract No. EY-76-C-02-1198.

---

[*] Present address: Thomas J. Watson Research Center, IBM Corporation, Box 218, Yorktown Hts., N.Y. 10598.

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

[2] P. C. Allen and D. Lazarus, Phys. Rev. B 17, 1913 (1978).

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

[4] C. C. Liang, J. R. Rea, A. V. Joshi, and D. L. Foster, J. Solid State Chem. 22, 171 (1977).

[5] C. C. Liang and A. V. Joshi, J. Electrochem. Soc. 122, 466 (1975).

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

[7] W. Hayes and A. M. Stoneham, in *Crystals with the Fluorite Structure,* edited by W. Hayes (Clarendon, Oxford, 1974).

[8] G. A. Samara, Phys. Rev. B 13, 4529 (1976).

[9] R. T. Harley, W. Hayes, A. J. Rushworth, and J. F. Ryan, J. Phys. C 8, L530 (1975).

[10] R. W. Keyes, in *Progress in Very High Pressure Research,* edited by F. P. Bundy, W. R. Hibbard, and H. M. Strong (Wiley, New York, 1961), p. 70.

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

[12] J. Oberschmidt and D. Lazarus (unpublished).

[13] L. H. Brixner, Mater. Res. Bull. 11, 1453 (1976).

[14] W. Klement, Jr., and L. H. Cohen, J. Electrochem. Soc. 126, 1403 (1979).

[15] E. D. D. Schmidt and K. Vedam, J. Phys. Chem. Solids 27, 1563 (1966).

[16] R. W. Bonne and J. Schoonman, J. Electrochem. Soc. 124, 28 (1977).

[17] M. H. Dickens, W. Hayes, C. Smith, and M. T. Hutchings, in *Proceedings of the International Conference on Fast Ion Transport in Solids,* edited by P. Vashista, J. N. Mundy, and G. K. Shenoy (North-Holland, Amsterdam, 1979).

[18] S. M. Shapiro and F. Reidinger, in *Physics of Superionic Conductors: Topics in Current Physics,* edited by M. B. Salamon (Springer, Berlin, 1979).

[19] C. E. Derrington and M. O'Keeffe, Nat. Phys. Sci. 246, 44 (1973).

[20] V. M. Carr, A. V. Chadwick, and R. Saghafian, J. Phys. C 11, L637 (1978).

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

[22] M. Pailloux, A. Gervais, M. Jacquet, and M. Bathier, C. R. Acad. Sci. Ser. B 274, 991 (1972).

[23] G. M. Hood and J. A. Morrison, J. Appl. Phys. 38, 4796 (1967).