

## Activation volumes in the high-temperature region for silver chloride and silver bromide

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Measurements of ionic conductivity as a function of pressure have been made for solid AgCl and AgBr in the high-temperature region where non-Arrhenius behavior has been reported at normal pressure. The results show that the activation volume increases considerably with increasing temperature and decreases with increasing pressure. The large increase in the activation volume as a function of temperature can be explained by the onset of a gradual transition to a solid-electrolyte phase such as those found in many materials with the fluorite structure.

### I. INTRODUCTION

An anomalous increase in the ionic conductivity that takes place in the temperature range about 100 K below the melting point for silver chloride and silver bromide has been the subject of extensive studies.<sup>1-12</sup> Just below the melting temperature the ionic conductivity reaches about  $1 \Omega^{-1} \text{cm}^{-1}$  for silver bromide and  $10^{-2} \Omega^{-1} \text{cm}^{-1}$  for silver chloride, values that are comparable to those usually associated with solid electrolytes (superionic conductors). An anomalous increase has also been detected in the Arrhenius plots for tracer diffusion of silver and sodium ions,<sup>2,4</sup> but, surprisingly enough, none has been detected for some other cations.<sup>11</sup>

The ionic conductivity  $\sigma$  of an ionic crystal in the intrinsic temperature range, due to thermally activated Frenkel or Schottky defects, can be written as<sup>13</sup>

$$\sigma T = (\sigma T)_0 \exp\left[-\left(\frac{1}{2}\Delta H_f + \Delta H_m\right)/k_B T\right], \quad (1)$$

where  $T$  is the absolute temperature,  $\Delta H_f$  and  $\Delta H_m$  are the formation and migration enthalpies for the Frenkel or Schottky defects, and  $k_B$  is the Boltzmann constant. An upward bend in the plot of  $\ln(\sigma T)$  vs  $1/T$  as reported in AgCl and AgBr can be caused by many different effects such as defect interactions, the influence of additional defect species, a new defect mechanism, or an intrinsic temperature dependence of the migration or formation parameters for the defects.<sup>11</sup> These alternatives have been discussed in great detail in the literature.<sup>1-12</sup>

Valuable information on the nature of the crystal defects and the ion-transport mechanism can often be deduced from measurements of the pressure dependence of the ionic conductivity. The defect formation and migration volumes are defined by

$$\left[\frac{\partial \Delta G_f}{\partial p}\right]_T = \Delta V_f, \quad (2)$$

$$\left[\frac{\partial \Delta G_m}{\partial p}\right]_T = \Delta V_m, \quad (3)$$

where  $\Delta G_f$  and  $\Delta G_m$  are the Gibbs free energies for formation and migration of a defect. For an ionic conductor with Frenkel or Schottky disorder we get, for the intrinsic

temperature range,<sup>14</sup>

$$\Delta V = \frac{1}{2}\Delta V_f + \Delta V_m = k_B T \left[ \left[\frac{\partial}{\partial p} \ln R\right]_T + \kappa \gamma \right], \quad (4)$$

where  $\Delta V$  is the activation volume,  $R$  is the sample resistance,  $\kappa$  is the isothermal compressibility, and  $\gamma$  is the Grüneisen parameter.

AgCl and AgBr are well suited for a high-pressure study since no phase transitions take place in the solid phase until about 7 GPa.<sup>15</sup> Of the papers published on the pressure dependence of the ionic conductivity of AgCl (Ref. 16) and AgBr,<sup>17,18</sup> only one reports measurements in the high-temperature region where major deviations from Arrhenius behavior are found.<sup>17</sup> In the present work the pressure dependence of the ionic conductivity has been studied for the high-temperature region of AgCl and AgBr for pressures up to about 0.6 GPa.

### II. EXPERIMENTAL

The high-pressure system consisted of a conventional compressor-intensifier apparatus using argon gas as the pressure-transmitting medium. To minimize contamination the gas fed through a dry-ice cold trap before entering the internally heated sample cell (Tem-Pres Division, Leco Corporation). The pressure was measured with an accuracy better than  $\pm 1\%$  using a calibrated Harwood manganin gauge. Single crystals of pure silver chloride and silver bromide were kindly provided by R. Friauf. The crystals were stored in darkness and were normally handled in red light. The sample was placed between two silver electrodes and silver paint was in some cases applied between the sample and the electrode. On each of the silver electrodes a platinum-platinum 10%-rhodium thermocouple was spot-welded. The thermocouple feedthroughs provided a continuous thermocouple wire from the sample to outside the pressure cell. The temperature was measured using a Dana model 5330 digital voltmeter, and an ice bath was used for the reference thermocouple. The temperature readings were corrected for the pressure dependence of the emf of the thermocouples,<sup>19</sup> and the accuracy of the temperature measurements is estimated to be  $\pm 2$  K. The sample thickness was kept less than a few millimeters to avoid the large temperature

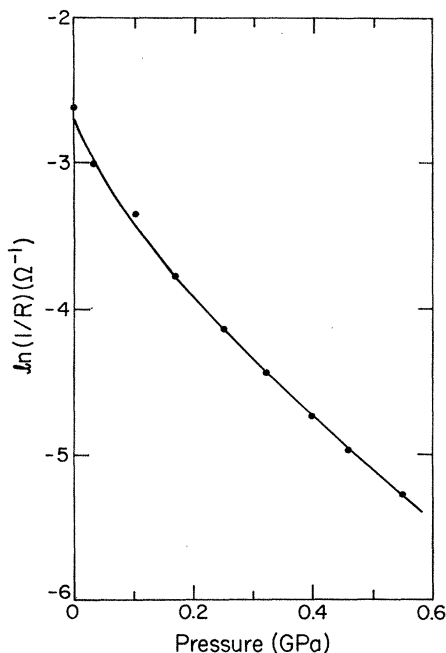


FIG. 1. Pressure dependence of  $\ln(1/R)$  for AgBr at 400°C. The curve serves only as a guide for the eye.

gradients that are common for internally heated pressure vessels. The sample resistance was measured using a Hewlett-Packard model HP-4262A LCR meter and a four-wire technique, where the thermocouple leads also served as the current and potential leads for the resistance measurements. Since nonblocking electrodes were used, the impedance was not frequency dependent for the frequencies used in this work, 1–10 kHz, and the impedance simply equals the sample resistance.<sup>20,21</sup>

In Fig. 1 the  $\ln(1/R)$ -versus-pressure curve is shown for silver bromide at 400°C. For both AgCl and AgBr there is a curvature in the conductivity plots, and the curvature increases with increasing temperature. The curvature is, however, almost absent for the lowest-temperature runs for AgCl. Activation volumes were calculated from Eq. (4) for a number of temperatures and pressures using least-squares fits; the results are presented in Table I. In Figs. 2 and 3 examples of the pressure and temperature dependence of the activation volume are shown.

Compressibility values of  $2.27 \times 10^{-11} \text{ m}^2 \text{ N}^{-1}$  for AgCl and  $2.42 \times 10^{-11} \text{ m}^2 \text{ N}^{-1}$  for AgBr, and Grüneisen-parameter values of 1.92 for AgCl and 2.27 for AgBr,<sup>22,23</sup> were used in the calculation of  $\Delta V$ , but the total contribution from  $k_B T \kappa \gamma$  [Eq. (4)] is only 0.2–0.3  $\text{cm}^3 \text{ mol}^{-1}$ , so possible uncertainties in these values are, in fact, of little importance in evaluating the activation volumes. The accuracy of the  $\Delta V$  values are estimated to be  $\pm 10\%$  for both AgCl and AgBr.

### III. DISCUSSION

Two exceptional features in the high-temperature region for AgCl and AgBr are the curvature in the  $\ln(1/R)$ -versus-pressure plots and the considerable increase in  $\Delta V$  as a function of increasing temperature. The curvature in the  $\ln(1/R)$ -versus-pressure plot implies a decreasing  $\Delta V$  with increasing pressure, as shown in Fig. 3. For an ionic crystal such an effect could be caused by errors in the temperature measurements, a contribution of anionic or electronic conductivity, or the presence of two competing transport mechanisms.<sup>24–26</sup> The reasonable experimental errors in this work are far too small to account for the observed curvature, and the only previous measurements performed in this temperature range also showed a distinct curvature in the  $\ln\sigma$ -versus-pressure plots.<sup>17</sup> The electronic conductivity is known to be negligible in these materials, and, since the anion conductivity has been shown to be very low,<sup>4,17,27</sup> neither of these two effects can be invoked to account for the curvature.

If, for an ionic crystal, one transport mechanism dominates at low temperature and another at high temperature, this fact could give conductivities such as those shown schematically in Fig. 4(a), where it is assumed that the type of defect is the same for all temperatures and that the migration enthalpy is larger for the high-temperature transport mechanism than for the low-temperature one. The two curves shown represent the conductivities at two pressures,  $p_2 > p_1$ . Since Eq. (4) is strictly valid only if a single transport mechanism is operative, we will here denote  $\Delta V$  as the apparent activation volume.  $\Delta V$  is approximately proportional to the length of the vertical bars in Fig. 4(a), and is shown as a function of temperature in Fig. 4(b). At both high and low temperatures the  $\Delta V$  value is constant since only one transport mechanism dominates, and in the intermediate-temperature region

TABLE I. Measured apparent activation volumes  $\Delta V$  for AgCl and AgBr. Also shown is the melting temperature  $t_m$  according to Ref. 22.

Pressure (GPa)	$\Delta V$ AgCl ( $\text{cm}^3 \text{ mol}^{-1}$ )					$t_m$ (°C)	$\Delta V$ AgBr ( $\text{cm}^3 \text{ mol}^{-1}$ )					$t_m$ (°C)
	350°C	400°C	430°C	450°C	470°C		350°C	400°C	430°C	450°C	470°C	
0.1	12.2		14.1			468	18.8	31.2				445
0.2	11.9	12.4	14.0	18.6		478	17.4	23.8	25.9			457
0.3	11.9	12.4	13.5	16.9	20.5	489	15.5	22.1	24.9	25.4		469
0.4	11.7	12.2	13.5	15.1	15.8	499	13.6	20.3	23.7	23.7		481
0.5	11.1	12.7	12.6	14.5	13.7	509	13.1	18.8	23.4	22.7	33.0	493
0.6					13.4	518		16.5	18.4	20.7		504

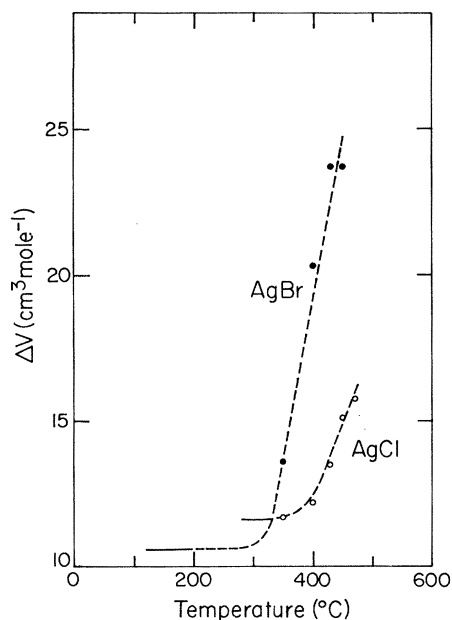


FIG. 2. Apparent activation volumes as a function of temperature at 0.4 GPa. The solid lines show  $\frac{1}{2}\Delta V_f + \Delta V_{mi}$  according to literature data (Refs. 16 and 18).

where both mechanisms coexist, we find a rapidly increasing value of  $\Delta V$  with increasing temperature. Not only the  $\ln(\sigma T)$  vs  $1/T$  plot but also the  $\ln(1/R)$  versus-pressure plot would have a curvature in the intermediate-temperature region, with  $\Delta V$  decreasing with increasing pressure. The trend of our measured  $\Delta V$  values shown in Fig. 2 are similar to those shown in Fig. 4(b), except that our  $\Delta V$ 's do not approach a constant value at high temperatures. Our values do show the pressure dependence expected for this type of change.

Frenkel defects are known to dominate in both AgCl and AgBr, and the cation transport takes place by both collinear and noncollinear interstitialcy jumps as well as by a vacancy mechanism.<sup>4</sup> This situation is thus much more complicated than the one shown in Fig. 4(a), but an estimate of the increase in  $\Delta V$  caused by a change in

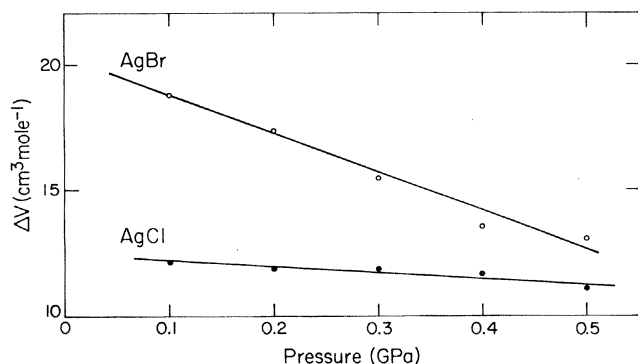


FIG. 3. Apparent activation volumes as a function of pressure at 350°C. The straight lines serve only as a guide for the eye.

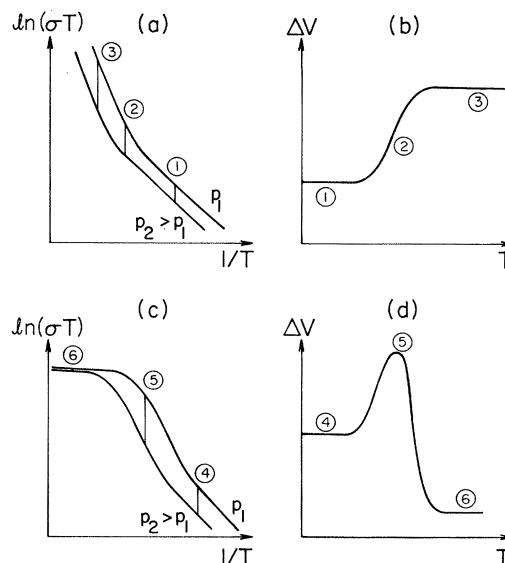


FIG. 4. Apparent activation volume resulting from changes in the ionic conductivity shown schematically in the case of (a) and (b) change in transport mechanism or (c) and (d) a gradual transition to a solid-electrolyte phase. The figures are explained further in the text.

transport mechanism can be obtained using literature data for the Frenkel formation volume  $\Delta V_f$  and the migration volume for interstitialcies  $\Delta V_{mi}$  and vacancies  $\Delta V_{mv}$ , respectively (see Table II). The  $\Delta V$  values for the two plateaus in Fig. 4(b) can then be calculated as  $\frac{1}{2}\Delta V_f + \Delta V_{mi}$  and  $\frac{1}{2}\Delta V_f + \Delta V_{mv}$ , and using the values in Table II, we find that  $\Delta V$  would increase from 11.6 to 13.1  $\text{cm}^3 \text{mol}^{-1}$  for AgCl. For AgBr the increase would be from 10.6 to 12.5  $\text{cm}^3 \text{mol}^{-1}$ , using the data of Lansari and Beyeler,<sup>18</sup> and from 10.6 to 15.4  $\text{cm}^3 \text{mol}^{-1}$ , using Kurnick's data.<sup>17</sup> Since the increases in our measured apparent activation volumes (see Table I) are considerably larger than the above values for both AgCl and AgBr, a change from one transport mechanism to another could not apparently explain the observed increase in  $\Delta V$ . It is thus more likely that the large  $\Delta V$  values are due to changes related to the formation of defects.

High-pressure experiments offer an opportunity to distinguish between Frenkel and Schottky disorder, since it has been shown from both experimental studies and from theoretical calculations that the formation volume for

TABLE II. Formation volume  $\Delta V_f$  and migration volume for vacancies  $\Delta V_{mv}$  and interstitialcies  $\Delta V_{mi}$  for AgCl and AgBr according to the literature. All values are in  $\text{cm}^3 \text{mol}^{-1}$ .

	AgCl (Ref. 16)	AgBr (Ref. 17)	AgBr (Ref. 18)
$\Delta V_f$	16.7	16	14
$\Delta V_{mv}$	4.7	7.4	5.5
$\Delta V_{mi}$	3.25	2.6	3.6
$\Delta V_f/2 + \Delta V_{mi}$	11.6	10.6	10.6

Frenkel defects is less than the molar volume, while that for Schottky defects is larger than the molar volume.<sup>28-31</sup> A change from Frenkel to Schottky disorder would thus give a sharp increase in  $\Delta V$ , and it appears, superficially, that a large concentration of Schottky defects at high temperatures is consistent with the present results (cf. Refs. 17 and 32). It has, however, been shown that the disorder is of Frenkel type also at high temperatures for both AgCl (Refs. 3, 4, 8, 33, and 34) and AgBr.<sup>4,34,35</sup> The large increase in  $\Delta V$  can thus not be explained by a change from Frenkel to Schottky disorder, and we therefore must consider whether there are any other possible explanations for the large values for the apparent activation volume.

The ionic conductivities of AgCl and AgBr are very large indeed, as high as those of the best solid electrolytes. However, AgCl and AgBr lack one characteristic property of solid electrolytes: the small temperature and pressure dependence of the ionic conductivity. This difference arises from the fact that in AgCl and AgBr the high conductivity is due to a high concentration of thermally activated, rather than structural, defects. In solid electrolytes the immobile ions form a regular space lattice in which the mobile ions can move easily between several available sites separated by low-energy barriers. This leads to an ionic conductivity which is only slightly temperature and pressure dependent, since the equations corresponding to Eqs. (1) and (4) have contributions only from the migration enthalpy and volume.

It is of interest to compare AgCl and AgBr to AgI. In AgI three phases exist at normal pressure. The most well known is the solid-electrolyte phase,  $\alpha$ -AgI, which is stable for temperatures above 147°C at normal pressure. For pressures between 0.4 and 10 GPa, a rocksalt-structure phase, fcc AgI, is stable. This phase is isostructural with AgCl and AgBr (space group  $Fm\bar{3}m$ ). The ionic conductivity in fcc AgI is similar to that in AgCl and AgBr, with the difference that at high temperatures and pressures a gradual change to solid-electrolyte-like conductivity takes place in fcc AgI.<sup>26</sup> This gradual change is similar to the increases in conductivity reported for the fluorite materials which show a diffuse transition to a solid-electrolyte phase,<sup>14,28,36,37</sup> e.g., PbF<sub>2</sub>. In Fig. 4(c) such a gradual change to a solid-electrolyte-like phase is shown. In this case, the apparent activation volume first increases and reaches a peak, then it decreases to a value of the order of a migration volume, as shown in Fig. 4(d). Apparent activation volumes such as those in Fig. 4(d) have been reported for BaF<sub>2</sub>,<sup>37</sup> PbF<sub>2</sub>,<sup>28</sup> and the high-pressure phase fcc AgI.<sup>26</sup> The  $\Delta V$  value at the peak in Fig. 4(d) should not be accorded too much physical significance when it comes to distinguishing between different defect properties, since the large value is a result of the onset of solid-electrolyte conductivity and is not to be associated with some definable defect formation or motion volume (cf. the discussion by Hayes and Boyce for the temperature dependence of the ionic conductivity under similar conditions<sup>38</sup>). The type of change shown in Fig. 4(c) results in decreasing  $\Delta V$  values with increasing pressure in the low-temperature region and increasing  $\Delta V$  values with increasing pressure in the high-temperature region.

Since for AgCl and AgBr no downward bend such as the one in Fig. 4(c) has been detected in the conductivity plots at normal pressure,<sup>4</sup> the region close to the melting transition was investigated at high pressure to see if the increased melting temperature under pressure would allow for a change such as that in fcc AgI. No downward bend in the  $\ln(\sigma T)$ -vs- $1/T$  curves or decrease in  $\Delta V$  with increasing temperature was, however, found, and the  $\Delta V$  values decreased with increasing pressure at all temperatures. In spite of this, our  $\Delta V$  values may still be a result of the onset of a gradual transition to a solid-electrolyte phase, which, however, is not completed before the melting temperature is reached. There are many similarities between AgBr and the solid-electrolyte materials which show such a gradual increase in the conductivity. The most obvious similarity is the high conductivity in AgBr, about  $1 \Omega^{-1} \text{cm}^{-1}$ , close to the melting point, and only slightly lower than that of the best conducting solid electrolytes at comparable temperatures. Other unusual physical properties have been reported for the high-temperature regions in AgCl and AgBr and in fluorite materials that have a gradual transition, e.g., anomalies in the elastic constants<sup>39,40</sup> and an increase in the thermal conductivity.<sup>41,42</sup>

To explain the non-Arrhenius behavior of the ionic conductivity in AgCl and AgBr, it has been suggested that the Gibbs free energy for formation of Frenkel defects decreases more rapidly than expected at high temperature. This implies that, e.g., the formation enthalpy is temperature dependent.<sup>1-12</sup> Such an effect would also lead to a temperature dependence of the formation volume. In a recent theoretical paper the free volume of formation for AgCl was calculated as a function of temperature,<sup>10</sup> as shown in Fig. 5. If only one transport mechanism is presumed to be operative in this region, Eq. (4) can be used to calculate  $\Delta V_f$  from our data in Table I and the  $\Delta V_m$  values in Table II—if  $\Delta V_m$  is assumed to be temperature independent. Using our values at 0.1 GPa, we derive  $\Delta V_f$  values of 17.9 and 21.7  $\text{cm}^3 \text{mol}^{-1}$  at 350 and 430°C, somewhat larger than the values in Fig. 5 and the

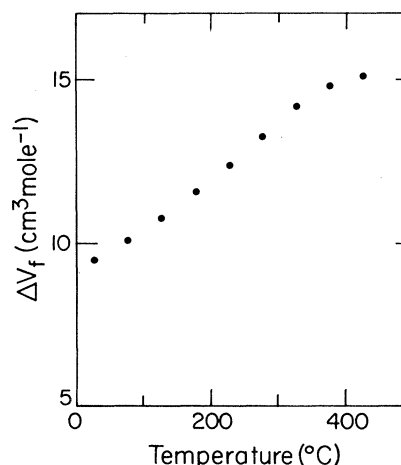


FIG. 5. Temperature dependence of the formation volume for Frenkel defects according to theoretical calculations (Ref. 10).

value found by Abey and Tomizuka<sup>16</sup> ( $16.7 \text{ cm}^3 \text{ mol}^{-1}$ ) at lower temperatures. The theoretical data also show a more or less continuous increase of  $\Delta V_f$  as a function of temperature over the temperature range from 27 to 427°C, whereas our results indicate that  $\Delta V_f$  is more or less temperature independent up to about 350°C, and then increases rapidly at higher temperatures (cf. Fig. 2). A comparison between our results and the theoretically calculated data is complicated by the fact that, due to lack of compressibility data for the high-temperature region of AgCl, the theoretically calculated  $\Delta V_f$  values are probably too small.<sup>10</sup>

#### IV. CONCLUSIONS

It has been shown in this work that the rapid increase of conductivity and activation volume as a function of increasing temperature in the high-temperature region of AgCl and AgBr can be explained by the onset of a gradual

transition to a solid-electrolyte phase similar to that observed in many materials with the fluorite structure. The detailed nature of the transition to the solid-electrolyte phase in the fluorides is still unresolved<sup>43</sup> and it is possible that an intrinsic temperature dependence of the thermodynamic parameters related to the formation and migration of the crystal defects might contribute to such a transition.

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