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Anomalous high-temperature ionic conductivity in the silver halides

J. K. Aboagye* and R. J. Friauf

Department of Physics, University of Kansas, Lawrence, Kansas 66045

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The ionic conductivity of pure AgCl and AgBr crystals has been measured carefully for a range of temperatures of 300 °C below the melting point. The usual cation-Frenkel-defect model is used, including contributions from vacancy and from both collinear and noncollinear interstitialcy jumps. Coulomb interactions are treated by the first-order Debye-Hückel-Lidiard (DHL) corrections, and further constraints are also introduced to keep the calculated results consistent with data from doped conductivity and tracer-diffusion measurements. Parameters for formation and mobility of defects are obtained from a least-squares fit of the conductivity in an intermediate temperature range up to 150 °C below the melting point. When these parameters are used to extrapolate to higher temperatures, the observed conductivity shows a large excess over the extrapolated values, amounting to nearly 100% at the melting point. The size of the anomaly is expressed in terms of a correction $-\Delta g$ to the free energy of formation needed to bring observed and calculated values of the conductivity into agreement. In both halides it is found that Δg increases rapidly and exceeds the values provided by the DHL corrections (as well as those from the extended-interaction theory of Sevenich and Kliewer for AgCl) by more than a factor of 2 at the highest temperatures. It is concluded that long-range Coulomb interactions are not sufficient to account entirely for the observed anomaly, and it is surmised that some other physical process, such as a general softening of the lattice, must also be present.

I. INTRODUCTION

It has frequently been observed that the ionic conductivity of the silver halides exhibits a peculiar behavior in the high-temperature region. At a temperature of about 100–150 °C below the melting point, the conductivity begins to rise anomalously above the value extrapolated from lower temperatures. This behavior is strikingly apparent in the overall conductivity plots of Figs. 1 and 2. This anomalous rise in the conductivity has been attributed by some workers in the field, particularly, Lidiard[1] and Sevenich and Kliewer,[2] to the long-range Coulomb interactions between the defects, whereas other people, particularly, Teltow and his group,[3-5] have suggested that this phenomenon is caused by a general loosening of the crystal lattice.

The charged point defects in an ionic crystal are influenced by long-range Coulomb interactions in the same manner as for ions in liquid electrolytes, and a version of the original Debye-Hückel theory has been adapted by Lidiard[1] for this situation. The dominant effect is to increase the defect concentration: there is a tendency for a positive defect to be surrounded by a cloud of negative defects, and vice versa, and the average formation energy is consequently lowered. In addition the mobilities are reduced slightly because the defect and its oppositely charged Debye-Hückel cloud are pulled in opposite directions by the electric field. Since the increase in concentration predominates, an anomalous rise in conductivity is predicted by this Debye-Hückel-Lidiard (DHL) theory.

An interesting aspect of the behavior of the silver halides is the unusually large defect concentration at high temperatures, about 0.2% in AgCl at the melting point and nearly 2% for AgBr. This feature is reflected by the large conductivities in Figs. 1 and 2: a 1-cm cube of AgBr has a resistance of only a few ohms at the melting point! With such a high concentration one needs a better theory than the first-order DHL theory. The DHL theory has been refined by Allnatt and Cohen[6] by using a cluster-expansion approach. Using the results of Allnatt and Cohen, Sevenich and Kliewer[2] have done extensive calculations for defects in AgCl. In the present work we set out to check the application of the first-order DHL theory and of the extended theory of Sevenich and Kliewer. In this way we could establish the adequacy or inadequacy of the long-range Coulomb interactions as applied to the silver halides.

As noted in the abstract, defect parameters were obtained by fitting the conductivity in an intermediate temperature range, where the DHL corrections are small and the first-order theory is adequate. Extrapolation to higher temperatures should give the behavior of the conductivity if all formation and mobility enthalpies and entropies are independent of temperature and if the DHL corrections are adequate. On the basis of these assumptions we compare the extrapolated conductivity to the experimental results and find that an appreciable anomaly still remains, namely, the experimental measurements are still larger than the extrapo-

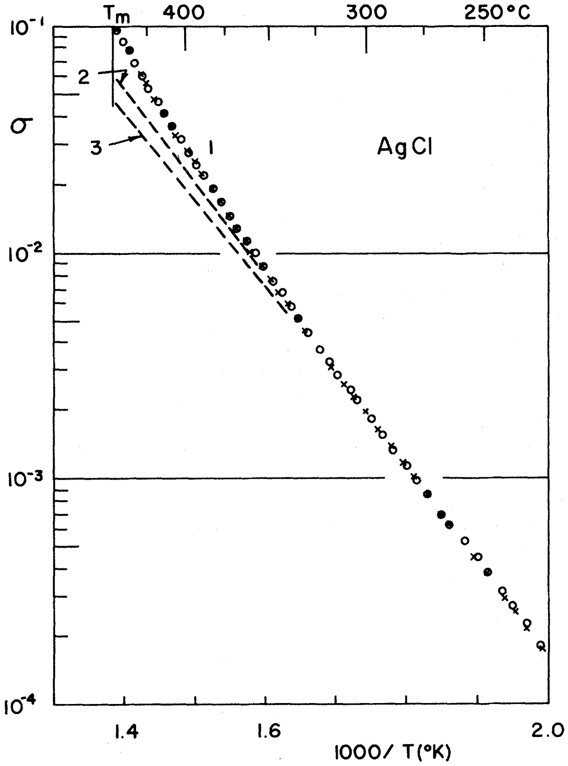

FIG. 1. Ionic conductivity of AgCl. 1, experimental measurements (O, X); 2, calculated with DHL corrections; and 3, simple theory (without DHL corrections).

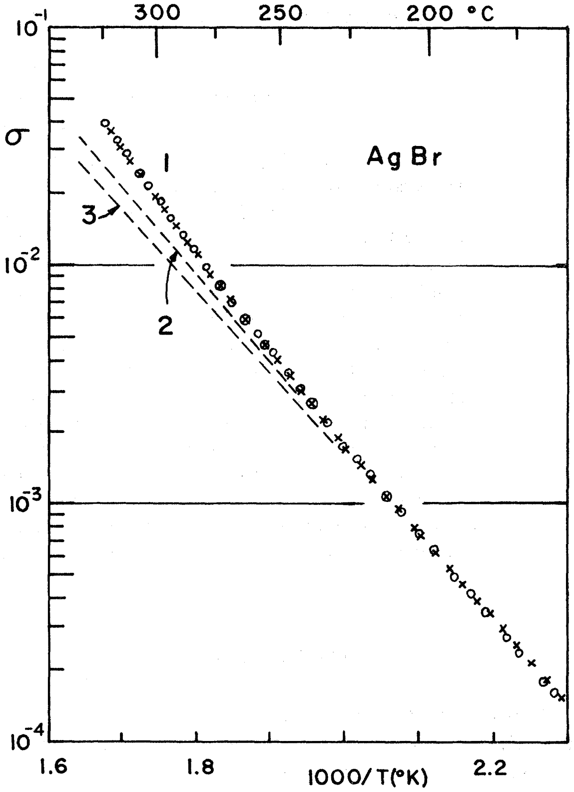

FIG. 2. Ionic conductivity of AgBr. 1,2,3—as in Fig. 1.

lated values by a significant amount. We then provide a measure for the excess conductivity by determining how many defects are needed to account for the observations (with no increase in extrapolated mobilities). The number of additional defects is therefore a direct measure of the discrepancy between the extrapolated theory and the experimental results.

II. EXPERIMENTAL PROCEDURE AND RESULTS

A. Sample preparation

In order to obtain the purest possible material, silver chloride and silver bromide were prepared in the laboratory by reaction of silver nitrate and the appropriate acid. The silver nitrate used in this preparation was obtained as special product X491 from the Eastman Organic Chemical Sales Div., Rochester, N.Y. Reagent-grade HCl and HBr obtained from Fisher Scientific Co. were distilled several times to remove trace amounts of heavy metals. The silver halide powder was then obtained by slow precipitation from dilute solutions of the silver nitrate and the corresponding acid. The preparation of the precipitate and the drying were all done in a dark room under red safelight because of the light sensitivity of the silver halides.

AgCl and AgBr single crystals were grown from their respective powders by a modification of the Bridgman method. The powder was sealed under vacuum into a long quartz tube about 14-mm i.d. with a tapered point at one end. During crystal growing the tube was rotated at about 3 turns/min and withdrawn from the furnace at a rate of 3 mm/h. The withdrawal of the tube was stopped after 25 h, and the tube was shattered to remove the crystal ingot.

Conductivity samples from these crystals were machined on a lathe to a diameter of 9 mm and a length of 10 mm. After the crystal dimensions were measured by a measuring microscope, electrodes were applied by painting the ends of the sample with a DuPont silver conducting paint (electronic grade 4817) and allowing this to dry.

B. Conductivity measurements

The sample holder for conductivity measurements is shown in Fig. 3. It is seen that in the heated portion of the apparatus the only materials present are quartz and silver, apart from the thermocouple; this minimizes the possibility of contamination from impurities that might otherwise come from the surrounding materials. The absence of contamination from the surroundings or the electrodes was indicated by the fact that there were no observations of long time changes in the conductivity. Data were taken from measurements made with increasing temperature, but values were reproducible at check points at 25 °C intervals on cooling.

The sample holder was evacuated and filled with helium to a pressure of about 1 atm, and was heated to the desired temperature in a Leeds and Northrup thermocouple calibration furnace. The furnace temperature was controlled with a thermocouple placed near the furnace winding and a chart recorder; temperature variations at the sample were less than 0.01 °C. The sample temperature was measured with a Chromel-Alumel thermocouple, which was welded to the lower silver electrode and which had previously been recalibrated *in situ* against a standard platinum thermocouple.

Resistance measurements were made with a General Radio 1615-A capacitance bridge at frequencies of 1–10 kHz in order to avoid polarization effects. The resistance standard was a series of General Radio decade resistors with an accuracy of 0.1%. Initially resistance measurements were made at 5 °C intervals after stabilizing the furnace temperature. Finally, it was decided to raise the temperature continuously at a rate of 12 °C/h and to take readings at intervals of about 10 min or 2 °C. Under these conditions the results were in agreement with those obtained at stabilized temperatures.

C. Results

Figures 1 and 2 give over-all results for two single crystals of AgCl and AgBr, respectively. There is a slight curvature at all temperatures because of contributions from several types of defect mechanisms, but the anomalous rise in the 100 °C immediately below the melting point is readily apparent. From these figures we see that even though the DHL theory works better than the simple theory it still does not account for all of the observed anomaly.

III. ANALYSIS OF DATA

A. Calculation of conductivity

There is a preponderance of evidence from many sources, such as conductivity experiments in pure and doped crystals,[3,4,7-9] diffusion measurements for both cation[10-13] and anion[10,14] tracers, and comparison of lattice and thermal expansion,[15] that silver Frenkel defects predominate in the silver halides. Hence we consider contributions to the conductivity from three transport mechanisms: cation vacancy jumps along with collinear and noncollinear interstitialcy jumps for interstitial silver ions. Let N be the number of silver ions per unit volume; e is the charge of electron; kT is Boltzmann's constant times absolute temperature; a_0 is the nearest-neighbor cation-anion distance; $R=\sqrt{2}\,a_0$ is the closest distance of approach of two defects in DHL theory; ϵ is the dielectric constant; κ_D is the DHL screening constant; ν_0 is a standard lattice vibration frequency; x_{00} (x_0) is the equilibrium concentration of Frenkel defects without (with) DHL interactions; x_v, x_i are mole fraction of silver vacancies, interstitial silver ions; c, x_k are mole fraction of divalent impurities, impurity-vacancy complexes; μ_v, μ_i are mobility for vacancy, interstitial motion; μ_1, μ_2 are mobility for collinear, noncollinear interstitialcy motion; $\phi=\mu_i/\mu_v$ is the mobility ratio; $\kappa=2\mu_1/3\mu_2$ is the ratio of interstitialcy frequencies; $g_F=h_F-Ts_F$ is the Gibbs free energy, enthalpy, entropy for the formation of Frenkel defect pair; $\xi=\chi-T\eta$ is the Gibbs free energy, enthalpy, entropy for association of a divalent ion-cation vacancy complex; $\Delta g_v=\Delta h_v-T\Delta s_v$ is the Gibbs free energy, enthalpy,

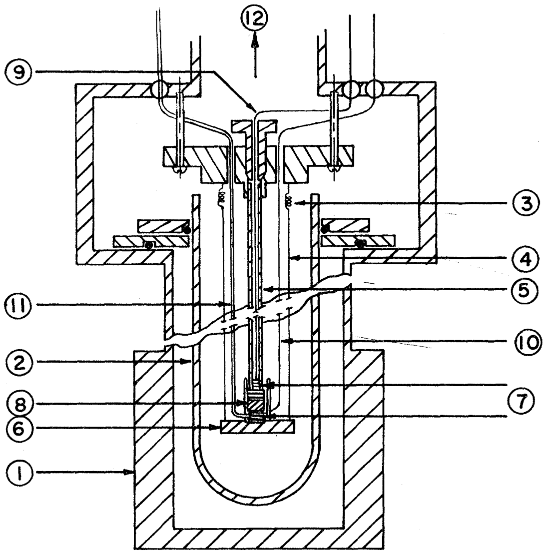

FIG. 3. Sample holder for conductivity measurements. (1) Inconel heat sink, (2) outside quartz tube, (3) stainless-steel springs, (4) silver wires, (5) quartz tube for sample support, (6) quartz plate, (7) solid silver electrodes, (8) sample, (9) high lead, (10) ground lead, (11) thermocouple wires, (12) to vacuum. O-ring seals are shown as solid circles.

entropy associated with a vacancy jump; and Δg_1, Δg_2 are similar expressions for collinear, noncollinear interstitialcy jumps.

The condition for thermodynamic equilbrium for Frenkel defects without consideration of DHL interactions is expressed by

$$x_v x_i = x_{00}^2(T) = 2e^{-g_F/kT} \tag{1}$$

and the association of divalent impurities and cation vacancies is governed by

$$x_k[x_v(c - x_k)]^{-1} = 12e^{\xi/kT}. \tag{2}$$

Also for charge neutrality one requires

$$x_v = x_i + c - x_k . \tag{3}$$

The mobilities are expressed by

$$\mu_v = 4(e\nu_0 a_0^2/kT)e^{\Delta s_v/k}\, e^{-\Delta h_v/kT}, \tag{4}$$

$$\mu_i = \mu_1 + \mu_2 , \tag{5}$$

where

$$\mu_1 = 2(e\nu_0 a_0^2/kT)e^{\Delta s_1/k}\, e^{-\Delta h_1/kT}, \tag{6}$$

$$\mu_2 = 4(e\nu_0 a_0^2/kT)e^{\Delta s_2/k}\, e^{-\Delta h_2/kT}. \tag{7}$$

The conductivity is given, in general, by

$$\sigma = eN(x_v \mu_v + x_i \mu_i). \tag{8}$$

For the pure crystal with $x_v = x_i = x_{00}$, we have

$$\sigma_0 = eNx_{00}(\mu_v + \mu_i). \tag{9}$$

If one includes the DHL theory,[1] it is convenient to introduce a screening length κ_D^{-1}, where

$$\kappa_D^2 = 8\pi(Ne^2/kT)(x_v/\epsilon), \tag{10}$$

and to define an interaction energy

$$\Delta g_{DH} = e^2\kappa_D[\epsilon(1 + \kappa_D R)]^{-1} \tag{11}$$

and an activity coefficient γ by

$$\ln\gamma = -\Delta g_{DH}/2kT. \tag{12}$$

Then the mass action relations in Eqs. (1) and (2) are changed to

$$\gamma^2 x_v x_i = \gamma^2 x_0^2(T) = x_{00}^2(T), \tag{13}$$

$$x_k[\gamma^2 x_v(c - x_k)]^{-1} = 12e^{\xi/kT}. \tag{14}$$

With the equation of charge neutrality, Eqs. (13) and (14) can be combined to give

$$(c/x_{00}) = (\zeta - \gamma^{-2}\zeta^{-1})(1 + \gamma^2\zeta H), \tag{15}$$

where

$$\zeta = x_v/x_{00}, \; H = 12x_{00}e^{\xi/kT}. \tag{16}$$

Thus, starting with c, $x_{00}(T)$, and ξ at some temperature, one can iterate for γ and ζ in Eqs. (12) and (15). Then x_v can be obtained from Eq. (16) and x_i from Eq. (13).

The mobilities are also affected by the Coulombic interactions because each defect and its oppositely charged Debye-Hückel cloud are pulled in opposite directions by the electric field. This effect reduces the mobilities by the Onsager-Pitts mobility drag factor[1]

$$G = 1 - e^2\kappa_D[3\epsilon kT(\sqrt{2} + 1)(1 + \kappa_D R)(\sqrt{2} + \kappa_D R)]^{-1}, \tag{17}$$

and the mobilities become

$$\mu_v' = G\mu_v, \; \mu_i' = G\mu_i. \tag{18}$$

The general expression for the conductivity is then

$$\sigma = eNG(x_v \mu_v + x_i \mu_i), \tag{19}$$

where x_v and x_i must be obtained from Eqs. (12) and (15), which include the first-order DHL corrections for the concentrations.

B. Introduction of constraints

The conductivity in Eq. (19) depends on 11 parameters (h_F, s_F, c, χ, η; Δh_v, Δs_v, Δh_1, Δs_1, Δh_2, Δs_2). If all of these vary freely, an excellent fit can be obtained to the conductivity of our nearly pure crystals, but the values predicted by such a fit for the mobility ratio ϕ and the ratio of interstitialcy frequencies κ do not agree with results obtained from other experimental information. For one fit for AgBr between 163 and 234 °C, for instance, the predicted values without constraints were too large for ϕ by (10–50)% and for κ by more than a factor of 5.

Since it does not seem reasonable to ignore this other information completely, we have incorporated some constraints in our fitting procedure as follows. In terms of the ratio of interstitialcy jump frequencies, which is determined from the temperature variation of the correlation factor for silver diffusion,[11,13] the interstitial mobility can be written

$$\mu_i = \mu_1 + \mu_2 = (1 + 1.5\kappa)\mu_2. \tag{20}$$

For the mobility ratio, which is obtained from the analysis of conductivity measurements on doped crystals[3,8] and which is also needed to obtain κ, we have

$$\phi = \mu_i/\mu_v = (1 + 1.5\kappa)\phi_2, \tag{21}$$

where $\phi_2 = \mu_2/\mu_v$ should have a simple Arrhenius temperature dependence with an activation energy of $\Delta h_2 - \Delta h_v$. The conductivity from Eq. (19) then becomes

$$\sigma = eNG\mu_v[x_v + x_i(1 + 1.5\kappa)\phi_2]. \tag{22}$$

For AgCl, ϕ was obtained from the work of Abbink[8] and κ from the work of Friauf and Weber.[13]

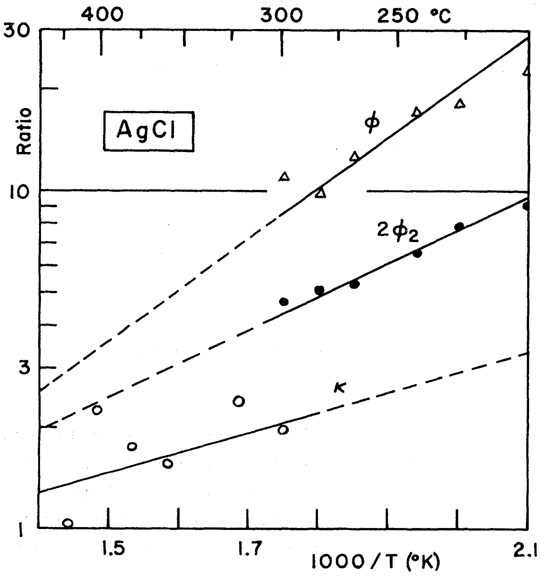

FIG. 4. Mobility ratios for AgCl. Ratio of interstitial to vacancy mobility $\phi = \mu_i/\mu_v$. Ratio of noncollinear interstitialcy to vacancy mobility $\phi_2 = \mu_2/\mu_v$. Ratio of collinear to noncollinear interstitialcy jump frequency $\kappa = 2\mu_1/3\mu_2$.

For AgBr, ϕ was taken from the work of Teltow[3] including DHL corrections and κ from the work of Friauf.[11,13] In both cases ϕ_2 was calculated from smoothed curves of ϕ and κ, and a least-squares fit of $\ln\phi_2$ vs $1/T$ was used for interpolation and extrapolation. Figures 4 and 5 show the experimental data and temperature ranges for the determination of ϕ, ϕ_2, and κ.

For both halides the table of dielectric constant versus temperature was taken from the work of Smith.[16] The table of nearest-neighbor distance versus temperature was taken from the work of Fouchaux and Simmons[15] for AgCl and from the work of Lawn[17] for AgBr. Curves of these data were fit with appropriate polynomials for interpolation and extrapolation.

C. Procedure for fitting

The conductivity as obtained from Eq. (22) is now a function of seven parameters (h_F, s_F, c, χ, η; Δh_v, Δs_v). The values of (Δh_1, Δs_1, Δh_2, Δs_2) are fixed by the constraints on ϕ and κ. The above seven parameters are determined from a least-squares-fitting program in which the parameters are varied in sequence until the root-mean-square deviation F becomes a minimum. F is defined as

$$F = 100\left((L-1)^{-1} \sum [\ln(\sigma T)_{\text{calc}} - \ln(\sigma T)_{\text{expt}}]^2\right)^{1/2}, \qquad (23)$$

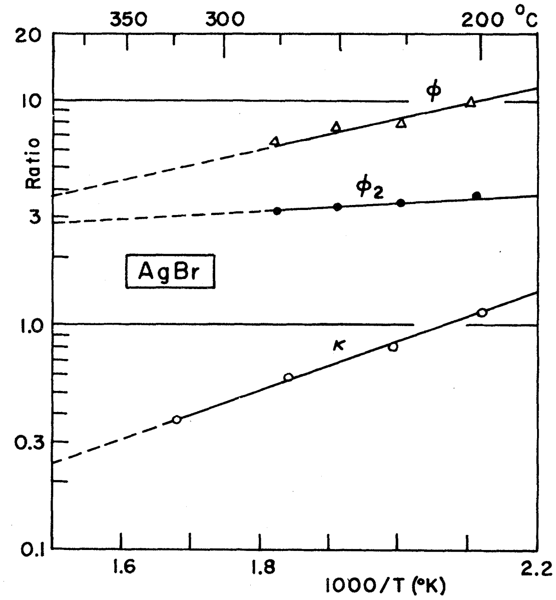

FIG. 5. Mobility ratios for AgBr. Symbols are defined in Fig. 4.

where T is the temperature at which the data points are being analyzed and L is the number of data points.

The conductivity fit is confined to an intermediate temperature range, where the first-order DHL theory is adequate and where corrections for impurities are also small. The upper and lower temperature limits are determined by the χ^2 test discussed in Sec. III D. For AgCl, the useful temperature range is 200–300 °C, and for AgBr, 170–245 °C. First the conductivity fit is carried out with the impure crystal analysis while allowing all remaining parameters to vary, including the impurity concentration c. For both AgCl and AgBr, c turns out to have reasonable values of about 1.7 ppm. There is no significant difference between the parameters obtained for different samples (except for the association entropy η in a few cases) as indicated by the results in Table I. Next the fit is carried out with the pure crystal analysis. In this case the average h_F and s_F obtained from the impure crystal analysis are kept constant and only Δh_v and Δs_v are varied. These last two parameters are finally averaged for all samples. The over-all consistency of the analysis is shown in Table I.

Since the calculation of both the concentrations and the mobilities from the parameters is a highly nonlinear process involving transcendental functions, it is desirable to use some auxiliary observations to ensure that the fitting process is behaving reasonably. One such check is to use two different sequences for varying the seven ad-

TABLE I. Consistency of parameters for conductivity fitting for different samples. Four samples of each type of crystal are included. Error limits show maximum, rather than standard, deviations.

Parameter	AgCl Impure	AgCl Pure	AgBr Impure	AgBr Pure
h_F (eV)	1.452 ± 0.002		1.134 ± 0.001	
s_F/k	9.37 ± 0.02		6.54 ± 0.01	
Δh_v (eV)	0.275 ± 0.001	0.275 ± 0.001	0.324 ± 0.001	0.324 ± 0.001
$\Delta s_v/k$	−0.635 ± 0.005	−0.640 ± 0.001	1.155 ± 0.004	1.153 ± 0.001
χ (eV)	0.62 ± 0.01		0.66 ± 0.04	
η/k	0.69 ± 0.02		8.1 ± 0.2	
c (ppm)	1.7 ± 0.2		1.7 ± 0.1	

justable parameters; for this purpose the first sequence was $(h_F, s_F, \Delta h_v, \Delta s_v, c, \chi, \eta)$ and the second was $(s_F, h_F, \Delta s_v, \Delta h_v, \eta, c, \chi)$. In general, the parameter values obtained from a fit do not depend on the sequence used if the parameters have been varied long enough. As an example the parameters obtained from the above two sequences for a doped crystal of AgCl are shown in Table II.

Another check on finding a good minimum in the multidimensional parameter space is shown in Fig. 6. It is clear that a well-defined minimum exists for variation of each parameter (this is not always true at the beginning of the parameter variation). The actual minimum point for each parameter is determined by fitting a fourth-order polynomial to the five lowest points on each curve.

D. Testing goodness of fit

At higher temperatures one finds that the deviation between experimental and predicted conductivities rises very rapidly, and at the melting point the deviation may be as large as (40–100)% (see Fig. 2 of Ref. 18). Thus, one is led to the conclusion that the high-temperature data cannot be included in the analysis, that is, the conductivity theory even with the inclusion of the DHL corrections is not able to provide a satisfactory description of the observations in this temperature range. A similar difficulty occurs to a lesser extent at very low temperatures, even when the presence of divalent impurities is taken into account. It becomes important, therefore, to have a reliable test as to whether a conductivity fit is good or bad. The procedure for applying χ^2 tests for this purpose has been given elsewhere,[18] but the principal ideas are outlined briefly below.

A qualitative indication of the goodness of fit is given by deviation plots as shown in Fig. 7. The sizable, and obviously systematic, deviations in Fig. 7(a) suggest strongly that this is *not* a good fit: either the model is inappropriate, or the

TABLE II. Consistency of parameters for conductivity fitting for different sequences. The two sequences for this doped sample of AgCl are defined in the text.

Parameter	First sequence	Second sequence
h_F (eV)	1.4469	1.4467
s_F/k	9.443	9.443
Δh_v (eV)	0.2743	0.2742
$\Delta s_v/k$	−0.6169	−0.6175
χ (eV)	0.6255	0.6257
η/k	9.648	9.655
c (ppm)	24.82	24.88

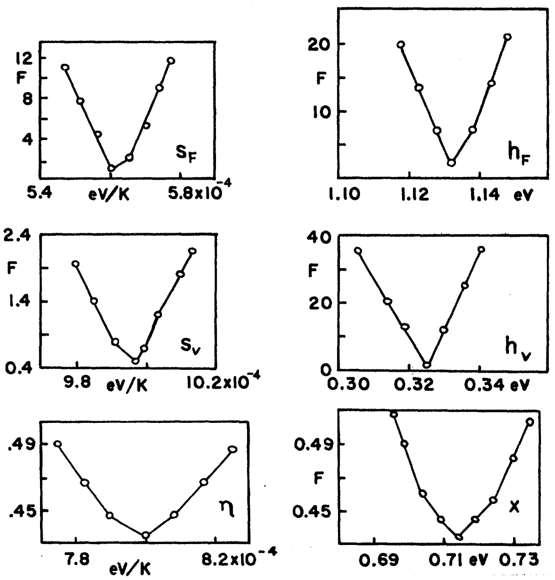

FIG. 6. Behavior of root-mean-square deviation *F* with variation of parameters. In each case the indicated parameter is varied over the range as shown, while all other parameters are held constant.

proper values of the parameters have not yet been obtained. At the end of the fitting procedure in Fig. 7(b), the smaller, and apparently random, deviations suggest that a good fit has been obtained. What is needed now is a quantitative statistical test for the goodness of fit.

The first problem is to determine whether the deviations are, indeed, random, and if so, what is their size. This is done by applying a χ^2 test to the deviations of Fig. 7(b), for instance, for the intermediate temperature range where it is expected that an adequate fit can be obtained with the proposed model. The set of deviations is tested to determine the probability that the deviations are distributed according to a normal error curve, with a mean deviation m and a standard deviation σ_0 to be determined from the data.[19] By pooling data for several different samples for each kind of crystal, we obtain about 30 data points, which are divided into 5 or 6 groups according to the size of the deviation. For AgCl we find $m = 0.004\%$, $\sigma_0 = 0.39\%$, and $\chi^2 = 0.95$ for two degrees of freedom, giving a satisfactory confidence level of 60%. The results for AgBr are $m = -0.002\%$, $\sigma_0 = 0.43\%$, and $\chi^2 = 2.54$ for three degrees of freedom, giving a confidence level of 50%. Furthermore, the calculated values of σ_0, 0.39%, and 0.43% for AgCl and AgBr, respectively, are quite consistent with an error analysis of the experimental procedure. It is estimated that overall errors in the conductivity arising from temperature uncertainties, sample dimensions, and resistance measurements may amount to about 0.5%.[18]

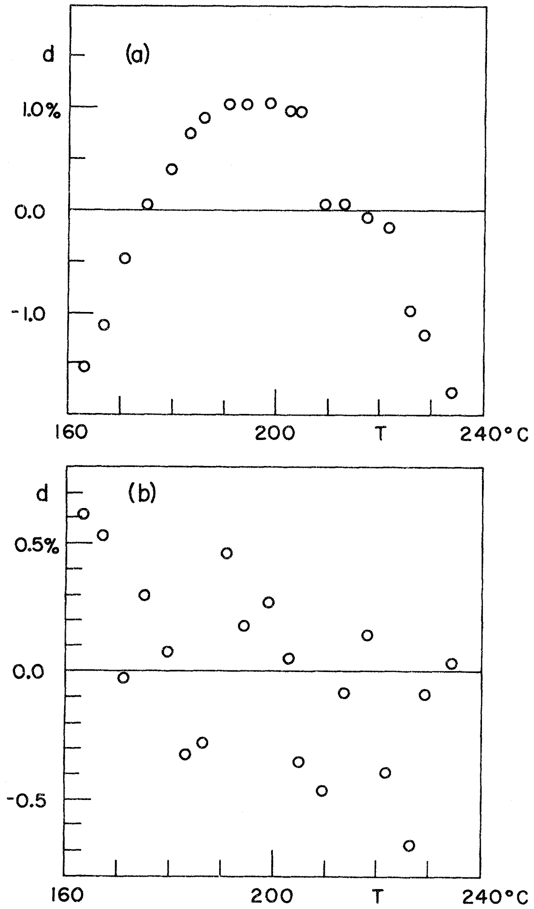

FIG. 7. Deviation plots for conductivity fits for a sample of AgBr in the intermediate temperature range. (a) At an early stage of adjusting the parameters in the fitting procedure. (b) At the end of the fitting procedure after the parameters have been adjusted to obtain the best fit. (Note the change in the scale of deviations.)

On the basis of the above analysis we assume that each deviation d_i has a normal error distribution with standard deviation $\sigma_i = \sigma_0$ and mean $m = 0$. In this situation we find that a quantity defined by

$$\chi^2 = \sum_i \frac{d_i^2}{\sigma_i^2} = \frac{1}{\sigma_0^2} \sum_i d_i^2$$

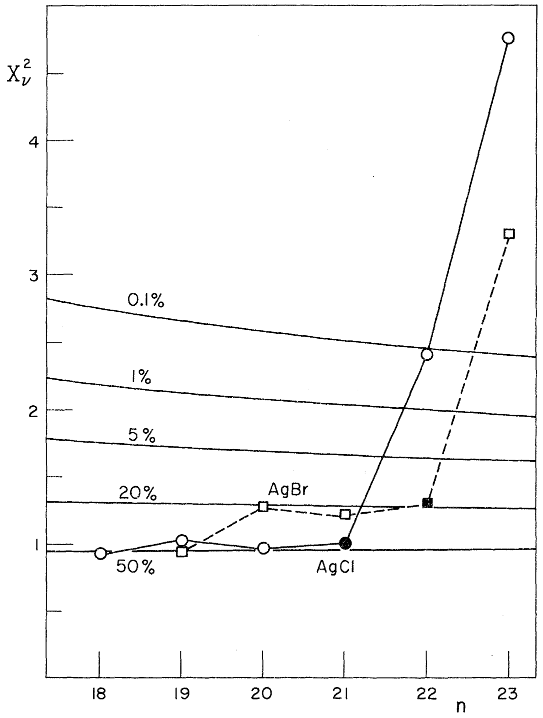

FIG. 8. χ^2 test for conductivity fits for AgCl and AgBr. As additional data points are included at the upper end of the intermediate temperature range, the reduced χ_ν^2 increases markedly. The solid points indicate the upper temperature limit selected for determination of the parameters. The solid lines show confidence levels for $n-6$ degrees of freedom, where n is the number of data points.

should have a χ^2 distribution,[20] and we consider this sum as a measure of the goodness of fit. The χ^2 test is then used to determine the limiting temperature as follows. First a fit is obtained for a reasonable temperature range, and χ^2 is calculated to ensure that the fit is reasonable. Then the additional data points are added one by one at the upper end of the temperature range, in steps of 5 °C, and a new fit and a new value for χ^2 are calculated. The results for each type of crystal are illustrated in Fig. 8. The sharpness of the rise of χ^2_ν upon encroachment into the higher-temperature region is striking. Here χ^2_ν is defined as χ^2/ν where ν is the number of degrees of freedom. As a consequence of the above test, any possible ambiguity in choosing the upper temperature is certainly not more than 5 °C. Results also show that there is no uncertainty at all in the values of the parameters obtained from the fit, even if the range extends far enough to give an unacceptably large value of χ^2_ν.

IV. RESULTS OF THE ANALYSIS

A. Fit at intermediate temperatures

Tables III and IV for AgBr give values for the parameters obtained from the fitting process at intermediate temperatures. The parameters are obtained from the fitted parameters and the constraints according to

$$\Delta h_1 = \Delta h_v + \Delta h_\kappa + \Delta h_{\phi_2} , \tag{24}$$

$$\Delta s_1 = \Delta s_v + \Delta s_\kappa + \Delta s_{\phi_2} + k \ln 3 , \tag{25}$$

$$\Delta h_2 = \Delta h_v + \Delta h_{\phi_2} , \tag{26}$$

$$\Delta s_2 = \Delta s_v + \Delta s_{\phi_2} , \tag{27}$$

which follow from Eqs. (20) and (21) and the definitions of ϕ and κ. All motional entropies are referred to the standard vibrational frequency of 5.8×10^{12} Hz.[21]

Corish and Jacobs[22] have determined the defect parameters for AgCl by analyzing conductivity curves over a large portion of the intrinsic temperature range. Their general procedure is quite similar to ours, and their results are also in good agreement in most cases. They ran into difficulty with Δh_2 and Δs_2 for the noncollinear interstitialcy, however, and obtained widely different values for the two different samples. Most of this trouble may be due to the fact that these two parameters are determined primarily by the curvature of the conductivity plot in the high-temperature region, much of which may be caused by the failure of the DHL theory rather than by contributions from the noncollinear interstitialcy jumps.

The only surprising feature of our results is the value of $\Delta h_1 = -0.014$ eV for AgCl, a negative activation enthalpy being unexpected and unphysical. (The result is nonetheless within the experimental range of 0.008 ± 0.020 eV reported by

TABLE III. Defect parameters for AgCl.

Parameter [a,b]	Aboagye and Friauf [c]	Corish and Jacobs [d]	Weber and Friauf [e]	Weber and Friauf [f]
h_F	1.452	1.471	1.44	1.25
s_F/k	9.41	10.1	9.4	6.0
Δh_v	0.275	0.288	0.27	0.35
$\Delta s_v/k$	−0.640	−0.500	−1.38	0.25
Δh_1	−0.014	0.052	0.008 ± 0.021	0.114 ± 0.022
$\Delta s_1/k$	−3.81	−2.74 (avg)	−3.76	−1.64
Δh_2	0.104	0.308, 0.688	0.132 ± 0.050	0.260 ± 0.046
$\Delta s_2/k$	−3.24	−0.147, +6.40	−3.15	−0.55
Δh_i (avg)			0.045	0.16

[a] Enthalpies are given in eV and entropies in e.u. (entropy unit).

[b] All motional entropies are referred to a standard vibrational frequency of 5.8×10^{12} Hz (Ref. 21).

[c] This work.

[d] Conductivity analysis includes DHL theory (Ref. 22).

[e] Calculated (Ref. 13) with mobility values from Abbink (Ref. 8), whose conductivity analysis includes DHL theory.

[f] Calculated (Ref. 13) with mobility values from Müller (Ref. 5), whose conductivity analysis is done with the simple theory without DHL interactions.

TABLE IV. Defect parameters for AgBr.

Parameter [a,b]	Aboagye and Friauf [c]	Weber and Friauf [d]	Weber and Friauf [e]
h_F	1.134	1.28	1.06
s_F/k	6.55	12.2	6.1
Δh_v	0.325	0.30	0.34
$\Delta s_v/k$	1.16	−0.28	1.02
Δh_1	0.043	0.058 ± 0.003	0.064 ± 0.006
$\Delta s_1/k$	−3.18	−3.64	−3.38
Δh_2	0.278	0.274 ± 0.017	0.245 ± 0.018
$\Delta s_2/k$	1.35	0.45	−0.18
Δh_i (avg)		0.17	0.15

[a] Enthalpies are given in eV and entropies in e.u. (entropy unit).

[b] All motional entropies are referred to the same standard vibrational frequency as for AgCl (see Table III).

[c] This work.

[d] Calculated (Ref. 13) with mobility values from Taltow (Ref. 3), whose conductivity analysis includes DHL theory.

[e] Calculated (Ref. 13) with mobility values from Müller (Ref. 5), whose conductivity analysis is done with the simple theory without DHL interactions.

Weber and Friauf.[13]) In any case a very small value of Δh_1 is inevitable in our analysis because of the use of the mobility ratios from Abbink.[8] His values, which are obtained with consideration of the DHL corrections, are appreciably larger than those reported by other workers not using these corrections,[13] but lead to an average interstitial contribution that is nearly independent of temperature ($\Delta h_i = 0.045$ eV). Müller,[5] on the other hand, worked in the low-temperature region to avoid the use of the DHL corrections and obtained even larger values of mobility ratios, but also with a greater temperature dependence ($\Delta h_i = 0.16$ eV). From consideration of his results on AgBr as well, it appears that his attempt to circumvent use of the DHL theory was partially, but not completely, successful, and hence his results for the temperature dependence may be somewhat unreliable. In conclusion, we can only say that the combination of our analysis with Abbink's results yields a value of Δh_1 for AgCl that is very nearly equal to zero.

B. Extrapolation to high temperatures

To extrapolate to the high-temperature region, we propose to assume that all parameters, that is all enthalpies and entropies, both for formation and mobility, are independent of temperature. Also, as mentioned earlier, we cannot continue the analysis to higher temperatures in the usual way since the first-order DHL corrections are not large enough to account for all of the observed anomaly in the conductivity; see Figs. 1 and 2, where it appears that an even greater concentration of defects is needed than that predicted by the DHL theory.

We can provide this larger concentration in a formal way by introducing an extra interaction energy Δg_{extra} such that[2]

$$[\exp(\Delta g_{\text{extra}}/2kT)]\sigma_{\text{theory}} = \sigma_{\text{expt}} , \tag{28}$$

where σ_{theory} is calculated using first order DHL corrections for both concentrations and mobilities. Thus we compare the experimental conductivity to the predicted value by calculating

$$\Delta g_{\text{extra}} = 2kT(\ln\sigma_{\text{expt}} - \ln\sigma_{\text{theory}}) . \tag{29}$$

Since σ_{theory} already includes the effect of the first-order DHL corrections on the concentrations, the total free-energy change required to account for the observed results is then given by

$$\Delta g = \Delta g_{\text{DHL}} + \Delta g_{\text{extra}} , \tag{30}$$

where Δg_{DHL} is given by Eq. (11).

In following this procedure, we are ascribing all of the additional anomaly in the conductivity to an additional enhancement of the concentration of defects, without consideration of any further changes in the mobilities. This approach seems reasonable, at least as a first approximation, since the influence of the long-range Coulomb interactions has a much larger effect on concentrations than on mobilities in the first-order DHL theory. Concentrations are increased by as much as a factor of about 3 for AgBr, for instance, whereas the mobility drag factor decreases the mobilities by less than 10% in all cases.

Results for extrapolation to high temperatures are summarized in Figs. 9 and 10, which show the interaction energy Δg needed to account completely for the observed anomaly at high temperatures in terms of enhanced defect concentrations. Δg_{DHL} is the interaction energy obtained from the DHL theory alone. The interaction energy Δg_{SK} has been calculated by Sevenich and Kliewer for AgCl.[2] There still exists difficulty in performing similar calculations on AgBr, presumably because of the larger defect concentrations.[23]

C. Conclusions

Obviously, the DHL theory is not able to account entirely for the high-temperature ionic conductivity of the silver halides. Even the much improved calculations of Sevenich and Kliewer[2] on AgCl do not seem to change the picture appreciably: Fig. 9 shows that Δg_{SK} is only slightly larger than Δg_{DHL},

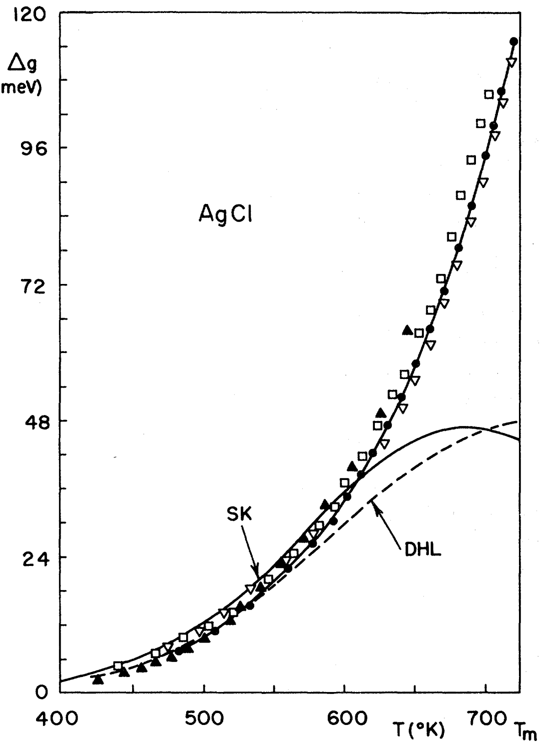

FIG. 9. Conductivity anomaly for AgCl (T_m=450 °C =723 °K). $-\Delta g$ is the additional free energy needed to increase the defect concentration enough to bring the extrapolated conductivity up to the observed values. Points show experimental results, Δg_{DHL} is from the DHL theory of Eq. (11), and Δg_{SK} is from the extended calculations of Sevenich and Kliewer (Ref. 2).

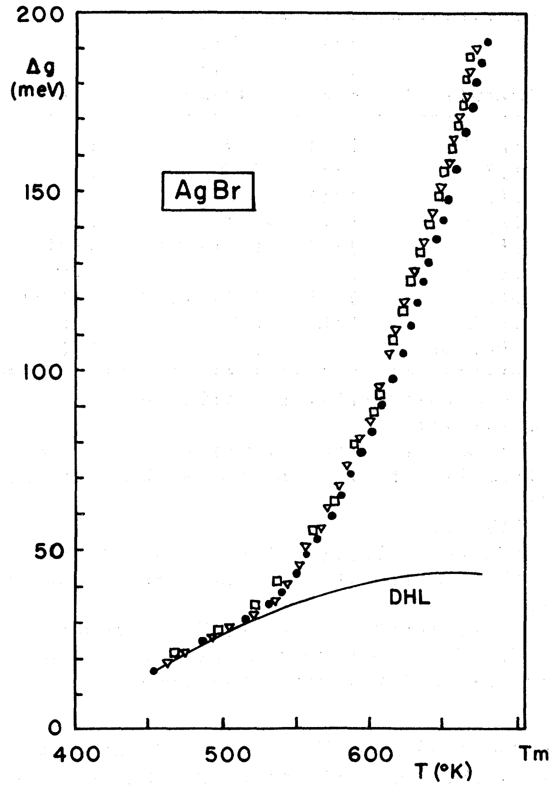

FIG. 10. Conductivity anomaly for AgBr (T_m =428 °C = 701 °K). See Fig. 9 for the legend.

whereas the experimental results require a Δg more than twice as large as Δg_{DHL}. The difficulty in attempting to calculate Δg_{SK} for AgBr, where the defect concentrations are an order of magnitude larger than for AgCl, may suggest that even the calculations on AgCl perhaps suffer from convergence problems and are correspondingly unreliable.[23] Unless something of this sort is supposed, however, there appears to be no way in which long-range Coulomb interactions can account for all of the high-temperature anomaly in the conductivity. It is clear from Figs. 9 and 10, nevertheless, that the DHL corrections do make a noticeable contribution in this temperature region, and therefore any theory that ignores these effects is incomplete.

The remaining question, then, is what physical process is causing the part of the anomaly that cannot be explained by the DHL theory. A reasonable possibility is that there is a general softening of the lattice, a sort of premelting phenomenon. This has been suggested for many years by Teltow's group,[3-5] and is also indicated by changes in a number of other physical properties as the melting point is approached—loss of mechanical hardness, decrease in velocity of sound, and greatly enhanced thermal diffuse scattering of x rays. In these circumstances it seems very possible that both the formation and jump energies may decrease appreciably with temperature. Such a behavior could be included in our calculations by introducing an explicit temperature dependence for h_F, Δh_v, etc. This would cause enhanced defect concentrations and also increased mobilities, with both effects leading to a further increase in conductivity. At present this suggestion is only speculative, but it is hoped that a more quantitative evaluation can be carried out in the future.

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*Present address: Dept. of Physics, University of Cape Coast, Cape Coast, Ghana.

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