

methods of measurement of the two-magnon-process contribution to the uniform precession linewidth are in good agreement. At 300 and 4.2°K both methods of measurement showed the two-magnon-process contribution to be less than 0.10 Oe, and the differences between the results of the two methods of measurement to be not far from the experimental error of the measurements. In the sample used here, relaxation of the uniform precession mode at either 300 or 4.2°K was not predominantly via the two-magnon process, but at the latter temperature this is probably due to broadening of the linewidth by paramagnetic impurities.

ACKNOWLEDGMENTS

The author gratefully acknowledges many valuable conversations with Dr. R. D. Myers during the course of this work. The author also wishes to express his appreciation to Dr. G. R. Jones for several beneficial discussions and for communication prior to publication of his ideas on the effects of surface roughness on resonance linewidths. The results obtained from the computer programming of O. R. Cruzan and A. Hausner were very helpful in the analysis of the measurements and are greatly appreciated.

Measurements of Thermal Expansion and Thermal Equilibrium Defects in Silver Chloride*

ROBERT D. FOUCHAUX† AND R. O. SIMMONS

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois

(Received 6 July 1964)

Linear thermal expansion of silver chloride has been measured by simultaneous macroscopic and x-ray methods on the same sample and the same temperature scale ($\pm 0.1^\circ\text{C}$). The two expansions agree within the experimental error of about 3×10^{-6} throughout the measurement range, from -62°C to within 4° of the melting point. This implies that the equilibrium concentrations of Schottky defects are less than 9×10^{-6} and that their enthalpy of formation is greater than 1.45 eV. This limit is consistent with results of Compton for chlorine diffusion. Results of other workers for high-temperature variations in ionic conductivity, thermal expansivity, silver diffusivity, and heat capacity can be interpreted in terms of a single species of defect, the cation Frenkel defect. An empirical Mie-Grüneisen equation of state represents, by a suitable choice of fitting parameters, the measured expansion of silver chloride when defect concentrations are small. However, the values of the fitting parameters appear to be inconsistent with those to be expected from the Grüneisen phenomenological theory. Because the concentrations of Frenkel defects are relatively large, an extrapolation method applied to the thermal expansion can be used to estimate their formation enthalpy as 1.4 eV. Further analysis is consistent with the suggestion that the defects make an explicit contribution to the thermal expansion coefficient of the crystal.

I. INTRODUCTION

SPECULATIONS on the equilibrium-defect structure of silver halide crystals at high temperatures¹⁻⁵ mention the possibility of appreciable concentrations of Schottky defects. Experimenters who measured heat capacity,⁶ thermal expansion,⁷ and ionic conductivity⁸

have also given interpretations requiring appreciable Schottky-defect concentrations. Unfortunately, these arguments either (1) contain rather arbitrary assumptions concerning the behavior of the hypothetical defect-free crystal, (2) depend upon an uncertain separation of the presumed effects of the Schottky defects from those of the larger concentrations of cation Frenkel defects known to be present,^{9,10} or (3) do not permit quantitative estimates of the equilibrium-defect concentrations to be made.

There is a type of experiment in which such arbitrariness is not present. It has been shown¹¹ for a cubic

* Supported by the U. S. Atomic Energy Commission.

† Present address: Department of Physics, Lehigh University, Bethlehem, Pennsylvania. This paper is based in part on the Ph.D. thesis presented by R. D. F. at the University of Illinois, Urbana, Illinois.

¹ A. W. Lawson, *Phys. Rev.* **78**, 185 (1950).

² F. Seitz, *Rev. Mod. Phys.* **23**, 328 (1951); see also *Phys. Rev.* **56**, 1063 (1939).

³ J. W. Mitchell, *J. Appl. Phys.* **33**, 406 (1962); see also *Phil. Mag.* **40**, 249, 667 (1949).

⁴ A critical review has been given by A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 20, p. 246.

⁵ H. F. Fischmeister, *Trabajos Reunion Intern. Reactividad Solidos*, 3°, Madrid, 1956 I, 321 (1957).

⁶ K. Kobayashi, *Phys. Rev.* **85**, 150 (1952); *Sci. Rept. Tohoku Univ., First Ser.*, **34**, 112 (1950).

⁷ W. Zieten, *Z. Physik* **146**, 451 (1956).

⁸ C. H. Layer, M. G. Miller, and L. Slifkin, *J. Appl. Phys.* **33**, 478 (1962).

⁹ I. Ebert and J. Teltow, *Ann. Physik* **15**, 268 (1955).

¹⁰ W. D. Compton, *Phys. Rev.* **101**, 1209 (1956); W. D. Compton and R. J. Maurer, *Phys. Chem. Solids* **1**, 191 (1956).

¹¹ J. D. Eshelby, *J. Appl. Phys.* **25**, 255 (1954); *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 3, p. 79; R. W. Balluffi and R. O. Simmons, *J. Appl. Phys.* **31**, 2284 (1960); K. Fischer and H. Hahn, *Z. Physik* **172**, 172 (1963).

TABLE I. Equilibrium defect concentrations x at the melting temperature, and defect formation enthalpies h in silver chloride.

Investigator	Method	x_F (Frenkel)	x_S (Schottky)	h_F (Frenkel) (eV)	h_S (Schottky) (eV)
Lawson ^a	Strelkow's dilatometric expansions ^b analyzed into "normal" and "anomalous" contributions, the latter attributed to defects, possibly of Schottky type.	...	See method	...	≥ 0.62
Seitz ^c	Inference of vacancy condensation at fusion to yield dislocation pattern producing tail in the fundamental optical absorption. h_F estimated from ionic-conductivity data.	d	$\sim 10^{-3}$	1.08	$\sim h_F + 0.4$
Kobayashi ^e	Specific heat. "Excess" enthalpy attributed to defects and resolved into two components.	7.5×10^{-3}	$\sim 10^{-3}$	1.53	($\sim h_F$)
Ebert and Teltow ^f	Ionic conductivity of pure and of doped samples, neglecting association of defects with the doping impurities.	3.5×10^{-3}	(g)	1.69	...
Ebert and Teltow ^f	Ionic conductivity with defect-impurity association taken into account.	1.5×10^{-3}	(g)	1.43	...
Zieten ^h	Macroscopic thermal expansion of pure and of doped samples. "Excess" expansion attributed to defects.	$\sim 6 \times 10^{-3}$	$\sim 3 \times 10^{-3}$	1.13	...
Fischmeister ⁱ	Comparison of measured macroscopic expansion to Grüneisen theory.	0.98
Mitchell ^j	Inference that at high temperatures, anion-vacancy concentrations are sufficient for occurrence of observed dislocation climb after quenching.	(d)	See method
Layer, Miller, and Slifkin ^k	Enhanced ionic conductivity of quenched crystals.	(d)	$> 3 \times 10^{-5}$
Nicklow and Young ^l	X-ray lattice expansion compared to Strelkow's dilatometric measurements. ^b	(d)	$< 9 \times 10^{-4}$ ^m	$0.80 < h_F < 1.47$...
Lawn ⁿ	X-ray lattice expansion compared to Zieten's macroscopic measurements. ^h	(d)	2×10^{-3}	0.76; 0.94	...

^a See Ref. 1.^b See Ref. 17.^c See Ref. 2.^d Assumed predominant, but no concentration given.^e See Ref. 6.^f See Ref. 9.^g Schottky disorder considered as possible cause for anomalous rise in ionic conductivity near the melting temperature.^h See Ref. 7.ⁱ See Ref. 5.^j See Ref. 3.^k See Ref. 8.^l See Ref. 15.^m See footnote 18.ⁿ See Ref. 16.

crystal that the relative linear expansion $\Delta L/L$ as measured by a macroscopic method, and the relative change in x-ray lattice constant $\Delta a/a$ will be equal if the number of ionic sites is unchanged. This result holds regardless of the value of the dilations produced around individual defects, provided only that a sufficiently dense random distribution of defects is present and that the crystal is not externally constrained. When the Frenkel defect (an interstitial cation and the resulting silver vacancy¹²) is formed, it may dilate the crystal lattice, but it leaves the total number of substitutional ionic sites unchanged. On the other hand, the Schottky defect (anion and cation vacancies¹³) not only dilates the crystal because of relaxation of the ions around the vacancies¹⁴ but also produces two new substitutional ionic sites per defect. If new sites are

generated, then

$$\Delta N/N = 3(\Delta L/L - \Delta a/a), \quad (1)$$

where $\Delta N/N$ is the fractional increase in the number of substitutional ionic sites. Therefore, sufficiently accurate measurements of both types of expansion, made on the same temperature scale as a crystal is heated, will unequivocally separate the effects of Frenkel defects and of the lattice from those effects which accompany the creation of new ionic sites.

Nicklow and Young¹⁵ and Lawn¹⁶ measured x-ray lattice expansions of silver chloride up to the melting point. By comparing their expansions with macroscopic measurements by others,^{7,17} they drew conflict-

¹² J. Frenkel, Z. Physik **35**, 652 (1926).¹³ W. Schottky, Z. Physik. Chem. **B29**, 335 (1935).¹⁴ N. F. Mott and M. L. Littleton, Trans. Faraday Soc. **34**, 485 (1938).¹⁵ R. M. Nicklow and R. A. Young, Phys. Rev. **129**, 1936 (1963). We want to thank these authors for a copy of their paper prior to its publication.¹⁶ B. R. Lawn, Acta Cryst. **16**, 1163 (1963).¹⁷ P. G. Strelkow, Physik Z. Sowjetunion **12**, 73 (1937).

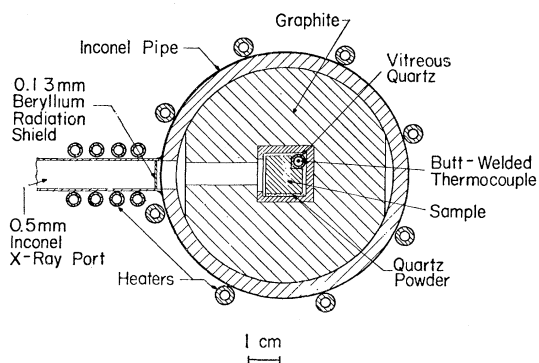


FIG. 1. Cross section of furnace core at the location of the x-ray crystal in the silver chloride bar. The sample is 53 cm long and the graphite 2.5 m long. The inconel pipe is insulated along a 3.5 m length and is supported at the ends only.

ing conclusions about the equilibrium defect content.¹⁸ Both of these comparisons, besides depending upon measurements of the lattice expansion of limited accuracy, are subject to objection on practical grounds. They rely upon the agreement between two temperature scales under different experimental conditions in two different laboratories. Because of the large thermal expansion coefficient, a temperature error alone of 1°C near the melting point could hide a Schottky defect concentration of 3×10^{-4} in silver chloride. Accurate comparisons are also complicated by effects such as differing sample purities, possible differences in physical constraint of the samples, and existing disagreement between the macroscopic expansion measurements at temperatures at which defect concentrations must be negligible.

We summarize the various speculations, results, and inferences from experiments on silver chloride in Table I.

The present work measured both the length and the x-ray lattice expansions of a bar of high-purity silver chloride over a broad temperature range. The general result of the present work is to confirm in the most direct and unambiguous manner that the dominant equilibrium disorder in silver chloride is of Frenkel type. Because the measurements define this dominance quantitatively, a number of interesting questions about the high-temperature properties of this crystal can be considered in some detail. We examine the possibilities of subordinate equilibrium defects not of Frenkel type, compare the present results critically with tracer diffusion and ionic conductivity measurements, compare the observed thermal expansion with existing phenomenological theory, and consider the possibility that the

¹⁸ Because Nicklow and Young do not quantify their statement of results, we compared the total expansions from 200 to 440°C of Nicklow and Young, and of Strelkow. Error limits were assigned according to the standard deviations and estimated temperature uncertainty given by Nicklow and Young, and estimated maximum error in length and temperature measurement by Strelkow. Converted to an uncertainty in expansion alone, these are $\delta(\Delta a/a) = 2 \times 10^{-4}$ and $\delta(\Delta L/L) = 1 \times 10^{-4}$, respectively.

thermal expansion coefficient of the crystal is altered by the presence of defects.^{7,19}

II. EXPERIMENTAL

The apparatus was similar to that used for expansion measurements on fcc metals by Simmons and Balluffi.²⁰ Certain modifications were however dictated by the chemical, mechanical, and thermal properties of silver chloride.

A. Sample

The sample bar was extruded at 4×10^4 kg/cm² with its final square cross section (see Fig. 1), straightened in a bakelite press, then recrystallized on fused quartz at about 440°C for twelve hours in a prepurified nitrogen atmosphere, and cooled to room temperature at 25°/h or slower. This method produced grains which, for the most part, extended across the entire cross section, and were 5 to 50 mm in length. A large grain with a [110] crystallographic axis within 3° of the sample face normal was chosen as the x-ray crystal. The bar was cut to its 53 cm final length with this x-ray grain in the middle.

Spectrographic analysis of the extruded silver chloride showed the following impurities present in ppm: Al, 10; Ca, <10; Cr, very faint trace; Cu, 3; Fe, 7; Mg, 3; Mn, very faint trace; Si, 3; Sn, 2; tested for but not detected were As, Au, Ba, Be, Bi, Cd, Co, Ga, Ge, Hg, In, La, Li, Mo, Na, Ni, Nb, Pb, Pt, Sb, Sr, Ti, Tl, W, V, Y, Zn, and Zr. The ionic conductivity of the extruded and annealed material, measured at 1000 cps and 23°C, averaged 0.89×10^{-7} ($\Omega\text{-cm}$)⁻¹, a value consistent with the spectrographic analysis.²¹ After the expansion experiments, the conductivity was essentially unchanged.

The entire bar was thoroughly cleaned, then portions of the ends were polished with 3% KCN solution on a flannel cloth to give a smooth surface. A series of pyramidal indentations of 70 μ base width were then spaced about 0.7 mm apart on each end to serve as reference marks.

B. Temperature Measurement and Control

A smooth square cross section fused quartz tube provided a flat nonreactive support essentially without restraint on the sample. Because of the low thermal conductivity of silver chloride, the axial butt-welded thermocouple was placed within this tube in a notch in the sample, as shown in Fig. 1.

¹⁹ M. F. Merriam, D. A. Wiegand, and R. Smoluchowski, *Phys. Rev.* **125**, 52, 65 (1962). These authors made photoelastic measurements; it has recently been shown that this technique may produce plastic deformation in the portion of the crystal examined [R. L. Wolfe and C. L. Bauer, *J. Appl. Phys.* **35**, 658 (1964)].

²⁰ R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **129**, 1533 (1963), and earlier papers.

²¹ F. C. Brown, *Phys. Chem. Solids* **4**, 206 (1958).

A significant error might be introduced by a thermal gradient in the sample bar at the exposed surface facing the x-ray port. Consequently, a beryllium radiation shield was installed covering the port. Its temperature was maintained well within 10° of the sample temperature at all times, this limit being sufficient to keep the x-ray grain surface temperature within 0.1° of the indicated temperature, as given by calculation and by independent experimental measurements of lattice parameter as a function of port heater power.²² Consequently, the x-ray and macroscopic measurements were made on the same temperature scale to within 0.1°C .

Five runs were made from room temperature to near the melting temperature and back. Temperatures were measured in these runs with a Pt-10%Rh versus Pt thermocouple. From calibration of this couple at the copper melting point²⁰ we expect that the indicated temperature at 455°C is correct within 0.4°C . One run was made from room temperature to -70°C and back, by pumping cold gaseous nitrogen into the furnace at each end. For this run the temperature was measured with a copper versus Constantan thermocouple.

Variations in temperature δT from the mean temperature along the sample length during the time required for a measurement were maintained such that $\alpha_T \delta T \leq 10^{-5}$, where α_T is the linear thermal expansion coefficient. This required that the temperature be controlled to $\pm 0.1^\circ\text{C}$ near 450°C . The temperature of the sample was changed at the rate of 25°C per hour or slower, in order to avoid thermal straining of the long soft bar and in order to allow quasiequilibration of the defect structure at each temperature.

C. Length-Expansion Measurement

The sample gauge length at 20.0°C was determined to 0.01 mm with a Wild-Heerbrugg cathetometer. Rigidly parallel filar micrometer microscopes²⁰ were then used to obtain about 120 sets of measurements of expansion at various temperatures, after the sample was annealed in place on its final support for more than 4 h at temperatures above 400°C .

Some difficulty in the length measurement was encountered, due to changes in the appearance of the reference indentations, due to reversible changes in the surface reflectivity and color with temperature, and, more troublesome, due to irreversible changes in the surface, especially on one end. After the experiment, visual inspection showed that this end of the sample was slightly darkened and the surface roughened. It is not understood why only one end showed this effect, since both ends were illuminated in the same manner with red light.

The first-cooling run and the second-heating run were considered as complete independent sets of meas-

urements, in which the same sets of indentations were used throughout. Data from the second-cooling run and later were pieced together to give a third independent set. For each such run the sample length at 20°C was recovered within about 8μ . The agreement of heating and cooling runs indicates that the defects were in equilibrium when measurements were made, and that no plastic deformation occurred. The sample could be moved freely by sliding throughout the measurements.

D. Lattice-Expansion Measurement

The x-ray lattice-expansion measurements were made by a back-reflection, oscillating-camera method using $\text{FeK}\alpha_1$ radiation ($\lambda = 1.93597 \text{ \AA}$) and a (440) reflection. About 140 exposures were made at various temperatures. The required exposure time varied from about 2 min at the lowest temperature to over 2 h at the highest.

During the course of the x-ray measurements it became apparent that the x-ray crystal had several small-angle grain boundaries with misorientations of less than $\frac{1}{2}^\circ$. The largest subgrain was about 7 mm wide, and two others of about 2 to 3 mm size were found by moving the sample and rotating the camera. Measurements above 300°C for the first two complete runs (1) showed three jumps in the apparent $\Delta a/a$ which could be correlated with adjustments of the sample position, (2) had individual deviations of more than five times the usual average deviation, and (3) gave generally different $\Delta a/a$ values than the later three runs. These anomalies were traced to an effective eccentricity in sample location with respect to the camera rotation axis, arising when the x-ray beam struck a subgrain boundary.²² Data above 275°C from the first two runs were therefore rejected and in run 3 and later the sample position was suitably adjusted to avoid any subgrain boundary.

As a test for a spurious $\Delta a/a$ due to x-irradiation, measurements were taken at 12°C before and after 21 h of continuous irradiation at the intensity used for all the x-ray exposures. These measurements agreed within 3 ppm, showing that there was negligible error in $\Delta a/a$ due to the irradiation. This conclusion is supported by the good reversibility of the x-ray measurements at all temperatures in the last three runs.

III. RESULTS

Using $a_{20} = 5.54939 \text{ \AA}$, we plotted the 34 values of $\Delta a/a_{20}$ in the range -61.5 to 200°C on a 1.0 by 2.5 m graph and drew a smooth curve through the points. The smoothed data were then used to prepare tables of $\Delta a/a_{20}$ versus T for various a_{20} in the range 5.54930 to 5.54980 \AA . Finally, we used a least-squares procedure, minimizing with respect to a_{20} the

²² R. D. Fouchaux, Ph.D. thesis, 1963, University of Illinois (unpublished).

TABLE II. Thermal expansion of silver chloride.

$T(^{\circ}\text{C})$	Present work						
	$10^6\alpha_{20}$	$10^3\Delta a/a_{20}$	$10^3\Delta L/L_{20}$	$10^3\Delta L/L_{20}^a$	$10^3\Delta L/L_{19\pm 2}^b$	$10^3\Delta a/a_{20}^c$	$10^3\Delta a/a_{20}^d$
	$a_{20}=5.5496 \text{ \AA}$					$a_{20}=5.5548 \text{ \AA}$	$a_{20}=5.5494 \text{ \AA}$
-62.5	...	-2.42 ^{e,f}
-50.0	2.83	-2.07	-2.1
-25.0	2.91	-1.35	-1.35 ^{e,f}
0.0	2.98	-0.61	-0.61	-0.5
25.0	3.05	0.15	0.15
50.0	3.12	0.93	0.93	1.0 ± 0.14^b	1.0
75.0	3.20	1.73	1.73
100.0	3.31	2.55	2.56	...	2.5	2.6	2.6
105.9	...	2.75	2.76	2.76
125.0	3.41	3.40	3.41
148.3	...	4.21	4.22	4.24
150.0	3.53	4.26	4.27	...	4.2	4.4	4.1
175.0	3.65	5.17	5.18
194.9	...	5.92	5.92	5.89
200.0	3.79	6.11	6.11	...	6.0	6.3	5.5
225.0	3.93	7.09 ^{i,f}	7.09 ^{i,f}
249.1	...	8.05	8.05	8.00
250.0	4.09	8.09	8.09	...	7.8	8.4	7.6
275.0	4.28	9.13	9.13
297.9	...	10.10	10.09	10.07
300.0	4.49	10.23	10.22	...	9.8	10.4	9.8
325.0	4.74	11.39	11.38
342.7	...	12.25	12.23	12.28
350.0	5.08	12.62	12.59	...	12.2	12.7	11.4
375.0	5.54	13.96	13.92
384.8	...	14.54	14.50	14.52
400.0	6.18	15.46	15.42	...	14.9	15.6	14.1
421.5	...	16.88 ^{k,f}	16.84 ^{l,f}	16.90
425.0	7.16	17.12	17.08	17.4	...
440.0	7.94	18.26	18.22	18.6	...
443.9	...	18.58	18.54	18.65
450.0	8.63	19.10	19.06	...	18.3	...	17.4

^a See Ref. 17.^b See Ref. 7.^c See Ref. 15.^d See Ref. 16.^e Errors on entries for $T \leq 200^{\circ}\text{C}$, ± 0.006 .^f Errors are deviation, defined in Eq. (2).^g Errors on entries for $T \leq 200^{\circ}\text{C}$, ± 0.012 .^h Errors are standard deviation given in Ref. 15.ⁱ Errors on entries for $225^{\circ}\text{C} \leq T \leq 400^{\circ}\text{C}$, ± 0.011 .^j Errors on entries for $225^{\circ}\text{C} \leq T \leq 400^{\circ}\text{C}$, ± 0.014 .^k Errors on entries for $421.5^{\circ}\text{C} \leq T \leq 450^{\circ}\text{C}$, ± 0.013 .^l Errors on entries for $421.5^{\circ}\text{C} \leq T \leq 450^{\circ}\text{C}$, ± 0.025 .

quantity

$$\bar{\delta}_{L-\bar{a}}^2 = \sum_{i=1}^n \delta_i^2 / (n-1), \quad (2)$$

where the subscript ($L-\bar{a}$) refers to the differences δ between the $n=41$ raw $\Delta L/L_{20}$ data points in the fitting range and the smoothed $\Delta a/a$ data. The best fit gave $a_{20}=5.54960 \text{ \AA}$ which is in satisfactory agreement with Berry's value of $a_{20}=5.54939 \pm 0.00018 \text{ \AA}$.²³ For the chosen value of a_{20} we had the following deviations in the fitting range: $\bar{\delta}_{a-\bar{a}}=6 \times 10^{-6}$ and $\bar{\delta}_{L-\bar{a}}=12 \times 10^{-6}$. The largest single $\delta_{L-\bar{a}}$ in the fitting range was 24×10^{-6} . The largest $\delta_{a-\bar{a}}$ were 11×10^{-6} (two points).

The above fitting range was chosen because 200°C is about the temperature at which $x_F=10^{-5}$. The fitting range should be as large as possible for good sensitivity in finding a fitting constant a_{20} , but must have concentrations of equilibrium thermal defects which are smaller than experimental error.

²³ C. R. Berry (private communication).

We used the slightly more cumbersome method of fitting raw $\Delta L/L$ data to the smoothed $\Delta a/a$ data, rather than the converse,²⁰ because of the smaller deviation of the $\Delta a/a$ data.

Data points for $\Delta L/L$ and $\Delta a/a$ for the entire temperature range of -61.5 to 451.7°C were plotted on a 5×2.3 m graph. Sixty $\Delta a/a$ measurements and 76 $\Delta L/L$ measurements were included. Table II shows values of $\Delta a/a_{20}$ and $\Delta L/L_{20}$ which are taken from the resulting smooth curves. Included for comparison are values from previous investigators. The work of Strelkow¹⁷ agrees with the present work within 1% of $\Delta L/L$ everywhere, while the values of Zieten⁷ and Lawn¹⁶ appear to be systematically lower and those of Nicklow and Young¹⁵ appear to be systematically higher.

The values from Strelkow were calculated from the expansions given for sample 1 in his Table 1, after the correction to 50.98 mm of an obvious misprint in the stated gauge length of his sample. The values of Zieten were read from his Fig. 2 of the earlier Ref. 7. We note

that his Fig. 1 in the later paper shows 464°C as the melting point; a correction of his temperature scale to put this at 455°C would tend to bring his expansion values into better agreement with other work. The values of Nicklow and Young were calculated from their Fig. 1 curve of lattice spacings using the value d_{20} shown on this curve. Their d_{20} gives $a_{20} = 5.5548 \pm 0.0006 \text{ \AA}$ which differs from Berry's value by 0.0054 Å. The values of Lawn were calculated from his Fig. 1 using $a_{20} = 5.5494 \text{ \AA}$.

Table II also includes smoothed values of the expansion coefficient $\alpha_{20} = (d/dT)(\Delta a/a_{20})$ obtained graphically. Not shown are values of Sharma and of Dutta and Dayal²⁴; their values lie generally about 1 to 2% lower.

Our errors shown in Table II are deviations, defined as in Eq. (2), taken in the temperature intervals indicated. The deviation of the x-ray data increases with increasing temperature primarily because the tangent of the Bragg angle decreases from about 6 at room temperature to about 3.9 near the melting point, which reduces the sensitivity of the measurements. The deviation of the macroscopic expansion data increases at higher temperatures because of the change in the appearance of the indentations mentioned in Sec. IIC.

Table II shows that in the range 200 to 350°C our expansions agree well within the statistical errors. Above 350° $\Delta a/a$ appears to increase slightly above $\Delta L/L$, but not much beyond the statistical error. The apparent small difference is of questionable significance (see Sec. IVB). Therefore, we take $|\Delta L/L - \Delta a/a| \leq 3 \times 10^{-5}$ at all temperatures.

IV. DISCUSSION

A. Schottky Defects

Two substitutional ionic sites are formed for each Schottky defect created. Therefore, from the definitions of Eq. (1), $x_S = \Delta N/N$. Hence our measurement, that $|\Delta L/L - \Delta a/a| \leq 3 \times 10^{-5}$, gives $x_S < 9 \times 10^{-5}$ under equilibrium conditions for all temperatures up to within 4°C of the melting point. This upper limit on equilibrium Schottky defect concentrations in silver chloride is based upon the well-defined experimental accuracy of the individual length and lattice expansion measurements.

Any presumed equilibrium concentration of Schottky defects will occur in the presence of higher concentrations of Frenkel defects. In the case of mixed Frenkel and Schottky disorder the electroneutrality condition becomes

$$x_{v+} = x_F + x_S, \quad (3)$$

where x_{v+} is the relative concentration of cation vacancies. There are also two "solubility product"

²⁴ S. S. Sharma, Proc. Indian Acad. Sci. **A32**, 268 (1950). B. N. Dutta and B. Dayal, Phys. Stat. Solidi **5**, 73 (1964).

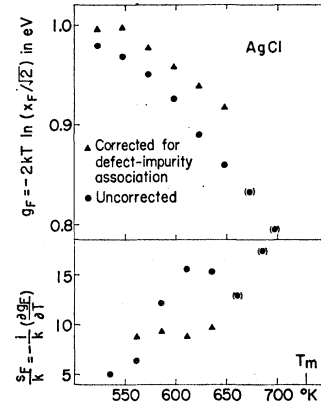


FIG. 2. Upper section shows free energy per Frenkel defect g_F derived from concentrations given by Ebert and Teltow (Ref. 9). The values given by triangles include a correction for association of defects and added cadmium ion impurities. Values given by circles neglect association. The lower section shows values of entropy of formation s_F , derived from first differences of the g_F values for each case.

relations,⁴

$$x_{v+}x_F = K_F^{-1} = l^{1/2} \exp(-g_F/kT) \quad (4)$$

and

$$x_{v+}x_S = K_S^{-1} = \exp(-g_S/kT), \quad (5)$$

which predict a suppression of the expected defect concentrations of one type in the presence of the other defect species. The vacancies are assumed mobile enough to insure thermodynamic equilibrium. l is an integer depending upon configurational entropy. Putting Eq. (3) in (5), and solving for g_S , the free energy of formation of a Schottky defect, we obtain

$$g_S = -kT \ln(x_S^2 + x_F x_S), \quad (6)$$

with the limit $x_S < 9 \times 10^{-5}$ obtained above, and $x_F = 1.5 \times 10^{-3}$ at 725°K; this gives $g_S > 0.98 \text{ eV}$.

It is more usual to speak in terms of an enthalpy of formation, h_S . This requires an estimate of the entropy s_S associated with the formation of a Schottky defect. Unfortunately, in the case of silver chloride, this is not a clearcut procedure. We illustrate the difficulty by considering first the entropy of the Frenkel defect.

The concentrations given by Ebert and Teltow⁹ allow g_F to be calculated using the expression obtained from Eq. (4), $x_F = \sqrt{l} \exp(-g_F/2kT)$, which assumes that the configuration of the interstitial site is independent of temperature and of defect concentration and neglects any possible suppression of x_F by Schottky defects. For elementary cube-centered interstitials $l=2$, while for $\langle 111 \rangle$ dumbell interstitials $l=4$. In Fig. 2 are shown values of $g_F(T)$ for the former case. Also shown are values of $s_F/k = -1/k(dg_F/dT)_P$ obtained from first differences of the free-energy points. The two different sets of values shown correspond to two different methods of analysis of the original ionic conductivity data (see Table I).

While magnetic resonance²⁵ and dielectric loss measurements²⁶ on silver bromide containing cadmium support the idea of association between the vacancies and the cadmium, the precise extent to which this association influences the conductivity is not clear at present. When association is neglected, Fig. 2 shows that s_F is not constant, but varies from 5 to 18 entropy units in the range of the measurements. The points marked by () were so marked by Ebert and Teltow because the method used in their experiments is less sensitive at those temperatures where the relative conductivity of the doped and pure materials is close to unity.

A fairly constant entropy $s_F \approx 9k$ for $T \leq 375^\circ\text{C}$ is obtained from the model which takes association into account. This value of entropy is near the measured values of s_S in alkali halides, which lie in the range 5 to $9k$.²⁷ Such lower entropy values are probably more representative of values expected for the case of dilute solutions of defects.

From the above considerations we take $s_S > 7k$ which gives $h_S = g_S + Ts_S > 1.45$ eV. This value is consistent with a theoretical estimate of 2.0 eV by Kurosawa.²⁸

B. Remarks on $(\Delta L/L - \Delta a/a) < 0$

We note from Table II that the mean lattice expansion is apparently slightly larger, at the highest temperatures, than the mean length expansion. It is worthwhile to consider briefly several possible contributions to this apparent small excess of interstitials, although the present measurements have not conclusively demonstrated such an effect in silver chloride.

(1) Compounds exhibiting deviations from exact stoichiometric composition may have excess interstitials, for example, Mg_2P^{29} and ZnO .³⁰ For silver chloride under the conditions of the present experiment (nitrogen atmosphere, temperature cycling, etc.) this appears a highly unlikely possibility.³¹ For small interstitial concentrations this is not excluded on an absolute basis by an experiment of the present type, however, which determines only changes in lattice parameter and length. A possible effect due to equilibration between metallic colloidal silver, silver vapor, chlorine gas, and silver chloride phases could be reversible, but is expected to be small.³²

²⁵ M. H. Cohen and F. Reif, in *Bristol Conference on Defects in Solids* (Physical Society, London, 1955), p. 44.

²⁶ J. Teltow and G. Wilke, *Naturwiss.* **41**, 423 (1954).

²⁷ H. Etzel and R. Maurer, *J. Chem. Phys.* **18**, 1003 (1950);

R. W. Dreyfus and A. S. Nowick, *J. Appl. Phys.* **33**, 473 (1962).

²⁸ T. Kurosawa, *J. Phys. Soc. Japan* **13**, 153 (1958).

²⁹ G. Brauer and J. Tiesler, *Z. Anorg. Chem.* **262**, 309, 319 (1950).

³⁰ G. Heiland, E. Mollwo, and F. Stöckmann, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 8, p. 191.

³¹ The slight photolytic darkening observed in parts of the sample caused no apparent irreversibility in either the macroscopic or x-ray measurements nor any change in x-ray lattice constant which could be ascribed to prolonged x irradiation.

³² C. Wagner, *Z. Elektrochem.* **63**, 1027 (1959).

(2) The detailed impurity analyses of the sample (Sec. IIA) revealed an impurity content of about 40 ppm. Impurities can, however, hardly be responsible for a disagreement between the expansion measurements at the highest temperatures. The several detailed tests described in Sec. II show that the impurity content was essentially independent of temperature and of time during the experiment. Moreover, a number, if not all, of the impurities present enter the silver chloride lattice substitutionally.

(3) X-ray diffraction measurements necessarily must be performed on material near the surface of the sample, while the length expansion is measured on the bulk. A variety of subtle and awkward effects might therefore conspire to make $\Delta a/a$ appear different from $\Delta L/L$.^{20,22} As mentioned earlier, detailed consideration has not revealed any evidence that any such effects have influenced the results given in Table II.

(4) A mixed defect system, consisting of cation interstitials, cation vacancies, and anion interstitials would give $\Delta N/N < 0$. A calculation, using charge balance and the relevant solubility product relations in the manner of the calculation given for Schottky defects above, indicates that such a system would have enhanced cation interstitial concentrations and suppressed cation vacancies. While such a defect structure seems unlikely on the basis of ionic size considerations, equilibrium concentrations of about 10^{-4} anion interstitials are not inconsistent with the present measurements or with ionic conductivity and diffusivity results.^{9,10} Moreover, it is interesting to note that for the silver halides, the degree of the dominant equilibrium disorder decreases with decreasing atomic number of the halide. The α phase of silver iodide, stable between 145°C and the melting point of 555°C , has a bcc anion lattice containing cations distributed essentially at random among the 42 possible interstitial sites of an elementary cell.^{33,34} Next, silver bromide shows cation Frenkel disorder with a concentration $x_F \approx 1 \times 10^{-2}$ near the melting point.³⁵ Finally, silver chloride shows near the melting point only $x_F \approx 3 \times 10^{-3}$.⁹ More detailed and precise expansion studies of the bromide and iodide might therefore be worthwhile.

C. Comparison with Chlorine Diffusion Measurements

Compton¹⁰ measured diffusion of chlorine in silver chloride by the radioactive tracer method, from 324°C to near the melting point. He obtained for the activation energy, $Q = 1.61$ eV.

Since Tubandt's transport number measurements on silver chloride⁴ showed that the ionic conductivity in the structure-sensitive region is by cations, it appears that the enthalpy of motion of an anion vacancy h_-^m

³³ L. W. Strock, *Z. Physik. Chem.* **B31**, 132 (1935).

³⁴ S. Hoshino, *J. Phys. Soc. Japan* **12**, 315 (1957).

³⁵ J. Teltow, *Ann. Physik* **5**, 63 (1949).

is greater than that of a cation vacancy h_+^m . Assuming that the chlorine diffusion proceeds via a vacancy mechanism, we can then estimate an upper limit on $h_S = 2(Q - h_-^m)$. From the mobility results of Ebert and Teltow⁹ $h_+^m = 0.4$ eV, whence $h_S \leq 2.4$ eV, which is well above the lower limit of 1.45 eV estimated in Sec. IVA. The present results are therefore consistent with the chlorine diffusion results and a single vacancy diffusion mechanism as long as $h_-^m \leq 0.95$ eV.

D. Curvature of $\ln P$ versus T^{-1} Plots

We have extensive evidence that the cation Frenkel defect⁹ and an interstitialcy mechanism¹⁰ dominate the ionic conductivity σ above the intrinsic knee. Yet, the logarithmic plots of σ and of silver diffusivity versus T^{-1} clearly are not straight at the highest temperatures. For example, σ increases to 29% above an extrapolation of the linear portion of the data.⁹ Also, when "excess" thermal expansion coefficient,^{7,15,16} or "excess" heat capacity,⁶ are plotted versus T^{-1} the resulting curve usually turns upward at the high-temperature region. Sometimes it has appeared possible to decompose the curve of such a property P into two components which differ in slope and in absolute value.^{6,16}

The present measurements show that such a curvature in a $\ln P$ versus T^{-1} plot cannot be interpreted in terms of Schottky defects in concentrations greater than 90 ppm. It could merely reflect the striking fact that in silver chloride, Frenkel defects attain high concentrations near the melting point. The concentrations are related to the Gibbs free energy, $g = h - Ts$. Because $s = -(\partial g / \partial T)_p$, the apparent temperature dependence of the enthalpy is given by $(\partial h / \partial T)_p = T(\partial s / \partial T)_p = -T(\partial^2 g / \partial T^2)_p$. From Fig. 2 and the discussion of Sec. IV A, it appears possible that for Frenkel defects in silver chloride, $\partial^2 g / \partial T^2$ is not negligibly small.^{35a}

Because of the long range of the Coulomb forces, interactions between defects are likely to be important. In the case of interacting defects, the equilibrium constant K_F of Eq. (4) must be replaced by $K_F f_v f_i$, where the f are the activity coefficients. The Debye-Hückel theory of electrolytes,³⁶ in its simplest form, gives

$$\ln f_v = \ln f_i = -(\pi)^{1/2} (2e^2 / a \epsilon kT)^{3/2} (x_F)^{1/2} = \Delta g_F / 2kT, \quad (7)$$

where e is the charge of the defects, ϵ is the dielectric constant of the crystal. Using $x_F = 1.5 \times 10^{-3}$, $T = 725^\circ\text{K}$, $\epsilon = 13$, we obtain $\Delta g_F = 0.15$ eV, an appreciable amount.

^{35a} Note added in proof. This matter has been discussed for silver bromide by H. Schmalzried, *Z. Physik. Chem. N.F.* 22, 199 (1959). The authors are grateful to Professor Carl Wagner for bringing this work to our attention.

³⁶ For example, R. H. Fowler and E. A. Guggenheim, in *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1939), Chap. IX; see also T. Kurosawa, *J. Phys. Soc. Japan* 12, 338 (1957).

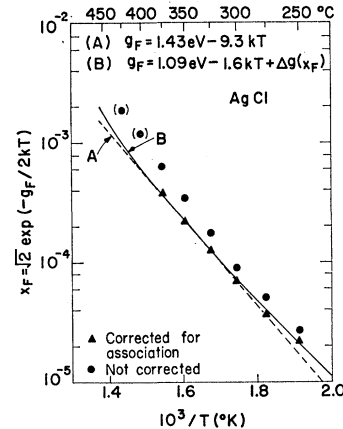


FIG. 3. Concentrations of Frenkel defects x_F in silver chloride. The values marked by circles neglect association between defects and added cadmium ion impurities, while the values marked by triangles include a correction for association (Ref. 9). Curve A is plotted using $h_F = 1.43$ eV given by Ebert and Teltow and neglects defect-defect interactions. Curve B shows the effect of including defect-defect interactions by a simple form of Debye-Hückel theory. Δg is given by Eq. (7) of the text.

While the Debye-Hückel theory is probably not strictly applicable in this situation, the magnitude of this contribution does not depend strongly on the particular interaction theory used.²² We also note that the correct value of the dielectric constant to be used at elevated temperatures is open to question.³⁷

In Fig. 3, curve A shows the dependence of x_F on temperature according to Ebert and Teltow,⁹ including corrections for association between the defects and the added divalent cation impurities, but neglecting defect-defect interactions. Curve B shows the temperature dependence of x_F if defect-defect interactions are included according to Eq. (7). It is interesting to compare the measured curvature in $\ln \sigma$ to curve B, which rises above linear curve A by 30% at the melting point. This close correspondence suggests that the curvature in $\ln \sigma$ arises from concentration effects, rather than from migration energy or mechanism changes.

It should be noted, of course, that for the simple interaction theory used the precise value of concentration at the melting point is quite sensitive to small inaccuracies in concentrations at lower temperatures. Also, the resulting apparent entropy term and the concentration-independent enthalpy term are smaller smaller than values of Sec. IVA.

Also shown in Fig. 3 are the concentrations inferred by Ebert and Teltow by neglecting defect-impurity association. These values of x_F at temperatures below 375°C yield a fit to Eq. (7) which increases without bound above about 425°C . We note that the Debye-Hückel radius, $(\epsilon a^2 kT / 32 \pi e^2 x_F)^{1/2}$, is approximately 5 \AA for an assumed $x_F(725^\circ\text{K}) = 3.5 \times 10^{-3}$. In this case

³⁷ A. R. Allnatt and M. H. Cohen, *J. Chem. Phys.* 40, 1871 (1964).

the error due to neglecting the effects of strain energy or of a minimum stable separation distance for a close pair of defects is doubtless appreciable.

E. Contributions to Thermal Expansion by Equilibrium Defects

Two distinct ways that equilibrium defects might contribute to the measured thermal expansion have been proposed. First, formation of the defects could add the volume $x_F v_F$,⁴ where v_F is the structural volume change produced by one defect (in units of the molecular volume $a^3/4$). The corresponding enhancement in linear expansion coefficient is given by

$$T^2 \Delta\alpha = (h_F v_F / 6k) x_F. \quad (8)$$

Second, it is possible that the thermal expansion coefficient itself is altered by the presence of defects.^{7,19} The relation proposed is

$$\Delta\alpha = (\alpha_L C) x_F, \quad (9)$$

where α_L is the expansion coefficient for a defect-free crystal, and C is a constant. If h_F , v_F , α_L , and C are weak functions of temperature, then logarithmic plots of $T^2 \Delta\alpha$ and of $\Delta\alpha$ versus T^{-1} will probably not both be identical in form to a $\ln x_F$ versus T^{-1} plot.

Earlier attempts to assess the magnitude of contributions by defects in silver chloride^{1,5,7,15,16} have been unsatisfactory in several respects. A major obstacle to any such attempt is the problem of obtaining an unobjectionable scheme giving values of α_L , in order that the defect contribution may be obtained by difference. In the absence of a rigorous theory appeal must be made either to (1) a temperature dependence of the resulting defect contribution to the expansion which agrees very closely with an independently measured enthalpy of formation of the defects in the same temperature range, or to (2) a reasonable magnitude for the resulting expansion which is in accord with an independently measured v_F or C , as defined above, and with an independent x_F . Unfortunately, for silver chloride no reliable theoretical values of v_F or C are available, and Table I shows that estimates of x_F and h_F from different experiments vary widely. It is agreed that the defects are relatively numerous, and the present work shows the Schottky defect contributions to be negligible, so we examine the present data in this light.

1. Expansion of Defect-Free Lattice $\Delta V/V_{20}$

We estimated $\Delta V/V_{20}$ by two independent extrapolation procedures. In the first, we put

$$\Delta V/V_{20} = \beta_{20} t + \frac{1}{2} (d\beta/dT)_{20} t^2 + \frac{1}{6} (d^2\beta/dT^2)_{20} t^3, \quad (10)$$

where $t = T(^{\circ}\text{C}) - 20$. β and its derivatives were determined graphically from the expansion data summarized in Table II. Values were $\beta_{20} = 9.225 \times 10^{-5}/^{\circ}\text{C}$, $(d\beta/dT)_{20}$

$= 9.50 \times 10^{-8}/(^{\circ}\text{C})^2$, and $(d^2\beta/dT^2)_{20} = 2.05 \times 10^{-10}/(^{\circ}\text{C})^3$.

In the second, we fitted an empirical Mie-Grüneisen equation of state to the expansion data in the interval 323 to 473°K. The equation is

$$(V_T - V_0)/V_0 = E_T/(Q - bE_T), \quad (11)$$

where V_T is the molecular volume at temperature T , $E_T = \int_0^T C_V dT$, and Q , V_0 , and b are parameters which are related to measurable quantities according to Grüneisen. Because the measured C_P contains a contribution from defects, we took for the defect-free lattice

$$C_P(\text{lattice}) = C_P(\text{meas.}) - h_F^2 x_F / 2kT^2, \quad (12)$$

evaluated using Ebert and Teltow's h_F and x_F in the case of no association (Table I and Fig. 3). Equation (12) neglects a small possible contribution to C_P arising because $(\partial h_F/\partial T)_P$ may not be zero. C_V was calculated from C_P measurements of Kobayashi⁶ by use of the Lindemann-Nernst equation

$$C_P - C_V = BC_P^2 T, \quad (13)$$

where $B = (V\beta^2/K_T C_P^2)_{T_{300}}$. B was calculated from the present expansion measurements, V from lattice parameter measurements of Berry,²⁸ and K_T , the isothermal compressibility, from elastic data of Arenburg.³⁸ C_V calculated in this manner increases monotonically from 12.1 cal/mole-deg at room temperature to 15.5 cal/mole-deg near the melting point.³⁹ The parameters were $V_0 = 41.9218 \text{ \AA}^3$, $Q = 163.7$ kcal/mole, and $b = 6.0$. The two resulting sets of $\Delta V/V_{20}$ values are similar; they are given in Table III.

Values of α_L were obtained from the volume expansions, Eq. (11) by numerical differentiation. They

TABLE III. Extrapolated volume expansion of silver chloride, as computed in Sec. IVE1 of text.

T °K	300 $\Delta a/a_{20}$ Measured	100 $\Delta V/V_{20}$	
		Eq. (10) ^a	Eq. (11) ^b
273	-0.183	-0.183	-0.179
323	0.279	0.281	0.276
373	0.765	0.770	0.759
423	1.278	1.278	1.276
473	1.833	1.834	1.825
523	2.427	2.415	2.407
548	2.739	2.718	2.712
573	3.069	3.030	3.025
598	3.417	3.352	3.347
623	3.786	3.684	3.679
648	4.188	4.026	4.021
673	4.638	4.379	4.372
698	5.136	4.742	4.733
723	5.730	5.117	5.113

^a Polynomial, Eq. (10).

^b Empirical equation of state, Eq. (11).

³⁸ D. L. Arenburg, J. Appl. Phys. **21**, 941 (1950).

³⁹ This is in disagreement with Nicklow and Young (Ref. 15) who used $C_P - C_V = TV\beta^2/K_T$ and assumed that V/K_T is constant. In the absence of reliable measurements of the temperature dependence of the compressibility of AgCl, the validity of the Lindemann-Nernst equation is uncertain in the present case.

TABLE IV. Linear thermal-expansion coefficients of silver chloride. α_T is the measured linear thermal-expansion coefficient at temperature T . α_L is the assumed expansion coefficient for a defect-free lattice; it was derived from Eq. (11) fitted in the range 323 to 473°K.

T (°K)	α_T ($10^{-5}/^{\circ}\text{K}$)	α_L ($10^{-5}/^{\circ}\text{K}$)
273	2.98	3.01
323	3.12	3.12
373	3.30	3.32
423	3.51	3.54
473	3.77	3.77
523	4.06	4.00
548	4.22	4.12
573	4.44	4.24
598	4.69	4.36
623	5.02	4.49
648	5.46	4.61
673	6.09	4.75
698	7.04	4.92
723	8.47	5.22

are given in Table IV, together with measured values of $\alpha_T = \alpha_{20}/(1 + \Delta a/a_{20})$ which are more appropriate for these analyses than α_{20} values.

According to Mie and Grüneisen,⁴⁰ $Q = V_0/\gamma K_0$ and $b = (m+n+3)/6$, where γ is the Grüneisen parameter $-d(\ln\omega)/d(\ln V)$, ω being a characteristic lattice vibration frequency, and m , n are exponents in the Mie form of the potential energy function $-A_1 r^{-m} + A_2 r^{-n}$. For silver chloride, $m=1$, $n=9.5$, so we might expect $b=2.25$. Using room temperature values in place of V_0 and K_0 , and the relation $\gamma = \beta V/K_T C_V$, we would expect $Q = C_V/\beta \approx 133$ kcal/mole. Thus the values of b and probably Q needed to fit the data are higher than those given by conventional Grüneisen theory. This result agrees qualitatively with the results of Fletcher, who showed for potassium chloride that reasonable choices of b and Q predict a thermal ex-

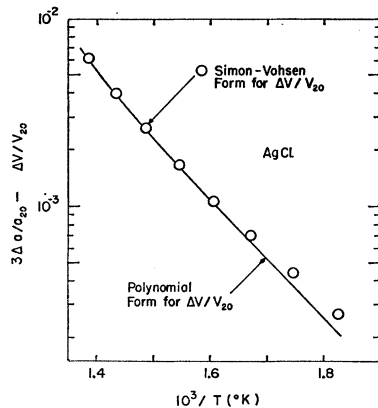


FIG. 4. Relative volume expansion arising from the presence of Frenkel defects in silver chloride. The solid curve was obtained by use of a polynomial extrapolation formula. The circles show values obtained by use of an empirical equation of state. See Sec. IVF of text.

⁴⁰ E. Grüneisen, in *Handbuch der Physik*, edited by H. Geiger and K. Scheel (Verlag Julius Springer, Berlin, 1926), Vol. 10, p. 1.

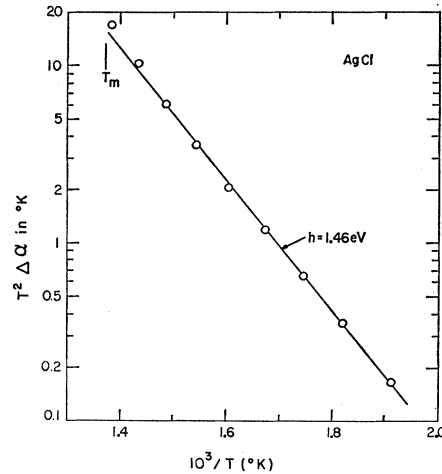


FIG. 5. Test for an enhancement of the linear thermal expansion coefficient, $\Delta\alpha$, by a structural volume change due to Frenkel defects. According to Eq. (8) of the text, this graph should resemble Fig. 3. The resulting temperature dependence is satisfactory over two decades. However, the resulting v_F values are definitely larger than the value 0.65 inferred from conductivity measurements under pressure (Ref. 43).

pansion coefficient which falls below the measured values.⁴¹

2. Defect Dilution v_F

An upper limit may be obtained on v_F by the assumption that $C=0$. Values of the presumed $x_F v_F = 3\Delta a/a_{20} - \Delta V/V_{20}$ are shown in Fig. 4 plotted versus T^{-1} . The very close agreement between the two extrapolation schemes is, doubtless, fortuitous. It is, however, similar to their agreement with experiment in the negligible defect range. A single straight line drawn through the points above 600°K has slope -0.70 eV, which suggests that $h_F = 1.40$ eV. Using from Table I Ebert and Teltow's values for $x_F(450^{\circ}\text{C})$ of 3.5×10^{-3} and 1.5×10^{-3} we get v_F limits of 1.8 and 3.5, respectively.

Alternatively, we can work with the expansion coefficient, using Eq. (8), still assuming that $C=0$. A plot of $T^2\Delta\alpha$ versus T^{-1} , using values of $\Delta\alpha = \alpha_T - \alpha_L$ from Table IV, is shown in Fig. 5. Applying Eq. (8) at the melting point with the x_F values used in the preceding paragraph yields the same v_F limits, which verifies consistency between the two approaches.⁴²

These limiting values for v_F are larger than a value 0.65 obtained by Abey and Tomizuka⁴³ from ionic conductivity studies of pure and of doped silver chloride under pressure, and than a rather uncertain

⁴¹ G. C. Fletcher, *Phil. Mag.* 2, 639 (1957); see also *Australian J. Phys.* 14, 420 (1961).

⁴² Nicklow and Young (Ref. 15) also employ expansion coefficients. Their $T^2\Delta\alpha$ values are *higher* at all temperatures than ours, and therefore lead to values of v_F larger than the present values. Their statement that the value of v_F derived from their analysis is 0.45 is not correct. It follows also that their discussion associated with this erroneous deduction is open to serious question.

⁴³ B. Abey and C. T. Tomizuka (to be published).

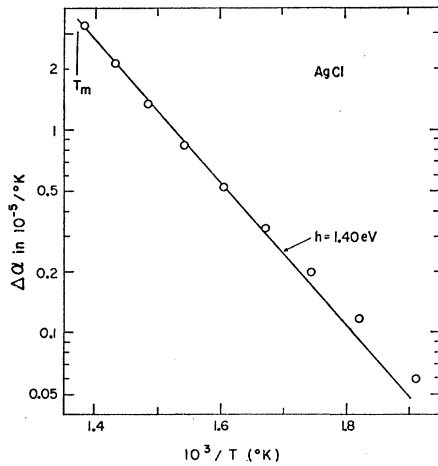


FIG. 6. Test for an explicit enhancement by Frenkel defects of the thermal expansion coefficient, as in Eq. (9) of the text. The resulting temperature dependence is satisfactory over a broad range. The magnitude of the enhancement cannot be precisely determined without better knowledge of the Frenkel defect concentrations, but it appears comparable to that observed for defects in x-rayed rocksalt (Ref. 19).

0.7 obtained by Zieten⁷ from doped silver chloride. Further, they are also larger than one expects from crude application of an elastic continuum model to estimate the dilations. It therefore appears that C is not negligibly small.

3. Explicit Change in α by Defects

Values of $\Delta\alpha$ [again from the Eq. (11) extrapolation] versus T^{-1} are shown in Fig. 6. The slope at high temperatures corresponds to $h=1.40$ eV, while at the lowest temperatures $\Delta\alpha$ lies somewhat above the straight line. For a value of $v_F=0.65$ and the range of

x_F values at the melting point shown in Table I, only $\frac{1}{6}$ to $\frac{4}{5}$ of this $\Delta\alpha$ is due to a structural expansion as considered in the preceding section. The remaining portion of $\Delta\alpha$, put in Eq. (9), yields at the melting point values for C lying between 20 and 350. A similar range of values for C is obtained at other temperatures. The result may be compared with a tentative $C=1500$ for thermally generated Schottky defects in rocksalt and a somewhat better established $C=14$ for x-irradiation induced defects in rocksalt.¹⁹

The reasonable temperature dependence of this analysis and the resulting approximate value for C therefore tend to confirm the rather surprising proposal of Merriam *et al.*¹⁹ It is at present not possible, however, either to judge in detail the merit of our extrapolation schemes or to narrow the uncertainty in the value of C , in the absence of precise and confirmed values for h_F and x_F in silver chloride.

Our conclusions are summarized in Table V.

TABLE V. Equilibrium defect properties of silver chloride at the melting temperature, concluded from the present work. (Symbols defined in Table I.)

x_F	x_S	h_F	h_S
Dominant	$<9 \times 10^{-5}$	1.4 eV	$1.45 < h_S < 2.4$ eV

ACKNOWLEDGMENTS

We are indebted to Professor F. C. Brown for advice and for equipment useful in sample preparation and manipulation, to Professor W. D. Compton, and K. L. Kliewer for helpful discussions. The Harshaw Chemical Company extruded the silver chloride bars and supplied the spectrographic analyses of the material.