

Thermal Expansion of AgCl[†]

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The thermal coefficient of expansion of AgCl has been measured as a function of temperature from 120 to 710°K (melting point = 728°K) by means of x-ray diffraction from small single crystals. Above 300°K the results agree well with the dilatometric measurements reported by Strelkow. Such agreement indicates that the concentration of Schottky defects in AgCl is not large enough to influence significantly the thermal expansion below 710°K. The thermal expansion for the entire temperature range is described rather well by Grüneisen's theory, (1) if it is assumed that thermally generated Frenkel defects contribute significantly to the high-temperature thermal expansion, and (2) if two parameters in the theory are chosen to give a good fit to the low-temperature ($T < 300^\circ\text{K}$) x-ray data. Attempts to determine the activation energy of the Frenkel defects from comparison of the thermal expansion data with theory indicate that certain constants of the theory are probably temperature dependent. Below 300°K the x-ray results differ significantly from the dilatometric results reported by Sreedhar. Low-temperature x-ray measurements of the thermal expansion of Al are, therefore, included and compared with existing data in the literature to demonstrate the validity of our experimental technique. The especially convenient experimental technique used is described.

INTRODUCTION

THE coefficient of thermal expansion of AgCl measured dilatometrically by Strelkow¹ increases quite rapidly at high temperatures. It was suggested by Lawson² that the entire increase of this coefficient above its value at room temperature is due to the thermal generation of point defects. As Fletcher³ has shown, at least for KCl, theory predicts some increase at high temperatures in the thermal expansion coefficient of a solid having no defects; although poor quantitative agreement between theory and experiment was found. In addition, Zieten⁴ has demonstrated, by dilatometric expansion measurements on AgCl samples doped with various concentrations of CdCl₂, that Frenkel defects contribute significantly to the high-temperature thermal expansion of AgCl below 420°K (693°K). The type of defects which contributed to the expansion above this temperature was uncertain but was speculated by Zieten to be Schottky.

In the present paper we report x-ray measurements of the thermal expansion coefficient of AgCl from 120 to 710°K. The results yield additional information about the type of defects which predominate in AgCl at high temperatures. We also calculate, using Grüneisen's theory, the high-temperature thermal expansion for AgCl after choosing two parameters in the theory to give a good fit to the low-temperature x-ray data. The difference between theory and experiment found at high temperatures is discussed in relation to the thermally generated defects and the probable temperature dependence of the Grüneisen constant.

The results obtained for the 120 to 300°K temperature range differ significantly from the dilatometric

results reported by Sreedhar.⁵ We therefore include our low-temperature x-ray expansion data for Al, which are in good agreement with the dilatometric results reported by Buffington and Latimer⁶ and by Bijl and Pullan,⁷ as evidence of the validity of our experimental technique.

THEORY

A brief search of the literature revealed that no strict theory of thermal expansion exists which can be compared easily with experiment. However, an approximate theory based on the Debye model of a solid was developed by Grüneisen⁸ from the Mie-Grüneisen equation of state for a solid,

$$VP + V(d\Phi/dV) = \gamma E_{\text{vib}}, \quad (1)$$

where V is the volume, P is the pressure; Φ is the potential energy of the solid when the atoms are at their equilibrium positions, and $\gamma = -(d \ln \Theta)/(d \ln V)$ is the Grüneisen "constant." E_{vib} is the vibrational energy of the atoms which, in the particular case of the Debye model, is given by $6RTD(\Theta/T)$ for a diatomic solid. $D(\Theta/T)$ is the Debye function, T is the absolute temperature, and Θ is the Debye characteristic temperature. If it is assumed (1) that Φ is a function of the volume only, and (2) that the atoms are at rest at $T = 0^\circ\text{K}$ (which makes $d\Phi/dV = 0$ there), then it follows³ from Eq. (1), via a Taylor series expansion of $V(d\Phi/dV)$ about V_0 , that

$$3 \frac{a - a_0}{a_0} \approx \frac{V - V_0}{V_0} = \frac{E_{\text{vib}}/Q}{1 - x(E_{\text{vib}}/Q)}, \quad (2)$$

⁵ A. K. Sreedhar, *J. Indian Inst. Sci.* **A36**, 186 (1954).

⁶ R. M. Buffington and W. M. Latimer, *J. Am. Chem. Soc.* **48**, 2305 (1926).

⁷ D. Bijl and H. Pullan, *Physica* **21**, 285 (1955).

⁸ E. Grüneisen, in *Handbuch der Physik*, edited by H. Geiger and Karl Scheel (Verlag Julius Springer, Berlin, 1926), Vol. 10, pp. 1-59.

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¹ P. G. Strelkow, *Physik Z. Sowjetunion* **12**, 77 (1937).

² A. W. Lawson, *Phys. Rev.* **78**, 185 (1950).

³ G. C. Fletcher, *Phil. Mag.* **2**, 639 (1957).

⁴ W. Zieten, *Z. Physik* **146**, 451 (1956).

where the zero subscript designates 0°K; Q is a constant given by $V_0/\gamma K_0$; x is a constant which is related⁹ to the form of the interaction potential Φ ; K is the compressibility; and a is the lattice parameter of the crystal. Although γ , and hence Q , is often assumed to be temperature independent, this assumption is not required for the derivation of Eq. (2).⁸ However, to simplify the present discussion, the possibility of a temperature-dependent γ will not be considered until later.

Thus, as Fischmeister¹⁰ has suggested, a plot of $a_0(a-a_0)^{-1}$ vs E_{vib}^{-1} should yield a straight line of slope $3Q$ and intercept $3x$. The use of such a plot at low temperatures, say below one or two times the Debye Θ , probably provides an adequate qualitative method for the comparison of theory with experiment. But, as Fletcher⁸ has pointed out, at high temperatures such a plot is relatively insensitive because the abscissa, E_{vib}^{-1} , is not linear in temperature, but varies more nearly as T^{-1} . Therefore, in comparison of theory with experiment, comparisons which involve the coefficient of thermal expansion explicitly seem to be more desirable.

A theoretical coefficient of thermal expansion is obtained from the Grüneisen theory by calculation of the temperature derivative of Eq. (2). Thus

$$3\alpha \approx 3 \frac{d}{dT} \left\{ \frac{a-a_0}{a_0} \right\} = \frac{(dE_{\text{vib}}/dT)_p}{Q[1-x(E_{\text{vib}}/Q)]^2}, \quad (3)$$

where α is the linear coefficient of thermal expansion and the "p" subscript means that the temperature derivative is taken at constant pressure. As E_{vib} is a function of volume and temperature,

$$\left(\frac{dE_{\text{vib}}}{dT} \right)_p = \left(\frac{\partial E_{\text{vib}}}{\partial V} \right)_T \left(\frac{dV}{dT} \right)_p + \left(\frac{\partial E_{\text{vib}}}{\partial T} \right)_V. \quad (4)$$

The calculation of $(\partial E_{\text{vib}}/\partial V)_T$ for a Debye model is given by Born and Huang.¹¹ The result is

$$(\partial E_{\text{vib}}/\partial V)_T = (\gamma/V)(TC_v - E_{\text{vib}}), \quad (5)$$

where $(\partial E_{\text{vib}}/\partial T)_V = C_v$, the specific heat at constant volume. Hence,

$$(dE_{\text{vib}}/dT)_p = 3\gamma\alpha(TC_v - E_{\text{vib}}) + C_v. \quad (6)$$

Combining Eqs. (3) and (6), one obtains

$$3\alpha = \frac{C_v}{Q\{1-x(E_{\text{vib}}/Q)\}^2 - \gamma(TC_v - E_{\text{vib}})}. \quad (7)$$

Thus, the determination of Q and x from a plot of $a_0(a-a_0)^{-1}$ vs E_{vib}^{-1} will permit a calculation of α

⁹ Assuming $\Phi = -Ar^{-m} + Br^{-n}$, Grüneisen gives $x = (m+n+3)/6$.

¹⁰ H. F. Fischmeister, *Acta Cryst.* **9**, 416 (1956).

¹¹ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), p. 50.

with Eq. (7). The result can be compared with experiment without the insensitivity problems inherent in the use of the $a_0(a-a_0)^{-1}$ plot for this purpose.

EXPERIMENTAL METHOD

The use of x-ray diffraction for the measurement of thermal expansion is by no means new.¹² Bond¹³ has recently described a particularly good diffractometer-type method for the determination of precision lattice parameters of single crystals. His method is, in principle at least, capable of being used for high-precision thermal expansion measurements. However, the particular experimental procedure and apparatus we have used offer certain advantages which have not been discussed elsewhere.

The thermal expansion measurements were made on small (maximum dimension $\lesssim 1$ mm) single-crystal samples with a Single Crystal Orienter¹⁴ (goniostat) and a General Electric XRD-5 x-ray unit. The measurements consisted of the determination of the diffraction angles for selected Bragg reflections at various temperatures. As a check on reproducibility, measurements were made both as the samples were cooled and as they were heated. No evidence was obtained of any systematic errors or hysteresis.

With the goniostat it is possible, with a single mounting of a sample, to orient a single crystal so that diffraction can be obtained from at least one of the equivalent sets of Bragg planes designated by a predetermined $\{hkl\}$. Such ease of sample orientation made it possible to maintain sample alignment, while the temperature was varied, by frequent reoptimization of the goniostat settings. Expansion measurement errors which occur as a result of changes in sample alignment due to expansion of the sample mount and parts of the instrument were thus eliminated. Significant changes in sample position were tested for by comparison of data obtained from different Bragg reflections, because for the collection of such data a rotation of the sample relative to the diffraction vector was required. The data were rejected from any run for which the results of this test indicated a change in sample position.

The use of small samples helped minimize thermal gradients and made possible the use of a temperature control technique (discussed later) which is relatively simple and which is especially good in a thermodynamic sense. The use of single crystals also essentially eliminates possible expansion effects due to grain boundaries and surface effects, such as might be found in a "powder" sample. Single-crystal samples of ultrapure and doped AgCl were obtained from F. Moser¹⁵ of the

¹² See for example: R. B. Jacobs and A. Goetz, *Phys. Rev.* **51**, 159 (1937); R. E. Glover, *Z. Physik* **138**, 222 (1954); P. D. Pathak and N. V. Pandya, *Current Sci. (India)* **29** (1), 14 (1960).

¹³ W. L. Bond, *Acta Cryst.* **13**, 814 (1960).

¹⁴ T. C. Furnas, Jr., *Single Crystal Orienter Instruction Manual* (General Electric Company, Milwaukee, 1957).

¹⁵ The preparation and purity of ultrapure AgCl samples are

Eastman Kodak Company. Optical-grade single-crystal AgCl material was obtained from the Harshaw Chemical Company. It was demonstrated for AgCl, by means of Laue photographs, that sample preparation¹⁶ did not introduce observable lattice distortion.

As an over-all check of the experimental technique, low-temperature ($T < 300^\circ\text{K}$) Al expansion data were obtained from a small single-crystal specimen prepared from a large single crystal of "pure" material by sawing, followed by extensive etching. The (333) Bragg reflection was used with Cu K_α radiation and the (222) reflection with Cr K_α radiation. Two independent runs were made with each reflection.

The low-temperature AgCl expansion data were obtained from the (600) and (444) Bragg reflections of three different samples with Cu K_α radiation. For one sample, the (440) was also observed. Possible effects of radiation-induced defects on the expansion measurements were considered. One sample doped with 5 ppm Cu was used. Data taken after differing x-ray exposures were compared for this and other samples. No effect larger than experimental error was observed. No residual darkening of the pure samples was observed. The high-temperature (300 to 710°K) AgCl data, obtained from one of the three samples used for the low-temperature measurements, were collected from the (600) and (600) reflections with Cu K_α radiation.

Temperature control was achieved by means of a gas stream, approximately 1 cm in diameter, directed onto the sample. In the 120-to-300°K temperature range the gas stream consisted of a mixture of dry air, initially at room temperature, and nitrogen gas which had been bubbled through liquid nitrogen. Temperature variation was obtained by variation of the air to nitrogen-gas ratio. An annular stream of dry air surrounded the cooling stream to minimize turbulence and, hence, sample frosting due to moisture in the room air.¹⁷ For temperatures above 300°K the gas stream consisted of an air stream heated by a single tubular furnace described elsewhere.¹⁸

Besides being convenient, temperature control by means of a gas stream has some additional advantages over other possible methods. The moving gas is a nearly perfectly agitated fluid bath with effectively infinite heat capacity and with excellent heat transfer properties. Thus, for the small pseudospheres used, the surface of the sample was rigorously held at the gas stream temperature.

In order that heat conduction problems be minimized, each sample was attached to the end of a glass fiber

described by N. R. Nail, F. Moser, P. E. Goddard, and F. Urbach, *Rev. Sci. Instr.* **28**, 275 (1957).

¹⁶ All cutting and shaping of the AgCl samples was done entirely by etching techniques. All mechanical methods tried hopelessly distorted the single crystals.

¹⁷ B. Post, R. S. Schwartz, and I. Fankuchen, *Rev. Sci. Instr.* **22**, 218 (1951).

¹⁸ R. A. Young, *Advances in X-ray Analysis* (Plenum Press, New York, 1961), Vol. 4, pp. 219-232.

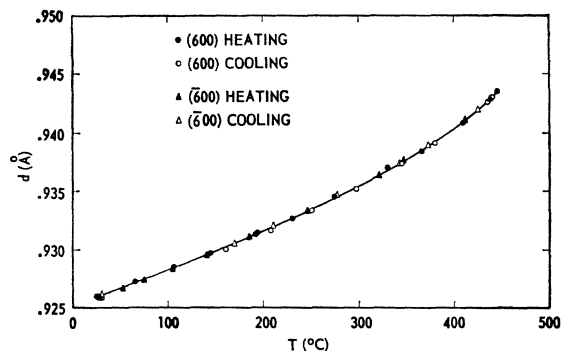


FIG. 1. Temperature dependence of d for the (600) and (600) reflections of AgCl. The standard deviation of the points from the curve is 0.0001 Å.

approximately 1 cm in length. Heat leaks along the fiber were assumed negligible, largely because the fiber, too, was partially bathed by the gas stream.

The temperature of both cooling and heating gas streams was determined with a calibrated chromel-alumel thermocouple having 3-mil-diameter leads. Temperature measurements made with differing dispositions of the thermocouple leads in the gas stream indicated that the temperature of the actual gas stream could be measured with an accuracy of $\pm \frac{1}{2}^\circ\text{K}$. Temperature measurements made with the sample removed indicated that at the sample position the temperature of the gas stream throughout a region several times the size of the sample was within $\frac{1}{2}^\circ\text{K}$ of the temperature indicated by the thermocouple in its normal position. Work done with similar gas-stream geometry and quartz specimens at 575°C indicated that the sample temperature in that case was probably uniform to within 1°K .¹⁹

RESULTS

For each Bragg reflection d , the Bragg plane spacing, was determined²⁰ from the diffraction angle vs temperature measurements and plotted as shown in Fig. 1. Graphically determined slopes were then used for calculation²¹ of the linear thermal coefficient of expansion.

¹⁹ R. A. Young, "Mechanism of the Phase Transition in Quartz," AFOSR Document No. 2569, Final Report, Contract No. AF 49 (638)-624, Project A-447, Engineering Experiment Station, Georgia Institute of Technology, 1962.

²⁰ The d spacing was determined from the angular position of the intensity maximum of the diffraction peak. Errors in the temperature dependence of d resulting from a possible temperature dependence of the peak shape were assumed negligible (the α doublet was always resolved). No extrapolation procedures common to precision lattice parameter measurement were required; only the change in d , not its absolute value, is needed with high precision. The agreement among results from different reflections, occurring at differing angles, attests to the validity of the procedures used for determination of the changes. The agreement among results for different specimens, for different wavelengths, for different heating or cooling cycles, and for different reflections including pairs 180° apart in sample orientations, show that the quantity measured is in fact the relative change in lattice parameter of the sample.

²¹ For $T < 500^\circ\text{K}$, the expression $(1/d)_{273}(dd/dT)$ was used to calculate α . The error introduced by the use of the 273°K value

sion, α , at various temperatures. Attempts to fit the data with polynomials of various degrees, with a high-speed computer, produced no more reliable slopes and were finally abandoned for a wholly graphical method.

The results obtained for the thermal expansion coefficient of Al are shown in Fig. 2. No systematic differences among results obtained from different runs and reflections were observed so the results were arithmetically averaged. The error bars in Fig. 2 represent the mean deviation from the mean. Our Al results agree well with the dilatometric results of Buffington and Latimer⁶ and of Bijl and Pullan.⁷

The AgCl results are shown in Fig. 3. Again, the results from different reflections were averaged arithmetically and the error bars represent the mean

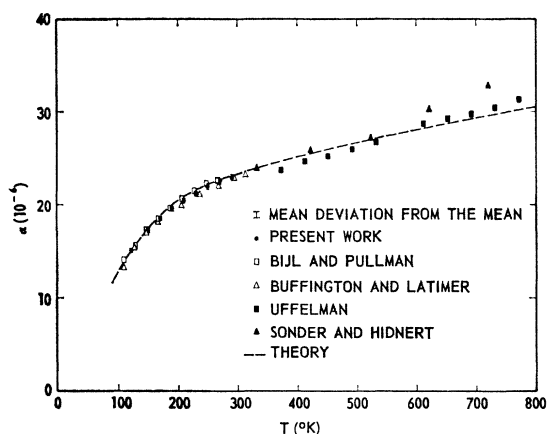


FIG. 2. Temperature dependence of the thermal expansion coefficient of Al. The theoretical line was calculated with Eq. (7) and Q and x from Fig. 4.

deviation from the mean. Our low-temperature results differ somewhat from Sreedhar's,⁵ while our high-temperature results agree well with Strelkow's¹ throughout. Since our low-temperature Al data agree well with those of Buffington and Latimer and with those of Bijl and Pullan, the difference between our low-temperature AgCl results and those of Sreedhar is real and is not due to errors associated with our experimental technique. The difference cannot be due to x-ray generated defects, for if the normal volume decrease caused by cooling the sample were opposed by a volume increase caused by increasing defect population,²² the apparent x-ray expansion coefficient would be smaller than that measured dilatometrically. Further, Sreedhar's low-temperature results are not consistent with the high-temperature data, as will be shown later by means of an appropriate $a_0(a-a_0)^{-1}$ vs E_{vib}^{-1} plot.

for $(1/d)$ was less than $\frac{1}{2}\%$. Above 500°K, d changed so rapidly that it was more appropriate to use $(1/d)_T(dd/dT)$.

²² The defect population would be expected to increase with decreasing temperature because of reduced annealing with little or no change in the defect generation rate.

The good agreement between our x-ray results and the dilatometric results of Strelkow indicates that the concentration of Schottky defects in AgCl below 710°K is not large enough to influence the thermal expansion significantly.

COMPARISON WITH THEORY AND DISCUSSION

For comparison of our expansion measurements with theory, plots of $a_0(a-a_0)^{-1}$ vs E_{vib}^{-1} for both Al and AgCl were first constructed for the low-temperature ($T < 300^\circ\text{K}$) range. The points were fit by a least squares procedure to a straight line. The resulting values for Q and x were then used to calculate the thermal expansion coefficient in the high-temperature range.

Values for a_0 were calculated from the experimental a_{120} with the low-temperature approximations of Eqs. (2) and (7). At 120°K, $x(E_{vib}/Q) \ll 1$ and $\gamma(TC_v - E_{vib}) \ll Q$; thus from Eq. (2)

$$3(a_{120} - a_0)/a_0 \approx (E_{vib}/Q)_{120}, \quad (8)$$

and from Eq. (7)

$$Q_{120} \approx (C_v/3\alpha)_{120}. \quad (9)$$

Therefore

$$\frac{3(a_{120} - a_0)}{a_0} \approx \left(\frac{E_{vib}}{Q}\right)_{120} \approx \frac{6R(120^\circ\text{K})D(\Theta/120)}{(C_v/3\alpha)_{120}}. \quad (10)$$

The validity of these approximations for the determination of Q and x is demonstrated by the fact that the Q 's obtained from Eq. (9) were within 1% of the Q 's obtained from the $a_0(a-a_0)^{-1}$ vs E_{vib}^{-1} plots. C_v in the 100 to 300°K temperature range was calculated from values of C_p given in the International Critical Tables²³

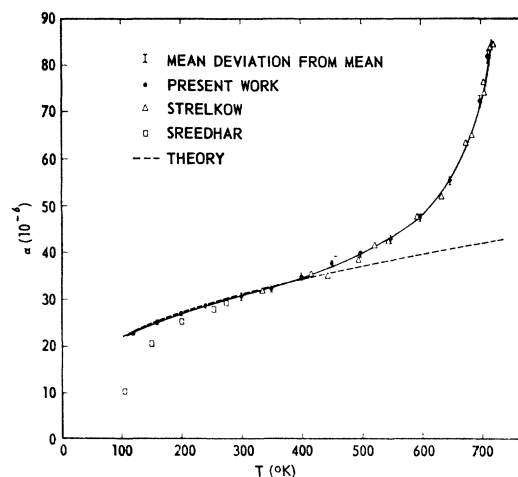


FIG. 3. Temperature dependence of the thermal expansion coefficient of AgCl. The theoretical line was calculated with Eq. (7) and Q and x from Fig. 5.

²³ International Critical Tables (McGraw-Hill Book Company, Inc., New York, 1929), Vol. 5, p. 97.

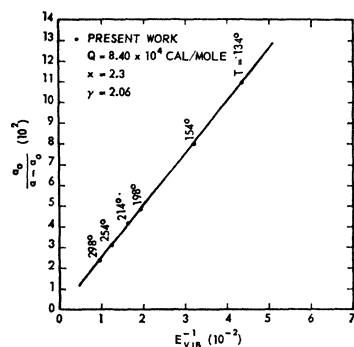


FIG. 4. Determination of Q and α for Al from a plot of the reciprocal of the lattice expansion versus the reciprocal of the vibrational energy in cal/mole.

with the expression

$$C_p - C_v = (9\alpha^2 VT)/K. \quad (11)$$

Room temperature values of V/K were used. All of the Al specific heat values used in this study were corrected for electronic contributions. It was assumed that up to the melting point the electronic specific heat is given by a constant times the temperature.²⁴ The value used for the constant was that measured by Howling, Mendoza, and Zimmerman,²⁵ 3.27×10^{-4} cal mole⁻¹ °K⁻². Values of Θ appropriate to the purpose were determined by comparison of the experimentally determined values of C_v in the 100 to 300°K temperature range with the Debye specific heat function, $C_v(\Theta/T)$.²⁶ For Al, $\Theta = 400^\circ\text{K}$ was obtained and for AgCl, $\Theta = 215^\circ\text{K}$ was obtained. E_{vib} was then calculated from tabulated values²⁶ of the Debye expression $D(\Theta/T)$, on the assumption that it is adequately given by Debye theory when the above-determined Θ values are used. Although the appearance of E_{vib} in Grüneisen's theory is independent of the model of a solid used, the tabulations of $D(\Theta/T)$ provide a convenient means for calculation of values for E_{vib} which are consistent with the experimental C_v .

The plot obtained for Al is shown in Fig. 4 and that for AgCl is shown in Fig. 5. The points fit straight lines very well. The results for Q and α are also shown in these figures, along with the γ calculated from Q with the expression $Q = (V_0/\gamma K_0)$ and room temperature values of V/K . Also on the plot for AgCl are three points which correspond to expansion measurements up to 400, 500, and 600°K. These high-temperature points are included to demonstrate the insensitivity, pointed out by Fletcher,⁸ of such a plot at high temperatures. The points are fit quite well with the straight line drawn through the low-temperature points, even though, as will be discussed later, thermally generated defects probably contribute significantly to the coefficient of thermal expansion above 400°K.

²⁴ K. Mendelssohn, *Cryophysics*, Interscience Tracts on Physics and Astronomy No. 7 (John Wiley & Sons, Inc., New York, 1960).

²⁵ D. H. Howling, E. Mendoza, and J. E. Zimmerman, *Proc. Roy. Soc. (London)* Ser. A **229**, 86 (1955).

²⁶ *Landolt-Börnstein Physikalisch-Chemische Tabellen*, First Supplement (Verlag Julius Springer, Berlin, 1927), p. 702.

In Fig. 6 is shown a plot similar to that in Fig. 5. The results for the coefficient of thermal expansion reported by Sreedhar⁵ were used to calculate a in the 100-to-300°K temperature range with the expression $(1/a)_T(da/dT)$ and our measurement of a at 300°K. His data were also used to calculate a_0 from the calculated a_{120} with Eq. (10). A single straight line will not fit both the high- and low-temperature portions of the data. In fact, for the high-temperature points to be consistent with Sreedhar's data, a larger expansion at high temperatures than is measured would be required, whereas the measured expansion is already thought to be "anomalously" large due to the probable contribution of thermally generated defects.

Calculations of α were made with Eq. (7) and with the values for Q , α , and γ given in Fig. 4 and Fig. 5. Since α is needed to calculate C_v [with Eq. (11) and measured values of C_p ²⁷] and vice versa, iterative calculations were generally required.²⁸ For $T < 300^\circ\text{K}$, Eq. (7) essentially reproduced (within 1–2%) the measured coefficients without iteration. For $T > 300^\circ\text{K}$ iterations were required in the calculations (a) for Al because measurements of α by different investigators^{29,30} did not agree; and (b) for AgCl because of the probable contribution of thermally generated defects to the expansion measurements.

The results of these calculations are compared with experiment in Fig. 2 and Fig. 3. The good agreement between theory and experiment for $T < 300^\circ\text{K}$ is not surprising since the expansion measurements in this

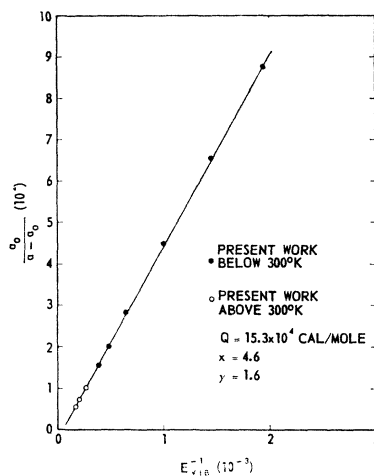


FIG. 5. Determination of Q and α for AgCl from a plot of the reciprocal of the lattice expansion versus the reciprocal of the vibrational energy in cal/mole.

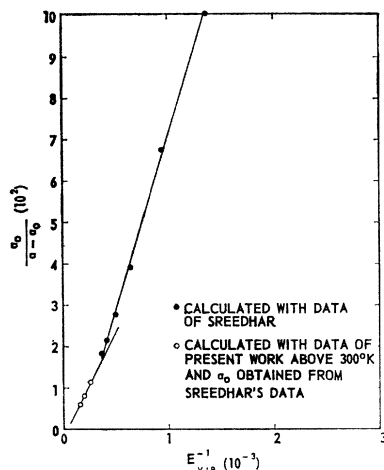
²⁷ For $T > 300^\circ\text{K}$ the C_p values reported by E. D. Eastman, A. M. Williams, and T. F. Young, *J. Am. Chem. Soc.* **46**, 1178 (1924) for Al and by K. Kobayashi, *Sci. Repts. Research Inst., Tohoku University, Series 1* **34**, 112 (1950) for AgCl were used.

²⁸ The values finally obtained for C_v of AgCl monotonically decreased from a value of 12.24 cal mole⁻¹ °K⁻¹ at 400°K to a value of 11.49 cal mole⁻¹ °K⁻¹ at 700°K. Such a decrease in C_v at high temperatures is not unexpected. See, for example, J. M. Keller and D. C. Wallace, *Phys. Rev.* **126**, 1275 (1962).

²⁹ W. H. Sonder and P. Hidnert, *U. S. Bureau of Standards Scientific Papers* **17**, 497 (1922).

³⁰ F. L. Uffelmann, *Phil. Mag.* (7) **10**, 633 (1930).

FIG. 6. Plot of the reciprocal of the lattice expansion, obtained for AgCl from the thermal expansion data of Sreedhar, versus the reciprocal of the vibrational energy in cal/mole.



temperature range were used to obtain Q and x . In the case of Al, reasonable agreement is also found at high temperatures. The agreement is as good as can be expected in view of the differences among the measurements of different investigators.

For AgCl the coefficient of thermal expansion increases much faster at high temperatures than is predicted by theory. An assumption which is consistent with the results of Zieten,⁴ and with the fact that our x-ray expansion measurements agree with those of Strelkow¹ up to 710°K (as close to the melting point, 728°K, as our measurements went), is that at least part of the difference between theory and experiment is due to the thermal generation of Frenkel defects.

If δ is the expansion, $(\Delta V)/V$, due to the thermal generation of Frenkel defects, then δ is expected to be of the form,³¹

$$\delta = A e^{-E/2kT}, \quad (12)$$

where E is the activation energy for the formation of a defect. The corresponding expansion coefficient, α' , can be expressed approximately³² as,

$$3\alpha' \approx d\delta/dT = (AE/2kT^2)e^{-E/2kT}. \quad (13)$$

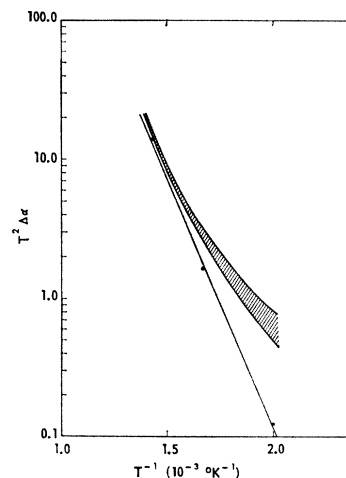
Thus if the difference, $\Delta\alpha$, between theory and experiment shown in Fig. 3 is due to the thermal generation of Frenkel defects, then $\Delta\alpha = \alpha'$ and a semilogarithmic plot of $T^2\Delta\alpha$ vs T^{-1} should be a straight line of slope $-E/2k$. Such a plot for AgCl is shown in Fig. 7. The shaded region corresponds to the possible range of values, consistent with experimental error, for the difference between theory and experiment. Since a single straight line will not fit both the high- and low-temperature portions of the plot, one might think that the curve represents the sum of two straight lines corresponding to two different activation energies. If tangents are drawn to the high- and low-temperature

portions of the curve, one obtains 33.9 kcal/mole and 18.3 kcal/mole, respectively, for these activation energies. The 33.9-kcal/mole value agrees well with the value 32.9 kcal/mole obtained by Ebert and Tetlow³³ from ionic conductivity measurements and with the value 35.2 kcal/mole obtained by Kobayashi^{27,34} from high-temperature measurements of C_p . The ionic conductivity measurements indicate that Frenkel defects associated with Ag^+ ion vacancies and interstitials are the predominant type in AgCl. Therefore, the 33.9-kcal/mole value obtained from the high-temperature portion of the $\log T^2\Delta\alpha$ vs T^{-1} plot probably corresponds to this type of defect.

The 18.3-kcal/mole value does not agree with any previously measured value for the activation energy for thermal generation of defects in AgCl. In addition, there are several reasons why the reality of this value is doubtful. It cannot be associated with the occurrence of a significant number of Schottky defects since the x-ray expansion measurements agree well with the dilatometric results of Strelkow. The generation of a significant number of Cl^- ion interstitials and vacancies also seems unlikely since one would expect a higher activation energy for this process because the ionic radius of the Cl^- ion is larger than that of the Ag^+ ion. Furthermore, Compton³⁵ has shown that no significant fraction of the ionic current in AgCl above 324°C can be attributed to Cl^- ions.

It seems most probable that only one activation energy occurs and that the apparent indication of a second is due to some not unexpected shortcomings of the theory in its present form. For instance, Estabrook³⁶

FIG. 7. Plot of the difference between the experimental and theoretical determinations of the thermal expansion coefficient of AgCl. The shaded region represents the possible range of values consistent with experimental error. The three points represent the difference after inclusion of some temperature dependence of the Grüneisen "constant" γ in the theoretical expression.



³¹ A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, pp. 246-349.

³² Does not include the variation of \bar{V} in $(\Delta V)/V$.

³³ I. Ebert and J. Tetlow, *Ann. Physik* **15**, 268 (1955). The value 32.9 kcal/mole was obtained by these authors from a measured value of 38.9 kcal/mole by taking into account the expected interaction between the thermally generated defects and the impurity ions introduced into the lattice to enhance the conductivity at low temperatures.

³⁴ K. Kobayashi, *Phys. Rev.* **85**, 150 (1952).

³⁵ W. D. Compton, *Phys. Rev.* **101**, 1209 (1956).

³⁶ J. N. Estabrook, *Phil. Mag.* **2**, 1421 (1957).

has concluded that the Grüneisen "constant," for a real solid increases at high temperatures. Such a change in γ would decrease Q and increase the calculated α . Since $\Delta\alpha$ at 500°K is only about 10% of its value at 700°K, a small increase in the calculated α would decrease $T^2\Delta\alpha$ much more at 500°K than at 700°K and thus would tend to straighten the curve in Fig. 7. For example, a 4.5% increase in γ ³⁷ will reduce $\Delta\alpha$ at 500°K by 81%, an amount which will make $T^2\Delta\alpha$ at 500°K lie on a line drawn tangent to the high-temperature portion of the $\log T^2\Delta\alpha$ vs T^{-1} plot. The temperature dependence of γ may well be stronger than linear. If it is assumed that γ increases as T^2 , the value of $T^2\Delta\alpha$ at 700°K is reduced only 10.4%. The $T^2\Delta\alpha$ values for 500, 600, and 700°K, obtained by iterative calculations based on the 4.5% correction to γ at 500°K and an assumed T^2 temperature dependence for γ are shown in Fig. 7. These points are well fit by a straight line which has nearly the same slope as does the best tangent to the high-temperature portion of the shaded curve. With this illustrative, and certainly not the best, correction for the temperature dependence of γ in the theoretical expression for α , only one activation energy is indicated. Further, its value, 33 kcal/mole, is in good agreement with the ionic conductivity and high-temperature C_p results mentioned above.

The temperature dependence assumed for γ is not necessarily valid. The T^2 dependence was chosen to demonstrate that even if a temperature dependence of $(d\gamma/dT)$ is allowed for, the correction to the calculated α is such that the $\log T^2\Delta\alpha$ vs T^{-1} plot is made more nearly linear. As is obvious, when the same 500° point is used and a linear dependence of γ on T is assumed, the 600° and 700° points fall between the straight line and the shaded region. Thus it is clear that an assumed temperature dependence of γ can have the effect of straightening out the $\log T^2\Delta\alpha$ plot, that the straightened curve will have a slope near to that of the tangent to the high-temperature portion of the original curve, and that neither the straightening effect nor the final slope are critically dependent on the exact choice of temperature dependence for γ .

The good agreement between the single activation energy finally obtained and those reported in the literature could be fortuitous, even though Zieten's⁴ dilatometric results with doped samples seem to rule out the possibility that the entire discrepancy between theory and experiment is due to an inadequate theory. Thus a determination of the volume change per defect implied by the $T^2\Delta\alpha$ plot is also desirable. If the number density, ρ (ratio of the number of defects to the number of lattice sites) of the thermally generated Frenkel defects is expressed as

$$\rho = Ce^{-E/2kT}, \quad (14)$$

³⁷ A change in γ of several percent seems quite reasonable. See, for example, T. H. K. Barron, *Ann. Phys. (N. Y.)* **1**, 77 (1957).

then A in Eqs. (12) and (13) is given by

$$A = (\Delta v/v)C, \quad (15)$$

where v is the average volume per atom and Δv is the volume increase which results from the generation of a single defect. The values of C reported for AgCl by Ebert and Teltow³³ from ionic conductivity measurements and by Kobayashi³⁴ from high-temperature measurements of C_p differ by a factor of 2. If the average of these values is used, 0.45 is obtained for $(\Delta v)/v$. This value seems reasonable, especially when compared with the value 0.55 obtained by Kurnick³⁸ for thermally generated Frenkel defects in AgBr from measurements of the pressure and temperature dependence of the ionic conductivity. Since the straightened $T^2\Delta\alpha$ plot yields satisfactory values for both $(\Delta v)/v$ and the activation energy, it is concluded that, up to 710°K, the observed thermal expansion is adequately accounted for by Grüneisen's theory (after the incorporation of a temperature dependence of γ) plus thermally generated Frenkel defects.

CONCLUSIONS

The present work has revealed the following points:

- (1) Schottky defects do not contribute significantly to the thermal expansion of AgCl up to 710°K (18° below the melting point).
- (2) Particularly when a temperature dependence of γ is incorporated, the Grüneisen theory adequately predicts the thermal expansion of Al and AgCl if two parameters in the theory, namely Q and α , are chosen to fit the data below 300°K and if it is assumed that thermally generated Frenkel defects contribute to the high-temperature expansion of AgCl. The nonlinearity in the plot of $\log T^2\Delta\alpha$ vs T^{-1} is most probably due to the use of a temperature-independent Grüneisen "constant" in the theoretical calculations and is not an indication of the occurrence of two types of thermally generated defects.
- (3) There is a significant difference between the x-ray and the existing dilatometric expansion data for AgCl below 300°K.

It was shown that the discrepancy between our x-ray low-temperature expansion data and the dilatometric data reported by Sreedhar for AgCl is not due to errors associated with our experimental technique. In addition, according to Grüneisen's theory, Sreedhar's results are somewhat inconsistent with the high-temperature expansion data. Therefore, it would be desirable to have additional low-temperature dilatometric measurements for AgCl.

- (4) The experimental technique used provides a convenient and valid x-ray determination of the thermal

³⁸ S. H. Kurnick, *J. Chem. Phys.* **20**, 218 (1952).

expansion coefficient of small single crystals. Errors due to changes, with temperature, of sample orientation and position are easily eliminated experimentally and temperature control by means of a gas stream is both convenient and especially good in a thermodynamic sense.

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Magnetic Properties of Superconducting Lead-Base Alloys

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Magnetization measurements have been made at 4.2°K on a variety of binary lead-base alloys, with the purpose of determining the effects of solutes, precipitates, and dislocations on superconducting properties. Increasing solute concentration results in increasingly broad magnetic transitions, the results correlating with normal-state electron mean free path in quantitative agreement with "negative surface energy" theories of Abrikosov and others. Magnetic hysteresis and trapped flux are small for annealed single-phase specimens, but are greatly increased by plastic deformation and by cellular precipitation. The maximum magnetic field to which superconductivity persists in these alloys is apparently determined by the electron mean free path, whereas extended defects such as dislocations and precipitates are primarily responsible for magnetic hysteresis and trapped flux.

INTRODUCTION

MAGNETIC flux is excluded from a bulk sample of "soft" superconductor until the thermodynamic critical field H_C is reached, at which field the flux penetrates abruptly and superconductivity is destroyed.¹ This magnetic behavior is reversible, flux being expelled from the specimen when the field is lowered below H_C . Although many superconducting elements and some dilute alloys approximate this ideal behavior, some elements (e.g., Nb, Ta, V) and most alloys and compounds do not, and have been termed "hard" superconductors. In hard superconductors, superconductivity persists to a field (H_N) greater than both H_C , which is calculable on thermodynamic grounds from calorimetric data, and H_{FP} , the field of initial macroscopic flux penetration. The magnetic behavior is often also highly irreversible. The magnetic properties of soft and hard superconductors have been reviewed by Shoenberg.² Two seemingly alternative models to explain hard or high-field superconductivity are now prominent in the literature: Mendelssohn's filamentary model and the "negative surface energy" model.

Mendelssohn Model

In fields between H_{FP} and H_N a hard superconductor is apparently neither entirely in the superconducting

state nor entirely in the normal state. Mendelssohn³ suggested that hard superconductors are inhomogeneous in microstructure and that this allowed development of a "sponge" structure consisting of interconnecting filaments of superconducting material separated by regions of normal material. If the filament dimensions are comparable to the penetration depth, superconductivity can then persist to high fields, and if they form a multiply connected network, magnetic hysteresis will result. Bean^{4,5} has recently extended this model to allow quantitative predictions of magnetic behavior, and has accounted for experimental results on bulk Nb₃Sn samples, including an observed dependence of magnetic hysteresis on bulk sample dimensions. A synthetic filamentary microstructure has been produced by pressing mercury into the pores of leached Vycor and the resultant properties were consistent with Bean's treatment.⁶ For the natural high-field superconductors, however, it was not clear what features of the microstructure served as the superconducting filaments. Several authors⁷⁻⁹ have suggested that dislocations play this role.

Several experimental results have raised difficulties about the filamentary picture of high-field super-

¹ It is assumed the specimen has zero demagnetizing coefficient and hence no "intermediate state" region.

² D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1960).

³ K. Mendelssohn, Proc. Roy. Soc. (London) **A152**, 34 (1935).

⁴ C. P. Bean, Phys. Rev. Letters **8**, 250 (1962).

⁵ C. P. Bean and M. V. Doyle, J. Appl. Phys. **33**, 3334 (1962).

⁶ C. P. Bean, M. V. Doyle, and A. G. Pincus, Phys. Rev. Letters **9**, 93 (1962).

⁷ R. W. Shaw and D. E. Mapother, Phys. Rev. **118**, 1474 (1960).

⁸ J. J. Hauser and E. Buehler, Phys. Rev. **125**, 142 (1962).

⁹ J. J. Hauser and E. Helfand, Phys. Rev. **127**, 386 (1962).