Linear Thermal Expansion Coefficient of the NaCl Phase of CsCl

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Linear Thermal Expansion Coefficient of the NaCl Phase of CsCl

Abstract
Cesium chloride undergoes a phase change from the low-temperature CsCl structure to the high-temperature NaCl structure at about 469°C.1 There is a volume increase of about 16% when the NaCl structure appears.1 The nature of the transition is of interest, as are the physical properties of the high-temperature phase. If sufficient high-temperature phase data are available for CsCl, calculations of the heat of transition can be made more accurately.

Keywords
cesium chloride, sodium chloride

Disciplines
Atomic, Molecular and Optical Physics | Physical Chemistry

Comments
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Linear Thermal Expansion Coefficient of the NaCl Phase of CsCl

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Cesium chloride undergoes a phase change from the low-temperature CsCl structure to the high-temperature NaCl structure at about 469°C.1 There is a volume increase of about 16% when the NaCl structure appears.1 The nature of the transition is of interest, as are the physical properties of the high-temperature phase. If sufficient high-temperature phase data are available for CsCl, calculations of the heat of transition can be made more accurately.2

The large volume change at the transition makes work with single crystals difficult, the crystals often breaking upon heating to only 100°C. Powdered CsCl was melted in air and poured into a brass mold coated with colloidal carbon. This resulted in polycrystalline rods, about 2 in. long and \( \frac{1}{4} \) in. in diameter, with an average grain diameter of 1 mm. Samples with larger grains than this usually broke during heating before any measurements could be made.

The dilatometer was a high-temperature modification of one used previously in this Laboratory.3 It measures length changes relative to fused silica by interferometry. The correction for the fused silica expansion4 is small. As a check, the thermal-expansion coefficient of a single crystal of KCl was measured in several 20°C intervals between 100° and 400°C. The results were 3% lower than the values obtained by x-ray diffraction by Glover5 in this temperature range.

The linear thermal-expansion coefficient of the low-temperature phase of CsCl, \( \alpha(T) = \frac{\Delta l}{l(T)} \Delta T \), where \( T \) is the average temperature in the interval \( \Delta T \), was determined to be \( 4.78 \times 10^{-5} \text{C}^{-1} \), between 50° and 150°C. This is within 5% of the temperature coefficient of lattice parameter expansion determined by Menary et al.,1 \( 4.98 \times 10^{-5} \text{C}^{-1} \).

As the phase change was approached, the length of the sample increased too rapidly to follow. The effects of the volume change took a long time to anneal out. The samples were held at 550°C for several days before measurements were begun. The length changes were followed as the temperature was cycled back and forth between 550° and 600°C. The average expansion coefficient between 570° and 590°C in the NaCl phase was \( 5.1 \times 10^{-5} \text{C}^{-1} \) with an estimated error of 10% based on the reproducibility. Upon cooling below the phase change the samples usually broke.

Just below the phase change the lattice parameter expansion coefficient1 is \( 6.6 \times 10^{-4} \text{C}^{-1} \) and the NaCl phase is seen to have a lower expansion coefficient than the more closely packed CsCl phase.

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On Imaginary Solutions to Three-Spin Spectra

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In the course of our investigation of the NMR spectra of thiophene and its derivatives, we have discovered a peculiarity in the analysis of general three-spin systems proposed by Castellano and Waugh.2 Their method of solution yields, in general, 40 independent sets of three coupling constants, and three chemical shifts which are consistent with the observed frequencies. The actual solution may be ascertained by comparing the intensities predicted from these sets with the observed intensities.3 In any given case, one or more of the 40 solutions may contain imaginary quantities and are preemptorily discarded on physical grounds; however, we have found several cases in which a slight change in the input parameters caused some of these complex solutions to become real.

Three-spin spectra may be characterized by three quartets associated with the fundamental frequencies of the three nuclei and with three combination lines. Having established such a grouping from the experimental spectrum, a set of eigenvalues is derived, consistent with the given grouping. These eigenvalues are the input parameters for the Castellano-Waugh procedure leading to the chemical shifts and coupling constants. Because of experimental error, the observed lines will in general not precisely fit into the required quartets and combination lines. In practice, one takes an average of the observed frequency spacings and derives an idealized, self-consistent set of lines. One may call such a set an adjusted set.

This averaging must be arbitrary to a certain degree. One could imagine a large number of such sets, differing from each other by small increments but all conforming to the observed spectrum within the experimental error.4 When one or more lines are missing, or when one is unable to resolve lines which lie close together, this arbitrariness is increased. Intuitively, one feels that this uncertainty would be reflected in the range of values one would obtain if all such sets were subjected...
to calculation. However, in the Castellano–Waugh procedure, this is not always the case for the real domain.

Table I lists the observed and two sets of adjusted frequencies for pure 2-iodothiophene at 40 Mc/sec. The average deviation between the two adjusted sets is 0.016 cps. Table II lists the two sets of eigenvalues derived from the adjusted sets in Table I with the sum of the coupling constants a maximum.

Eigenvalue set No. 1B yielded two real solutions. The one that is consistent with other data follows:

\[
\begin{align*}
\omega_A &= -6.80, \\
\omega_B &= -6.36, \\
\omega_C &= 13.16, \\
J_{AB} &= -1.26, \\
J_{AC} &= 5.36, \\
J_{BC} &= 3.67, \\
\end{align*}
\]

where A, B, and C are the 5, 3, and 4 protons, respectively, in 2-iodothiophene. The calculated intensities agree closely with those observed, with the average intensity unit. (The sum of the intensities is normalized to 12.00.)

Eigenvalue set No. 1A yielded no real solutions. The roots of the fourth-degree polynomial equation are

\[
\Omega_1 = -1.984528 \pm 0.004252i; \\
\Omega_2 = 4.486732 \pm 3.538255i.
\]

Note that the first pair of roots have only a very small imaginary component. The corresponding pair belonging to set No. 1B are \(\Omega_1 = -1.987975\) and \(\Omega_2 = -1.987980\).

The algebraic calculation used in the analysis may be viewed as a mapping or a transformation whereby points representing the input parameters in a multidimensional space are mapped into points representing the solutions in a multidimensional complex space. Since many different sets of eigenvalues can be constructed from a given grouping within the experimental error, there will be a corresponding number of points in the input parameter space, constituting an error volume. This volume is then mapped into four corresponding volumes in the solution space because there are four solutions to each set of eigenvalues. In the example cited, two such volumes in the solution space include both the real and the imaginary domain.

The first pair of solutions to the A set were complex and normally would have been discarded. Yet it is clear from the above that they must be considered to belong to error volumes in the solution space which also include real and, in principle, acceptable solutions. In fact, one of these real solutions turned out to be the actual solution to the problem.

It is apparent, therefore, that care must be exercised in simply discarding all complex solutions. This is especially true when the calculation is carried out by computer techniques which automatically reject any set which contains imaginary quantities. A similar situation was found to exist with 2-chlorothiophene in a 10% solution in CCl₄ at 60 Mc/sec, so that this phenomenon appears to apply in more than an isolated case.

3. Several sets may agree with the observed intensities. These may be distinguished by running the spectrum at a different frequency or in a solvent which appreciably changes the chemical shift.
4. In principle, an infinity of such sets could be constructed by making the next set differ only infinitesimally from the previous set.

Compare Ref. 2, p. 298.