Low Temperature Heat Capacity and Thermal Expansion of KCl Containing a Low Concentration of Li$^+$

J. G. Collins, S. J. Collocott, R. J. Tainsh,
C. Andrikidis and G. K. White

Division of Applied Physics, CSIRO, P.O. Box 218, Lindfield, N.S.W. 2070.

Abstract

The linear thermal expansion coefficient α from 180 mK to 36 K and the heat capacity per gram c_p from 0·5 to 10 K are reported for KCl containing approximately 100 ppm Li$^+$. Contributions to α and c_p attributable to the impurity have been identified and analysed on the basis of a model in which the Li$^+$ ions reside about 0·05 nm from the equilibrium cationic site in any of the $\langle 111 \rangle$ directions. There is consistent quantitative agreement with a Schottky-like term that arises from the eightfold degeneracy of the level splitting; the splitting parameter is 1·5 K. The large (~ 160) Grüneisen parameter associated with the impurity contribution is evidence for a quantum-mechanical tunnelling process, and agrees with values derived from independent measurements of the spectroscopic and dielectric responses of this system under pressure.

1. Introduction

Measurements of the heat capacity and linear coefficient of thermal expansion of crystals containing very low concentrations of homovalent impurity ions yield quantitative information about the physical environment of the isolated impurity and its dependence on pressure. As well as being of intrinsic interest, this information provides a basis for studying the properties of highly concentrated, interacting impurity centres, i.e. of some forms of disordered or glass-like systems (see e.g. Klein 1984).

Case *et al.* (1972) measured, in this laboratory, the linear coefficient of thermal expansion α between 2 and 30 K of NaCl containing OH$^-$ and CN$^-$ ions and KCl containing Li$^+$ ions. Results for KCl/Li$^+$ showed a temperature dependence that varied approximately as T^{-2} below about 6 K, suggesting that the high temperature side of a Schottky anomaly was being observed. When these results were combined with heat capacity measurements made on similarly doped material (Harrison *et al.* 1968), a very large Grüneisen parameter of about 300 was obtained, suggesting that a quantum-mechanical tunnelling mechanism was dominating the free energy of the crystal at these very low temperatures.

We have now extended the thermal expansion measurements for KCl/Li$^+$ downwards to the region of 100 mK in a newly commissioned ^{3}He–^{4}He dilution refrigerator to try to confirm this hypothesis. We have re-measured the thermal expansion from 2 to 36 K in a conventional ^{4}He capacitance dilatometer to confirm the long-term stability of the impure crystal, and we have measured the heat capacity per gram c_p of the sample from 0·5 to 10 K.

Within experimental error, the results of the combined measurements are consistent with deductions from a phenomenological model (Gomez *et al.* 1967) in which Li$^+$ ions are displaced about 0·05 nm from the substitutional cationic sites in one of eight equivalent $\langle 111 \rangle$ directions. The resulting dipole can tunnel quantum-mechanically 'around' the simple cube formed by the eight sites and can contribute a Schottky term to the free energy of the crystal. The model is very similar to that used by Devonshire (1936) (cf. Harrison *et al.* 1968) to describe rotational states of molecules in crystals.

Our results are consistent with a model based on an energy gap of about 1·5 K between four equally separated energy levels (degeneracies 1 : 3 : 3 : 1), and are in moderate agreement with earlier heat capacity measurements (Harrison *et al.* 1968) that give a splitting of 1·2 K and with spectroscopic studies that give splittings between 1·1 and 1·2 K (see e.g. the review by Barker and Sievers 1975). The Grüneisen parameter for the Schottky contribution is of the order of 160, which agrees with a value derived from measurements of far-infrared spectra and dielectric response of similar materials subjected to pressure (Kahan *et al.* 1976; Holland and Lüty 1979).

2. Experimental

Our sample was taken from boule No. 70331Q of KCl, given to us by Professor R. O. Pohl, Cornell University. It contained 0·5 mol % LiCl in the melt and was estimated by Pohl to have a concentration of Li$^+$ ions in the crystal of approximately $2-3 \times 10^{24}$ m^{-3}. Details of the sample preparation are given by Harrison *et al.* (1968).

Heat Capacity

The sample was 42·2 mm long by 20 mm square cross section and weighed 28·72 g. The heat capacity was measured in an adiabatic calorimeter (Collocott 1983) from 0·5 to 10 K with an inaccuracy of less than 1%.
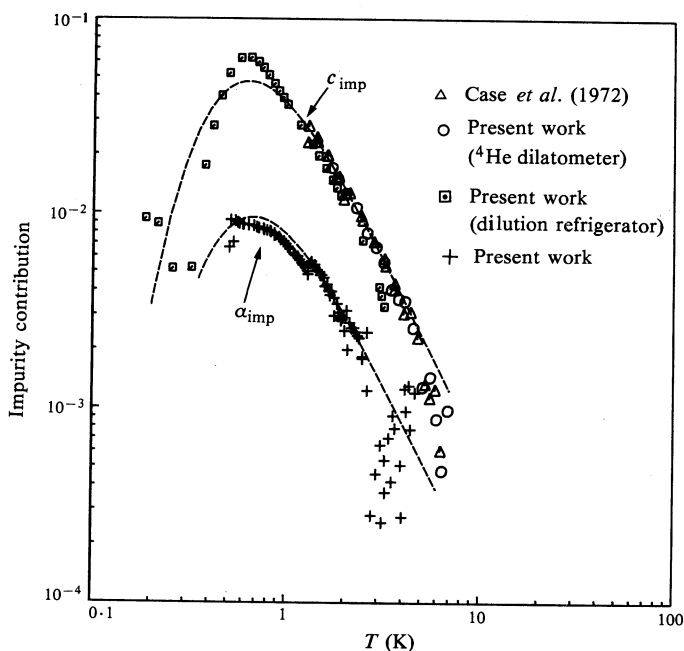
Thermal Expansion

The same sample was used for the thermal expansion measurements. The ^{4}He capacitance dilatometer (White and Collins 1972) was used to re-measure α from 1·6 to 36 K. A copper end-cap 8·42 mm thick was placed on top of the sample to bring the total length to the standard cell size of approximately 51 mm. The end-cap was connected to the base plate of the cell by a threaded copper screw through a hole drilled vertically through the sample. The screw was held lightly in position by a series of wavy washers below the base plate. This gave mechanical stability without constraining the sample. Values of α were obtained with probable errors of $\pm 0·01 \times 10^{-8}$ K^{-1} at 4 K increasing to $\pm 0·5 \times 10^{-8}$ K^{-1} at 30 K.

Expansion measurements in the dilution refrigerator were made in a new OFHC copper cell identical in design to that used in the ^{4}He dilatometer. The expansion cell was threaded into the base of the mixing chamber of the refrigerator. Temperatures were measured using a calibrated germanium resistance thermometer (Lake Shore Cryotronics Inc. model No. GR-200-30). The estimated error in α is about $\pm 2 \times 10^{-8}$ K^{-1} at 500 mK, decreasing to about $\pm 0·1 \times 10^{-8}$ K^{-1} at 2 K and increasing to about $\pm 0·5 \times 10^{-8}$ K^{-1} at 30 K.

3. Results

Heat Capacity

The measured values of c_p (mJ g^{-1} K^{-1}) were analysed by initially subtracting a harmonic lattice contribution c_D based on a Debye temperature of 235·1 K (Barron *et al.* 1957) for two ions per Bravais lattice point. The residual, higher-temperature values (above 6 K) were plotted as $(c - c_D)/T^5$ against T^2 to give an estimate of the coefficients of the leading correction terms in T^5 and T^7. Below 3 K this contribution is less than 1 μJ g^{-1} K^{-1}. This is within experimental error and does not affect the subsequent analysis; it is included for completeness. Barron *et al.* estimated a slightly smaller correction below 10 K in the pure material.

Fig. 1. Contribution to the specific heat capacity (mJ g^{-1} K^{-1}) and coefficient of linear thermal expansion of KCl/Li$^+$ (10^{-6} K^{-1}) attributable to the impurities. The broken curves are Schottky fits to the data with the splitting parameter $\Delta = 1\cdot5$ K and magnitudes 21·6 μJ g^{-1} K^{-1} (heat capacity) and 10·075 × 10^{-8} K^{-1} (thermal expansion).

The contribution, c_{imp}, remaining after subtracting the harmonic and higher-order terms, was attributed to the dipolar impurities:

$$c_{imp} = c - (1\cdot944 \times 10^6 \times \tfrac{2}{74\cdot56})\left(\frac{T}{235\cdot1}\right)^3 - 0\cdot37\left(\frac{T}{10}\right)^5 - 0\cdot28_5\left(\frac{T}{10}\right)^7 \text{ mJ g}^{-1}\text{ K}^{-1}.$$

The residual values c_{imp} are plotted against temperature on a log scale in Fig. 1 (upper curve); the considerable scatter above 3 K for values below 1 μJ g^{-1} K^{-1} is rounding error, and is magnified by the logarithmic scale.

A nonlinear, least-squares fit was made to the values of c_{imp} in Fig. 1 (shown as the broken curve) by using the Schottky expression

$$c_{imp} = \frac{(3\,k\,n/\rho)\,x^2\,\exp(x)}{\{\exp(x)+1\}^2}, \qquad x = \Delta/kT.$$

Here Δ is the energy-level splitting, k is Boltzmann's constant and n is the concentration by volume of Li^+ ions in the crystal of density ρ. We found $\Delta/k = 1 \cdot 55 \pm 0 \cdot 05$ K and $3\,k\,n/\rho = 20 \cdot 5 \pm 2 \cdot 4$ $\mu J\,g^{-1}\,K^{-1}$. Given a density of 2030 kg m^{-3} for KCl, we deduced an impurity concentration of approximately 10^{24} m^{-3}.

The measured values of $c(T)$ agree well with those of Harrison *et al.* (1968) for companion samples to ours. The impurity concentration we deduced is about half that estimated by R. O. Pohl (personal communication); we note that Harrison *et al.* also deduced from their heat capacity measurements impurity concentrations for their samples that were about 40% below values determined by spectrochemical analysis.
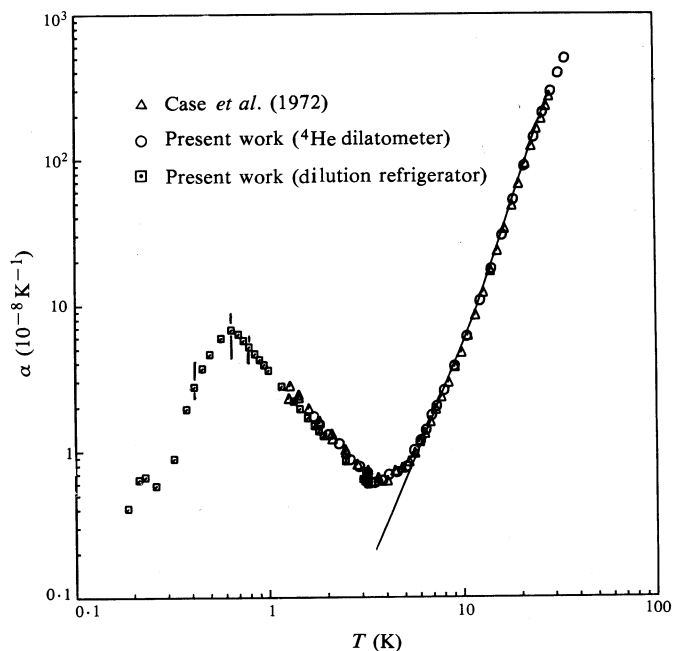

Fig. 2. Coefficient of linear thermal expansion of KCl containing 10^{24} m^{-3} Li^+ plotted as a function of temperature. The solid line is the linear expansion coefficient for pure KCl (White and Collins 1973). Error bars show uncertainty due to smoothing of the results.

Thermal Expansion

Results for the linear coefficient of expansion of KCl/Li^+ below 36 K are shown in Fig. 2 for three independent sets of measurements: $1 \cdot 3$–$28 \cdot 6$ K measured in 1971 in the ^{4}He capacitance dilatometer (Case *et al.* 1972), $1 \cdot 6$–$35 \cdot 8$ K in the same apparatus in 1985, and 180 mK–26 K in the new copper capacitance dilatometer in the ^{3}He–^{4}He dilution refrigerator.

The excellent agreement between the first two sets of measurements shows that the impure crystal has remained very stable over 15 years with no obvious segregation or aggregation of the Li$^+$-vacancy dipoles. There is also good agreement between these data and those obtained above 1 K from the dilatometer in the dilution refrigerator. This gives us confidence that the calibrations of the two cells are consistent. Below 1 K there is increasing scatter in the raw points, and the expansion coefficient data have been subjected to cubic spline smoothing as a function of ln T. There is some latitude in the smoothed values, depending upon the initial selection of knot temperatures. This uncertainty is shown by the error bars on the plot below 1 K.

The contribution to the linear expansion coefficient α_{imp} that is attributable to the Li$^+$ impurity was found by subtracting from the measured values an amount

$$10^8 \alpha_{KCl} = 4 \cdot 86 \left(\frac{T}{10}\right)^3 + 0 \cdot 7 \left(\frac{T}{10}\right)^5 \text{ K}^{-1}$$

(White and Collins 1973). The values of α_{imp} were least-squares fitted as functions of temperature to a Schottky expression, yielding a splitting parameter $\Delta/k = 1 \cdot 53 \pm 0 \cdot 1$ K and a pre-exponential factor $11 \cdot 5 (\pm 1 \cdot 0) \times 10^{-8}$ K^{-1}. The values of α_{imp} and the Schottky fit are shown as functions of temperature in Fig. 1 (lower curve).

A Grüneisen parameter

$$\gamma_{imp} = -(\partial \ln \Delta / \partial \ln V)_T = 3\alpha_{imp} B_s / \rho c_{imp}$$

was calculated for the impurity contribution. With values of 19·63 GPa for the bulk modulus B_s and 2030 kg m^{-3} for the density (these are values for pure KCl) we obtained

$$\gamma_{imp} \sim 160 \pm 20.$$

4. Discussion

Within experimental error both the excess heat capacity and the excess thermal expansion attributed to the Li$^+$-vacancy dipoles are described well by the phenomenological, four-level model of Gomez et al. (1967) with splitting parameter 1·5 K.

The particular form of potential introduced into the model by Gomez et al.—a double-harmonic-oscillator (DHO) model—cannot describe adequately the thermal expansion results. It yields for the level splitting parameter

$$\Delta = 2\pi^{-\frac{1}{2}} \hbar \omega \eta^{\frac{1}{2}} \exp(\eta),$$

where $2\pi\hbar$ is Planck's constant, ω is the fundamental oscillator frequency, and $\eta = m\omega x^2 / \hbar$ is the ratio of the barrier height to the zero point energy of the oscillator; here m is the mass of the Li$^+$ ion and $2x$ is the separation between the oscillator centres.

From this expression we derive γ_{imp} as

$$\gamma_{imp} = (\tfrac{3}{2} - \eta)(-\partial \ln \omega / \partial \ln V) + (1 - 2\eta)(-\partial \ln x / \partial \ln V).$$

Assuming that the well-spacing between neighbouring $\langle 111 \rangle$ Li$^+$ sites is $0 \cdot 10/\sqrt{3} = 0 \cdot 058$ nm and setting $\Delta/k = 1 \cdot 5$ K, we deduce

$$\eta = \text{(barrier height)}/\text{(zero point energy)} \sim 7, \qquad \omega = 12 \text{ THz}.$$

Holland and Lüty (1979) have shown that the dependence of well-spacing x on pressure (volume) is effectively zero for small applied pressures, so that a value for the volume dependence of the oscillator frequency ($\partial \ln \omega / \partial \ln V$) of about $+30$ is needed to reproduce the observed γ_{imp}. The volume dependence of ω is unknown; an educated guess, based on the observed behaviour of infrared vibrational frequencies under pressure, suggests that $\partial \ln \omega / \partial \ln V$ should be small and *negative*. This quantitative inadequacy of the single-parameter DHO model confirms the conclusion of Kahan *et al.* (1976), who found that it could not describe the pressure dependence of observed absorption lines in the far-infrared spectrum of the KCl/Li system.

As has been pointed out by Fischer and Klein (1980), the Grüneisen parameter for KCl/Li can be estimated from measurements of the pressure dependence of the far-infrared and dielectric responses for this system (Kahan *et al.* 1976; Holland and Lüty 1979). They obtained values of γ_{imp} between 200 and 300 from the lowest-lying points in these data, in order-of-magnitude agreement with the preliminary estimate of ~ 300 made by Case *et al.* (1972) from our 1971 thermal expansion measurements. Our revised value of ~ 160 is consistent with a value of ~ 150 that can be obtained from the results of Holland and Lüty for the dielectric response *in the limit as applied pressure goes to zero*. Although there must be considerable uncertainty on this limit due to curvature in the pressure dependence of Δ (cf. Fig. 15 of Holland and Lüty 1979), we regard the agreement as satisfactory.

Measurements contemporaneous with ours have recently been published by Dobbs and Anderson (1986). They deduced a value for γ_{imp} of $+150 \pm 15$ for samples containing between 60 and 150 ppm Li$^+$, in excellent agreement with our result.

Acknowledgments

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