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Low temperature anharmonicity in CsCl

Mattia Sist,^[a] Karl Frederik Færch Fischer,^[a] Hidetaka Kasai,^[b] and Bo Brummerstedt Iversen^{*[a]}

Abstract: Anharmonic lattice vibrations govern heat transfer in materials, and it is commonly assumed to be dominant at high temperature. The textbook cubic ionic defect free crystal CsCl is shown to possess an unexplained low thermal conductivity at room temperature (~1 Wm/K), which increases to ~13 Wm/K at 25 K. Through high resolution X-ray diffraction it is unexpectedly shown that the Cs atomic displacement parameter becomes anharmonic at 20 K.

In solids properties such as superconductivity, heat capacity and thermal conductivity are dictated by atomic motion within the crystal. The presence of anharmonic effects is becoming a decisive factor in inspecting thermoelectric performances,^[1] and in predicting the thermodynamic stability of specific phases.^[2] Anharmonicity corresponds to departure of a system from harmonic behaviour, which is mathematically represented by the linear proportionality between forces and atomic displacements.

“Engineering” anharmonicity^[3] potentially expands our capabilities to design new materials with low thermal conductivity. A large number of recent works highlights the link between particular bonding states^[1, 4] or high deformability of the lone-pair charge density^[5] to anharmonicity. In this context, CsCl, a “simple” ionic system, represents a notable exception. Caesium chloride represents the archetypal structural model of the so-called caesium chloride structure (B2, $Pm\bar{3}m$) as reported by numerous Inorganic Chemistry textbooks. The structure can be depicted as cubic with each corner occupied by an anion (or a cation), whereas the cation (or the anion) sits at the centre of the cell. Our study was initially motivated by the low thermal conductivity in crystalline CsCl, which is 1.0 W/(m K)^[6] at ambient conditions, i.e. lower than in well-known thermoelectric materials such as PbTe (2.2 W/(m K))^[7]. In these latter compounds the low thermal conductivity is rationalized in term of anharmonicity or static disorder.^[8] Information on the atomic displacements is routinely gathered from diffraction experiments, but it is usually limited to the Debye-Waller factor in the harmonic approximation. This is because departure from the harmonic potential is usually found at high temperatures,^[9] while most diffraction experiments are carried out at low temperatures. Moreover, quantification of anharmonicity requires high quality datasets, especially in terms of Q-space resolution,^[10] which due to thermal motion is difficult to measure at high temperature.

The site symmetry of Cs and Cl is $m\bar{3}m$. This implies that, in the harmonic approximation, the atomic displacement parameter (ADP) has to be isotropic, i.e. $U_{11} = U_{22} = U_{33}$ while mixed terms are zero, and the nuclear probability density function (NPDF) is spherical. In crystallography, deviations from harmonicity are usually modelled with the Gram-Charlier (GC) formalism,^[11] in which the harmonic Gaussian distribution is mathematically expanded. Up to 4th term, the site symmetry imposes that $D_{1111} = D_{2222} = D_{3333}$ and $D_{1122} = D_{1133} = D_{2233}$ whereas all other GC coefficients, D_{ijkl} , are zero. The implementation of GC coefficients allows deviations from the normal distribution, and for CsCl non-sphericity of the NPDF.

The maximum entropy method (MEM) is an unbiased reconstruction of the charge density from X-ray diffraction data.^[12] The nuclear-weighted X-ray maximum entropy method (NXMEM) has been recently introduced as a powerful tool to enhance the nuclear resolution from X-ray data.^[13] Here NXMEM offers a valuable model-free tool to corroborate findings from refinement of GC coefficients.

The evolution of the harmonic isotropic ADP, U_{iso} , of Cs and Cl with temperature is shown in Figure 1. From 20 to 100 K, $U_{iso}(\text{Cl}) > U_{iso}(\text{Cs})$. At $T > 100$ K the harmonic ADPs of the two atoms are comparable despite the large mass difference.

Figure 1 Isotropic atomic displacement parameters of Cs and Cl as a function of temperature. Error bars are smaller than the symbols. Roman numbers refer to the crystal number. Values at 100 K for crystal I and II perfectly overlap.

In the GC expansion to the fourth order the atomic site symmetry $m\bar{3}m$ imposes that the Debye-Waller factor is given by:

$$T = e^{\left(-8\pi^2 U_{iso} \frac{\sin^2 \theta}{\lambda^2}\right)} \left[1 + \frac{2\pi^4}{3} (D_{1111} h^4 + D_{1122} h^2 l^2) \right]$$

At all temperatures $D_{1111}(\text{Cl})$ and $D_{1122}(\text{Cl})$ are negligible and zero within 3 sigma, see supporting information. On the contrary, refinement of $D_{1111}(\text{Cs})$ and $D_{1122}(\text{Cs})$ leads to a substantial improvement of the statistical R-factors (Figure 2) and significantly improves the model according to the Hamilton test^[14] except at 300 K.

Inspection of the maximum and minimum Fourier difference residuals in the harmonic and anharmonic models shows

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Supporting information for this article is given via a link at the end of the document.

that inclusion of the GC terms substantially improves the model at low temperatures (Figure 3).

Figure 2 R and wR factors as defined in JANA2006 in the harmonic model and in the anharmonic model as function of temperature. Inclusion of the GC coefficients leads to a significant improvement of the model, especially at low temperatures. The definition of R and wR and numerical values of the R-factors are reported in the SI.

Figure 3 Maximum and minimal Fourier residuals in the harmonic model and in the anharmonic model as function of temperature. Numerical values are reported in the SI. Inclusion of the GC coefficients significantly improves the models at low temperatures but not at 200 K and 300 K.

The resulting anharmonic refinements are stable and lead to physically meaningful NPDFs. The dimensionless *ratio* anharmonic/harmonic contribution to the Debye-Waller factor decreases rapidly above 50 K rendering the overall ADP(Cs) more and more isotropic with temperature (Figure 4). The Fourier transform of the Debye-Waller factor yields the NPDF and it is shown in Figure 5.

In particular the nuclear probability density function of Cs is elongated along the $\langle 100 \rangle$ directions which, presumably, accounts for a preferred atomic displacement towards caesium atoms in adjacent cells and away from chlorine atoms (soft potential direction in the primitive cubic CsCl structure). We tend to exclude the presence of static disorder with Cs off-centering as the maximum of the NPDF(Cs) decreases smoothly with temperature. However, since diffraction only probes the time averaged electron/nuclear density, thermal motion and disorder cannot be decoupled.

Figure 4 “Significance” of the anharmonic contribution to the overall ADP(Cs). A logarithmic trendline has been added as guideline. The ratio D_{hkl}/U_{iso}^2 decreases rapidly above 50 K rendering the anharmonic contribution negligible at high temperatures.

Figure 5 Experimental nuclear probability density function (NPDF) of Cs in the (100) plane in a square of 0.25 x 0.25 (fractional coordinates); the color scale is logarithmic (0 to $\log(\text{NPDF}_{\text{MAX}})$) with 10 contours; at bottom of each picture the minimum and maximum in $\text{\AA}^{-3}$ in absolute scale are reported. The temperature is indicated in upper-right corner (20, 100, 200, 300 K have been obtained from refinement on crystal I, 50, 150 K have been obtained from refinement on crystal II).

The decrease of the anharmonic character with increasing temperature is unexpected since normally the opposite should occur.^[15] A bottom flatter in the $\langle 100 \rangle$ direction in the anharmonic potential energy curve might explain the low temperature NPDF anisotropy, while at RT temperature, for larger vibration the anharmonic potential energy branches resemble the harmonic one as observed in thermoelectric PbTe and SnTe.^[16]

The maximum entropy method (MEM) offers a non-biased reconstruction of the electron and nuclear density from X-ray and neutron experiments, respectively.^[12, 17] The MEM electron density is “dynamic” as it is not deconvoluted from thermal smearing effects. Features of MEM densities may be caused by bonding^[18] and/or by nuclear motion effects.^[19] In the present case, the diffuseness of the electronic cloud of Cs makes it impossible to recover signs of anharmonic displacements, even when using simulated anharmonic structure factors, see supporting information. The MEM analysis is not therefore explored further. Conversely, NXMEM substantially enhances the nuclear resolution from X-ray diffraction data.^[13] In the NXMEM algorithm the observed X-ray structure factors are transformed into the pseudo-nuclear structure factors. MEM computation on the

pseudo-nuclear structure factors yields an electron-weighted nuclear density. This latter is not quantitatively comparable to the NPDF as depicted from Fourier transform of the Debye-Waller factor since it inherently depends on the atomic scattering factors, i.e. on the number of electrons. As a consequence, even though Cs and Cl exhibit similar ADPs and NPDF maxima at 300 K, NXMEM densities are remarkably higher for Cs than for Cl as shown in Figure 6 and Figure 7. Nevertheless, the atomic nuclear shapes and the maxima positions in the NPDF and NXMEM are expected to be similar. In fact the non-sphericity in the NXMEM density is consistent with the NPDF as it is more pronounced at 20 K and it is virtually absent at $T > 100$ K. This further corroborates that the anharmonic contribution is significant at very low temperature while at room temperature the ADP of caesium is fully isotropic.

Figure 6 Experimental NXMEM density of Cs at $\chi^2 = 0.3$ as function of temperature (right-upper corner) in the (100) plane in a square of 0.25×0.25 (fractional coordinates) centred on the Cs atom; the color scale is logarithmic (0 to $\log(\rho_{\text{max}})$) with 10 contours; at the bottom of each picture the minimum and maximum in absolute scale are reported. The temperature is indicated in upper-right corner (20, 100, 200, 300 K have been obtained from refinement on crystal I, 50, 150 K have been obtained from refinement on crystal II).

Figure 7 Experimental NXMEM density of Cl at $\chi^2 = 0.3$ as function of temperature (right-upper corner) in the (100) plane in a square of 0.25×0.25 (fractional coordinates) centred on the Cl atom; the color scale is logarithmic (0 to $\log(\rho_{\text{max}})$) with 10 contours; at the bottom of each picture the minimum and maximum in absolute scale are reported. The temperature is indicated in upper-right corner (20, 100, 200, 300 K have been obtained from refinement on crystal I, 50, 150 K have been obtained from refinement on crystal II).

Overall the GC coefficient expansion and NXMEM show that the atomic displacement of Cs is anisotropic, and hence for the present cubic structure, anharmonic at low temperature. CsCl possesses a very low thermal conductivity at ambient conditions despite the NPDF being harmonic. The thermal

conductivity as a function of temperature has been measured down to 25 K to probe whether the appearance of anharmonicity constitutes a major contribution to the low thermal conductivity in CsCl. Our measurements confirm the very low thermal conductivity of CsCl at room temperature ($\kappa = 1.0(2)$ W/(m K)). At lower temperatures, however, the thermal conductivity increases. This means that the observed increase of anharmonicity at low temperature does not contribute significantly to a lower thermal conductivity. Fully harmonic ADPs have, actually, been observed even in systems with very low thermal conductivity [20]. It is worth stressing that despite the present work proves that the ADP of Cs is anharmonic at low temperatures, the populations of harmonic phonons with relatively high energy might mask anharmonic features in the NPDF at higher temperatures.

Figure 8 Thermal conductivity, κ , as function of temperature.

The present results have been derived from X-ray diffraction measurements with data collection taking less than two hours per temperature. Systematic effects such as absorption and extinction are strongly reduced by using high energy radiation and crystals of small dimensions. Overall, the present work shows that the combined approach of least-square fitting in reciprocal and direct space NXMEM analysis can be used to consistently reconstruct subtle anharmonic nuclear effects.

Anharmonicity is often found in the presence of a lone pair^[5b] and because of resonance bonding.^[4a] The low thermal conductivity of CsCl and the present findings on the anharmonic character of the Cs ADP constitute a remarkable exception, which calls for a more general theory on anharmonicity. The results furthermore highlights that the unusual low thermal conductivity in CsCl needs further scrutiny. CsCl is a simple crystal structure, and unlike thermoelectric materials such as PbTe^[21], SnSe^[22], and SnTe^[23] the crystals have limited defects and atomic disorder. Since anharmonicity is shown here to also be very limited at room temperature, the origin of the low thermal conductivity in CsCl remains to be understood.

Experimental Section

Two spherical single crystals grown from a saturated solution of CsCl were selected under a microscope and checked with a Bruker Apex

II single crystal diffractometer. Data collections were performed at beamline BL02B1, SPring8, Japan,^[24] employing a He gas cooling system. Data on crystal I (radius, $r = 10\ \mu\text{m}$) were measured at 20 K, 100 K, 200 K, 300 K ($\lambda = 0.24783\ \text{\AA}$), while data on crystal II (radius, $r = 20\ \mu\text{m}$) were measured at $\sim 17\ \text{K}$, 50 K, 100 K 150 K ($\lambda = 0.2496\ \text{\AA}$). Refinements on data collected at nominal 17 K produce U_{iso} and cell parameters that are compatible with $T \approx 70\ \text{K}$ probably due to an off-centring of the cooling nozzle and these data are therefore confined to the SI. The data were integrated, corrected for the Lorentz effect and polarization, and for absorption (empirical correction) with the Rigaku Rapid Auto software. The data were merged with Sortav^[25] and imported into JANA2006.^[26] Extinction^[27] represents a major issue in such perfect inorganic crystals, but it was however limited by the small dimensions of the crystals and the short wavelength employed. The extinction parameters were negative and therefore physically meaningless for crystal I (mosaic spread $g = -0.27(7)$ for type I model, particle size $p = -2.1(9)$ for type II as given in JANA2006), but slightly significant for crystal II ($g = 0.27(4)$) (see supporting information). MEM and NXMEM calculations were performed with the BayMEM software.^[28] The NXMEM calculations were stopped at $\chi^2 = 0.3$ and details are reported in the SI. The thermal conductivity was measured with a Physical Property Measurement System (PPMS) using the Thermal Transport Option (TTO)^[29] down to 25 K on a bar-shaped sample made from a pellet of CsCl pressed at 5 atm with a density of 97 % of the crystallographic density.

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CsCl

High resolution single crystal X-ray diffraction reveals highly unusual Cs anharmonicity in CsCl below 100 K which offers insight into the very low thermal conductivity of this simple crystal structure.