

The Temperature Dependence of the Debye–Waller Factor Near a Phase Transition: CsPbCl₃

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Abstract

By fitting effective one-particle potentials to Bragg neutron diffraction intensities measured by Sakata, Harada, Cooper & Rouse [*Acta Cryst.* (1980), A36, 7–15] for the cubic perovskite caesium lead chloride, CsPbCl₃, it has been established that, contrary to the results of Sakata *et al.*, the effective one-particle potentials for the Cl ion are neither independent of temperature nor of a highly anharmonic form. To the resolution limit of the data, collected out to $\sin \theta/\lambda = 0.58 \text{ \AA}^{-1}$, the one-particle probability density function of the Cl ion is singly peaked. It is proposed that the strong temperature dependence of the effective one-particle potentials, and the accompanying anomalous temperature behaviour observed for the mean-square displacements of the Cl and Cs ions above the anti-ferrodistortive phase transition temperature, result from soft-mode vibrations. The temperature dependence of the mean-square displacement in the presence of soft modes is derived and it is shown for the first time that a significant temperature-invariant component will be the main additional effect at temperatures well above the critical temperature. The Cl and Cs ions in CsPbCl₃ obey this derived mean-square displacement relationship.

1. Introduction

In recent years the interpretation of Debye–Waller factors (DWF's) from weakly anharmonic systems in terms of the parameters of an effective one-particle potential (OPP) has become an established technique (Dawson, Hurley & Maslen, 1967; Willis & Pryor, 1975). The effective OPP may be viewed as representing the mean field seen by the atom in question, resulting from the influence of all the other atoms in the crystal. For systems where the interparticle displacement correlations are not very large in magnitude the measured OPP parameters are found to be almost independent of temperature (apart from the minor effect of thermal expansion of the lattice), *e.g.* for SrF₂

(Mair, Barnea, Cooper & Rouse, 1974) and for Si and Ge (Roberto, Batterman & Keating, 1974).

In materials which undergo structural phase transitions the dynamics of the crystal may be highly anharmonic, so that perturbation theory about the harmonic case may no longer be applicable. In the vicinity of a structural phase transition it is also to be expected that the atomic motion will be characterized by interparticle correlations which are large in magnitude. The question arises as to whether the OPP formalism is still a useful one in the presence of such large interparticle correlations. Recognizing, however, that the DWF is an exact one-particle property of the system, we can still work within the framework of the OPP formalism, obtaining atomic OPP's at each individual temperature. The temperature dependence of the OPP's may then be related to the cooperative effects in the crystal.

CsPbCl₃ is a cubic perovskite which undergoes an antiferrodistortive, first-order phase transition at 320 K to the tetragonal phase. A second-order phase transition, to an orthorhombic structure, occurs at 315 K. The phase transitions are associated with the condensation of rotational modes of the PbCl₆ octahedra, the M_3 mode, depicted schematically in Figs. 1(a) and (b) being responsible for the phase transition at 320 K (Fujii, Hoshino, Yamada & Shirane, 1974). Figs. 1(a) and (b) show that the only atomic displacements directly affected by the M_3 mode are those of the Cl ions parallel to the xy plane. The phase transition at 315 K corresponds to the condensation of the Z_3 mode, see Fig. 1(c), which involves motion of the Cs atoms as well as the PbCl₆ rotations, and is anticipated in the cubic phase by a soft R_{25} mode (Fujii *et al.*, 1974).

Accurate neutron diffraction data have been collected for CsPbCl₃ over the temperature range 325–623 K by Sakata, Harada, Cooper & Rouse (1980), who applied corrections for extinction and thermal diffuse scattering. Refinements of the intensities were made by Sakata *et al.* at each temperature, using Debye–Waller factors which allowed for anharmonic effects by including contributions from the fourth cumulant of the atomic displacements (Johnson, 1970), *i.e.* by a

perturbation expansion about the harmonic case. In these refinements the only anharmonic term which was significant at each temperature was the anisotropic fourth cumulant for the Cl ions, corresponding to preferred motion of these ions in the x and y directions, consistent with the displacements expected for the M_3 mode.

The complicated character of the crystal dynamics is evident from the temperature dependence of the mean-square displacements (m.s.d.'s). These are displayed in Fig. 2, the m.s.d.'s being the experimental values obtained from the corresponding refined Debye-Waller B_U values tabulated by Sakata *et al.* (1980). In the figure $\langle u_{\parallel/\perp}^2 \rangle_{\text{Cl}}$ refer to displacement parallel/perpendicular to the xy plane (see Fig. 1a) of the Cl ion at the centre of the face $z = 0$. The curve $\langle u_{\parallel}^2 \rangle_{\text{Cl}}^{\text{S}}$ will be discussed in §4. Examination of the other curves shows that although the m.s.d. of the Pb ion, $\langle u^2 \rangle_{\text{Pb}}$, and the Cl ion perpendicular to the xy plane, $\langle u_{\perp}^2 \rangle_{\text{Cl}}$, follow the expected harmonic curve, the m.s.d.'s of the Cs ion, $\langle u^2 \rangle_{\text{Cs}}$ and of the Cl ion in the xy plane, $\langle u_{\parallel}^2 \rangle_{\text{Cl}}$, extrapolate linearly from the high-temperature values to give a positive non-zero intercept at 0 K. In the case of

$\langle u_{\parallel}^2 \rangle_{\text{Cl}}$ the intercept is very large. Also, the values of $\langle u_{\parallel}^2 \rangle_{\text{Cl}}$ rise away from the linear, high-temperature curve as the phase transition temperature, T_0 , is approached from above. Except for this anomalous behaviour near T_0 , Sakata *et al.* were able to fit their experimental $\langle u_{\parallel}^2 \rangle_{\text{Cl}}$ values with temperature independent highly anharmonic OPP models. They did not, however, test these OPP's on their original intensity data.

In the present study, the analysis of Sakata *et al.* (1980) is carried further. Highly anharmonic trial OPP's for the Cl ion are used in refinements of the intensity data sets at individual temperatures. Some of the trial OPP's correspond to multi-peaked one-particle probability density functions (PDF's) for the Cl ion and some to singly-peaked PDF's. The evidence from the Fourier syntheses of Sakata *et al.* (1980) (resolution limit of 0.58 \AA^{-1} in $\sin \theta/\lambda$, corresponding to 0.5 \AA in real space) and from the neutron diffraction work of Hutton, Nelmes, Meyer & Eiriksson (1979) at 325 K (resolution limit of 1.2 \AA^{-1} in $\sin \theta/\lambda$) suggests that the Cl ion PDF is singly peaked within the resolution of the experiments. As multiple peaking would be associated with the tendency of the Cl ion to vibrate about

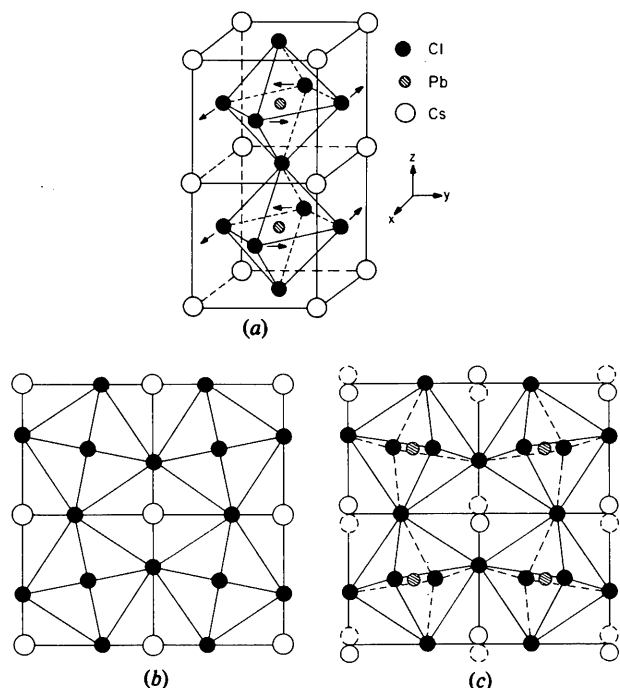


Fig. 1. (a) Two unit cells of the CsPbCl_3 structure showing the rotations of the PbCl_6 octahedra for an M_3 mode. In this diagram, rotation about the z axis is shown. The cubic symmetry of the crystal requires the presence of similar rotations about the x and y axes as well. (b) Projection on the xy plane showing the Cl ion displacements which become stabilized by condensation of the M_3 mode at 320 K. (c) As for (b), but showing the Cl and Cs ion displacements for the Z_3 mode which condenses at 315 K. [These figures are based on figures from Fujii *et al.* (1974).]

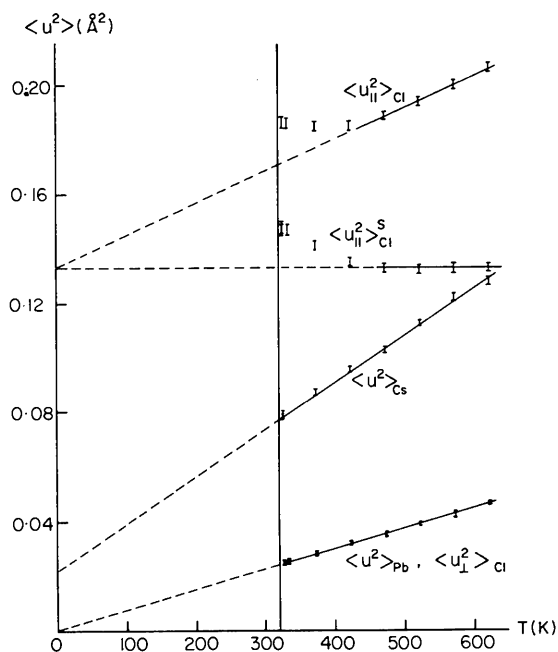


Fig. 2. Experimental mean-square displacements of the ions in CsPbCl_3 . $\langle u_{\parallel/\perp}^2 \rangle$ refer to displacements parallel/perpendicular to the xy plane (see Fig. 1a) of the Cl ion at the centre of the face $z = 0$. The Pb and Cs ions have cubic site symmetry and so their m.s.d.'s refer to an arbitrary direction. The curve $\langle u_{\parallel}^2 \rangle_{\text{Cl}}^{\text{S}}$ is the soft-mode contribution to $\langle u_{\parallel}^2 \rangle_{\text{Cl}}$, as discussed in §4. The values of the m.s.d.'s ($\langle u_{\parallel}^2 \rangle_{\text{Cl}}$, $\langle u_{\perp}^2 \rangle_{\text{Cl}}$, $\langle u^2 \rangle_{\text{Cs}}$ and $\langle u^2 \rangle_{\text{Pb}}$) were obtained from Table 1 of Sakata *et al.* (1980), where the corresponding refined Debye-Waller B_U values are tabulated for each temperature. Solid lines for $\langle u_{\parallel}^2 \rangle_{\text{Cl}}$, $\langle u_{\perp}^2 \rangle_{\text{Cl}}^{\text{S}}$ and $\langle u^2 \rangle_{\text{Cs}}$ are fits to the data using equation (10) and the parameter values quoted in §4.

Table 1. Trial highly anharmonic OPP's for Cl Ion displacement in the xy plane

OPP equation*	Type of OPP	Number of peaks in PDF	GOF†	R	R_w	Parameter values
(a) Au^6	Sextic (of form used by Sakata <i>et al.</i> , 1980)	1	12.8	8.88	20.7	$A = 0.39 (10^{-19} \text{ J } \text{Å}^{-6})$
(b) $A(u_\alpha^6 + u_\beta^6)$	Anisotropic sextic	1	11.9	8.01	19.3	$A = 0.73 (10^{-19} \text{ J } \text{Å}^{-6})$
(c) $Au^2 + B(u_\alpha^4 + u_\beta^4)$	Anisotropic quartic [Sakata <i>et al.</i> (1980) used isotropic form]	1 ($A \geq 0$) 4 ($A < 0$)	2.15	1.55	3.45	$A = 0.173 (10^{-19} \text{ J } \text{Å}^{-2})$ $B = 0.024 (10^{-19} \text{ J } \text{Å}^{-4})$
(d) $A\{(u_\alpha - d)^2 + (u_\beta - d)^2\}$	Anisotropic double quadratic	1 ($A = 0$) 4 ($A \neq 0, d > 0$)	2.22	1.57	3.57	$A = 0.203 (10^{-19} \text{ J } \text{Å}^{-2})$ $d = -0.007 (\text{Å})$
(e) $A_1(u_\alpha - d)^2 + A_2(u_\beta - d)^2$	Anisotropic elastic-sided square well	1 (flat-topped)	2.09	1.84	3.35	$A = 0.202 (10^{-19} \text{ J } \text{Å}^{-2})$ $d = -0.005 (\text{Å})$
(f) Au^2	Harmonic	1	2.48	1.93	4.03	$A = 0.191 (10^{-19} \text{ J } \text{Å}^{-2})$

* $u_{\alpha,\beta}$ are the components of the Cl ion displacements along axes rotated away from the crystallographic $a_{1,2}$ axes by $\pi/4$, the axis of rotation being the a_3 axis. u^2 is defined by: $u^2 = u_\alpha^2 + u_\beta^2$.

† Agreement factors are defined in terms of $\Delta_l = (I_{\text{obs}} - I_{\text{calc}})_l$ as follows: $\text{GOF} = \{\sum_{l=1}^n \Delta_l^2 / (n - m)\}^{1/2}$, $R = \sum_{l=1}^n |\Delta_l| / \sum_{l=1}^n I_{\text{obs},l}$, $R_w = \{\sum_{l=1}^n w_l \Delta_l^2 / \sum_{l=1}^n w_l I_{\text{obs},l}^2\}^{1/2}$ where there are n intensities, I , with weights w , and m is the number of least-squares parameters.

positions of local equilibrium which anticipate the structure of the low-temperature phase (see Bruce & Schneider, 1977; Bruce, 1980), the question whether multiple peaking occurs is of some importance. As well as seeking details of the structure of the Cl ion one-particle PDF, the present analysis tests the applicability of the OPP approach to a highly anharmonic system in which cooperative atomic motion is significant. A specific aim is to provide a model for the m.s.d. data of CsPbCl_3 which is consistent both with the observed intensity data of Sakata *et al.* (1980) and with the lattice-dynamical properties of the system.

2. Anharmonic one-particle potential models

The trial OPP's for the Cl ion motion in the xy plane used in the refinement of the intensity data of Sakata *et al.* (1980) are given in Table 1. All of them [except the harmonic model (f)] are capable of producing the temperature-dependent behaviour observed for $\langle u_{\parallel}^2 \rangle_{\text{Cl}}$, at least in the non-critical region above 450 K. The OPP's for the Pb and Cs ions and for the Cl ion displacement perpendicular to the xy plane were assumed to be of harmonic form. Model (a) of Table 1 and an isotropic form of model (c) were used by Sakata *et al.* to fit their $\langle u_{\parallel}^2 \rangle_{\text{Cl}}$ data above 450 K.* The anisotropic form of the OPP's (b) to (e) is such as to allow for the preferred motion of the Cl ion along the x and y directions, observed by Sakata *et al.* in the form of a refined fourth cumulant term for the Cl ion. Under the conditions given in column 3 of the table, OPP's (c)

and (d) have four minima, these being disposed symmetrically about the equilibrium position along the x and y axes, *i.e.* in the preferred directions of the Cl motion.

For models (a) to (c) numerical integration is necessary to compute the corresponding Debye-Waller factors, the method chosen being Gaussian quadrature. Models (d) and (e), which are related to four displaced harmonic oscillators with separation parameter d , have the advantage that they can be treated by analytical procedures. OPP's of forms (d) and (e) are depicted along the x (or y) axis in the one-dimensional diagrams

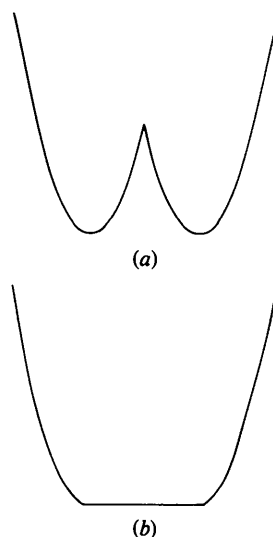


Fig. 3. (a) Double quadratic well, OPP (d) in Table 1, along x direction. (b) Elastic-sided square well, OPP (e) in Table 1, along x direction.

* Note that Sakata *et al.* did not fit these models to their intensity data, their fits being to the previously refined mean-square displacements only.

of Figs. 3(a) and (b), from which it can be seen that model (d) differs from model (e) only in the region between the minima, where (e) is flat. In other words, the difference between the models lies in the four-minimum or flat-bottomed nature of the OPP's or, correspondingly, the four-maximum or flat-topped nature of the one-particle PDF's. Equations for the Debye-Waller factor relating to these two models and detailed discussions of their properties, including the effect of the cusp in model (d), are given elsewhere (Mair, 1982).

The weights used in the refinements of the intensities were the reciprocal squared standard deviations of the observed intensities, obtained from Table 3 of Sakata *et al.* (1980). Results from the refinements of the intensity data are presented in columns 4 to 7 of Table 1. These results are for the data at 573 K for all models. For models (c) and (d) additional refinements were made at 473 and 333 K, respectively. Columns 4 to 6 give the agreement factors, defined below the table, and column 7 gives refined values of the OPP parameters.

The first conclusion (result 1) that can be made upon inspection of Table 1 is that only the models which can be reduced to a harmonic form are at all successful and, for these, the refined parameters represent small perturbations from the harmonic case, to account for the anisotropic Cl ion vibration. This result contradicts the conclusion of Sakata *et al.* (1980) that the Cl ion is vibrating in a (temperature independent) highly anharmonic OPP. The contradiction arises because Sakata *et al.* used only partial information in their highly anharmonic refinements, namely the mean-square displacement data, whereas the full sets of intensity data have been refined here.

A secondary result (result 2) from the model refinements in Table 1 is that the evidence is against multiple peaking in the one-particle PDF as, for the quartic oscillator, model (c), parameter A refined to a positive value. Models (d) and (e) were capable of fitting the data fairly successfully, model (e) being slightly preferred, but neither of them produced physically realistic values for the separation parameter, d , which became negative. The resolution of the data was 0.5 Å, so that multi-peaking in the PDF with a peak separation less than 0.5 Å cannot be ruled out.

Result 1 above presents us with the following apparent paradox. *At any particular temperature the Cl atoms are vibrating as if they were in a nearly harmonic effective OPP well whereas $\langle u^2 \rangle_{\text{Cl}}$ is behaving in a manner which is characteristic of a highly anharmonic OPP.* Noticing that the anisotropic nature of the Cl ion motion is probably indicative that the M_3 and R_{25} rotational modes are contributing to a considerable extent to the Cl vibration, even far from the phase transition, we turn to consideration of the possible effects of such cooperative motion on the OPP's.

3. Temperature dependence of the Cl ion PDF and effective OPP

We have seen in the previous section that the OPP for the Cl ion at any given temperature in the range studied is harmonic, to a first approximation, *i.e.* the OPP for any direction in the xy plane is, approximately,

$$V^{\text{Cl}} = \alpha^{\text{Cl}} u^2/2, \quad (1)$$

where α^{Cl} is the harmonic OPP coupling constant and u is a displacement in the xy plane, along the x direction, say. In this approximation,

$$\langle u^2 \rangle_{\text{Cl}} = k_B T/\alpha^{\text{Cl}}, \quad (2)$$

where k_B is the Boltzmann constant and T the temperature. We can see from (2) that only for a m.s.d. linear with temperature and which can be extrapolated to zero at 0 K will the harmonic coupling constant be constant with temperature. The observed trend for $\langle u^2 \rangle_{\text{Cl}}$ in Fig. 2 is therefore indicative of a highly-temperature-dependent OPP coupling constant, α^{Cl} . A less-pronounced temperature dependence is also expected for the harmonic OPP coupling constant of the Cs ion, α^{Cs} , whereas α^{Pb} and α^{I} will be essentially constant with temperature.

To show explicitly the temperature dependence of the Cl ion OPP, a flexible model for the one-particle PDF was used to refine the intensities at each temperature. The normalized PDF, $\rho_{\text{Cl}}(u_1, u_2, u_3)$, was chosen to be of the form

$$\begin{aligned} \rho_{\text{Cl}}(u_1, u_2, u_3) = & (1 - P)f(u_1, u_2, u_3, \sigma_1, \sigma_3) \\ & + P\{f(u_1 - d, u_2, u_3, \sigma'_1, \sigma_3) \\ & + f(u_1 + d, u_2, u_3, \sigma'_1, \sigma_3) \\ & + f(u_1, u_2 - d, u_3, \sigma'_1, \sigma_3) \\ & + f(u_1, u_2 + d, u_3, \sigma'_1, \sigma_3)\}/4, \quad (3) \end{aligned}$$

where

$$\begin{aligned} f(x, y, z, \sigma_1, \sigma_3) = & \exp \{-(x^2 + y^2)/2\sigma_1^2 - z^2/2\sigma_3^2\} \\ & \times [2\pi\sigma_1^2(2\pi\sigma_3^2)^{1/2}]^{-1}. \end{aligned}$$

It corresponds to a five-site disorder model (see also Megaw, 1969) in which a fraction $(1 - P)$ of the Cl ion occupies the central site and the remaining fraction occupies sites at displacements $\pm d$ away from it along the x and y axes. The spatial distribution at each site is given by the Gaussian function f . The disorder form of this model was chosen for convenience only, and does not indicate that five-site disordering is actually occurring.* The model should, rather, be interpreted as

* The Bragg diffraction data cannot distinguish between a 'split-atom' model representing a situation in which the atoms in each unit cell are *fixed* on one of the available multiple sites, the distribution being random when averaged over the crystal, and a model in which each atom is vibrating amongst the multiple sites around the mean position. However, the former model is not a realistic one, as the ordering of occupied sites occurring at the phase transition implies that mobility amongst the multiple sites must be possible.

a weakly anharmonic model for the Cl ion, with the anisotropic motion in the xy plane being specified by the extra parameters P , d and σ'_1 . (At temperatures below 400 K the intensities were, in fact, equally well fitted by a four-site model.)

The temperature dependence of the PDF along the x direction is shown in Fig. 4(a) (only four temperatures are shown to avoid crowding in the figure). Its single-peak nature is in accord with the results of the previous section. The effective OPP corresponding to each PDF of Fig. 4(a) may be obtained (in the classical régime) through the relationship

$$V(u) = -k_B T \ln \{\rho(u)\}, \quad (4)$$

and the resulting curves along the x direction are shown in Fig. 4(b). As anticipated at the beginning of this section the OPP curves appear nearly harmonic and are indeed temperature dependent. Fig. 4(b) shows a softening of the OPP's as temperature decreases, as compared with the quasi-harmonic effect of lattice expansion, where the softening occurs as T increases and is also a much smaller effect (see Mair *et al.*, 1974). The OPP behaviour in Fig. 4(b) and the behaviour of $\langle u^2 \rangle_{\text{Cl}}$ and $\langle u^2 \rangle_{\text{Cs}}$ in Fig. 2 can more reasonably be attributed to the presence of cooperative vibrational motion in the form of soft modes. The question which then arises concerns the form of the temperature dependence induced in the mean-square displacements as a result of the soft modes.

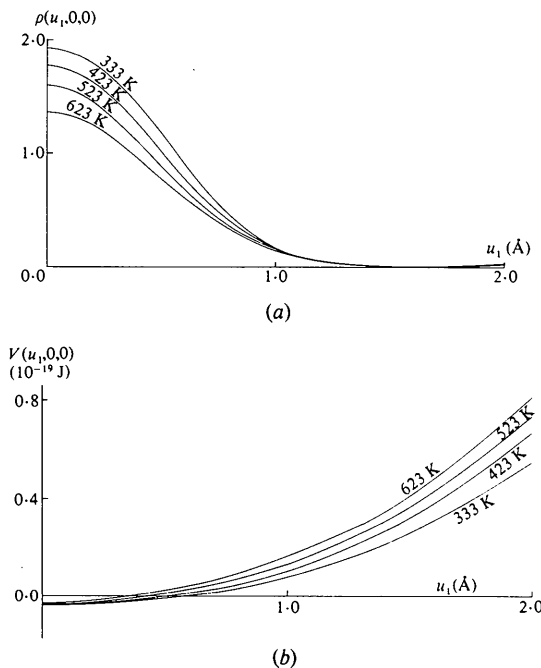


Fig. 4. (a) One-particle PDF's for Cl ion in x direction, $\rho(u_1, 0, 0)$, for 333, 423, 523 and 623 K. (b) Effective OPP's corresponding to the PDF's of (a).

4. The effect of soft modes

Fujii *et al.* (1974) have observed that the phonon frequencies for the modes M_3 and R_{25} decrease with temperature, *i.e.* they are soft modes. We shall consider the effect that such soft modes would have on the m.s.d.'s.

Meissner & Binder (1975) have shown that, for the classical régime and independent of the harmonic approximation,

$$\langle (\mathbf{Q} \cdot \mathbf{u})^2 \rangle = \frac{k_B T}{Nm} \sum_{\mathbf{q}_j} |\mathbf{Q} \cdot \mathbf{e}^j(\mathbf{q})|^2 \frac{1}{\omega_j^2(\mathbf{q}, T)}, \quad (5)$$

where \mathbf{Q} is the scattering vector, n the number of unit cells in the crystal and m the mass of the atom concerned. In the harmonic approximation, $\omega_j(\mathbf{q}, T)$ is the frequency of the normal mode (\mathbf{q}_j) and is independent of temperature, but in the general case it is a renormalized phonon frequency, with eigenvector $\mathbf{e}^j(\mathbf{q})$.

In the summation over modes (\mathbf{q}_j) we can separate out the frequencies associated with soft-mode behaviour, denoted by S , from the remaining essentially temperature-independent frequencies, denoted by R . Then

$$\langle (\mathbf{Q} \cdot \mathbf{u})^2 \rangle_2 = \frac{k_B T}{Nm} \sum_{\mathbf{q}_R} \frac{|\mathbf{Q} \cdot \mathbf{e}^R(\mathbf{q})|^2}{\omega_R^2(\mathbf{q})} + \frac{k_B T}{Nm} \sum_{\mathbf{q}_S} \frac{|\mathbf{Q} \cdot \mathbf{e}^S(\mathbf{q})|^2}{\omega_S^2(\mathbf{q}, T)}. \quad (6)$$

The first term in (6) is proportional to T and so has the same temperature dependence as in the harmonic approximation. For the second term we need to know the temperature dependence of the soft mode frequencies, $\omega_S(\mathbf{q}, T)$.

For the soft zone-boundary mode (M_3 for the phase transition at 320 K), the temperature dependence follows the Landau theory relationship,

$$\omega^2 = \omega_0^2(T - T_C)/T_C, \quad (7)$$

where T_C is the critical temperature for the transition and T is not so close to T_C that critical fluctuations are occurring [see Landau & Lifshitz (1958), Cowley (1980), Cochran (1960) for theory and Fujii *et al.* (1974) for supportive experimental evidence for (7) for CsPbCl_3]. Modes in the vicinity of the M point and also around the R point also show softening (Fujii *et al.*, 1974). We shall assume that they follow a relationship

$$\omega_S^2 = \omega_{0,S}^2(T - T_S)/T_S \quad (T_S < T_C), \quad (8)$$

where T_S is some temperature below T_C and varies with the distance in q space of the mode from the position of the soft zone-boundary mode. Experimental evidence from the closely related structure, K_2SnCl_6 (Vogt, Prandl & Reichardt, 1981), shows that (8) should be a reasonable approximation for our purposes. Evidence of such a relationship also exists for other substances

exhibiting soft-mode behaviour, *e.g.* PbTe (Alperin, Pickart & Rhyne, 1972), SbSI (Pouget, Shapiro & Nassau, 1979).

Substituting (8) into (6), we obtain, for the mean-square displacement,

$$\langle u^2 \rangle = aT + T \sum_s \frac{p_s}{T - T_s}, \quad (9)$$

where a, p_s are independent of temperature. For $T \gg T_s$ (and therefore $T \gg T_c$) this reduces to

$$\langle u^2 \rangle = aT + b \quad T \gg T_c, \quad (10)$$

where a, b are independent of temperature and neglected terms in (10) are of order T^{-1} . The second, constant, term in (10) is the contribution due solely to soft modes. Note that a result identical with (10) can be derived from (3) of Borsa & Rigamonti (1972), taken in the hydrodynamic limit. [Their equation (4), for T close to T_c , is obtained outside the hydrodynamic régime and is therefore beyond the range of validity of the Ornstein-Zernike theory on which it is based.]

The experimental evidence in CsPbCl₃ is consistent with (10). Fig. 2 shows the fit to the experimental $\langle u^2 \rangle_{\text{Cl}}$ for $T > 450$ K (solid line) with $a = 1.17 (15) \times 10^{-4} \text{ \AA}^2 \text{ K}^{-1}$, $b = 0.133 (8) \text{ \AA}^2$. The soft-mode contribution is also plotted separately ($\langle u^2 \rangle_{\text{Cl}}^s$) and is seen to be constant for $T > 450$ K. Below 450 K, the upturn in the soft-mode contribution indicates that the equation for the mean-square displacement in its original form, *i.e.* (9), is appropriate in this region.

Note that the slopes of $\langle u^2 \rangle_{\text{Cl}}$ and $\langle u^2 \rangle_{\text{Cl}}^s$ are similar. This indicates that the Cl ion vibration would be nearly isotropic in the absence of soft modes.

Recalling that the displacements of the Cs ion are associated with the condensation of the Z_x^+ mode at 315 K (Fig. 1c), it is not unreasonable to expect that the Cs ions in the cubic phase should also show the effects of soft-mode vibrations in their mean-square displacements. The fit to $\langle u^2 \rangle_{\text{Cs}}$ in Fig. 2, using $a = 1.72 (8) \times 10^{-4} \text{ \AA}^2 \text{ K}^{-1}$, $b = 0.022 (4) \text{ \AA}^2$ in (10) is consistent with the presence of such soft-mode behaviour for the Cs ion. In this case (10) fits the data right down to 325 K, indicating that the T_s in (9) are clustering around a much lower temperature than 325 K, *i.e.* the ω_s^2 contributing to $\langle u^2 \rangle_{\text{Cl}}$ are, on average, decreasing with temperature rather slowly [see (8)].

The Pb ion motion and the Cl ion motion perpendicular to the xy plane do not exhibit significant soft-mode effects, as the corresponding mean-square displacements can be fitted adequately by straight lines passing through the origin (Fig. 2). This result is not surprising as a net displacement of the Pb ions does not occur at either the 320 or 315 K phase transition and for the Cl ion there is no displacement perpendicular to the xy plane at 320 K and only one third of the ions are displaced in this direction at 315 K (see Fig. 1).

5. Conclusions

The analysis of neutron diffraction data from CsPbCl₃ presented here supports the lattice dynamical evidence that soft modes are contributing significantly to both the Cl and Cs ion vibrations. A similar interpretation can undoubtedly be made for the case of CsPbBr₃ (neutron diffraction data for which was also collected and analysed by Sakata *et al.*, 1980). In this case the Br ion vibration perpendicular to the xy plane may also be exhibiting soft-mode behaviour, although the evidence for this is on the borderline of experimental error. Neutron diffraction results for the perovskite RbCaF₃ (Bulou, Ridou, Rousseau, Nouet & Hewat, 1980) also seem to be consistent with a large soft-mode contribution to the F ion mean-square displacement in the cubic phase.

Multi-peaking in the one-particle probability density function of the Cl ion has not been detected to within the resolution limits of the data (0.5 Å), a result which is in accord with the conclusions of Sakata *et al.* (1980) and Hutton *et al.* (1979). The probability density function at each temperature, although slightly extended in the x and y directions, is approximately Gaussian in shape.

The effective one-particle potential approach to analysis of data from a system in which large interparticle correlations are present has proven very useful. By observing the degree to which the OPP's are quadratic and the fact that they vary strongly with temperature, becoming 'softer' as the temperature decreases, it has been possible to establish that soft modes are contributing substantially to the vibration of selected ions throughout the whole temperature range of the measurements.

Using the Cl and Cs ions of CsPbCl₃ as examples, it has been shown here for the first time that, when the temperature is sufficiently far above the phase transition temperature, a temperature-independent component enters into the expression for the mean-square displacement of an atom whose vibration is influenced by soft modes. This result opens up new possibilities for the use of Bragg diffraction measurements in obtaining lattice dynamical information. In contrast with the information obtainable from neutron inelastic scattering data, the Bragg diffraction results can separate out the vibrational behaviour of each atomic species.

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The Fourier Transform of Actin and Other Helical Systems With Cumulative Random Angular Disorder

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Abstract

A general class of helical disorder exists which can be described by cumulative random angular motions of subunits. This disorder affects layer-line intensities and widths by a factor proportional to n^2 , the square of the order of the layer line. The result explains several features of actin and polytetrafluoroethylene (Teflon) transforms, and may be relevant to other helical systems.

We have described the angular motions of subunits in the F-actin helix (Egelman, Francis & DeRosier, 1982) based upon image analysis of electron micrographs. In this paper we will present an analytic treatment of the effect of this form of disorder on the transform of such a structure. Because this treatment appears to explain features of other disordered systems (such as Teflon above the 292 K transition), we believe that it may be applicable to many helical structures.

Whereas the subunit positions in an ideal helix can be described by

$$r_j = r_0$$

$$z_j = j \Delta z$$

$$\psi_j = \psi_{j-1} + \Delta\psi = j \Delta\psi,$$

we will deal with a particular form of disordered helix where subunit positions are described by

$$r_j = r_0$$

$$z_j = j \Delta z$$

$$\psi_j = \psi_{j-1} + \Delta\psi + \delta_j = j \Delta\psi + \sum_{k=1}^j \delta_k. \quad (1)$$

Fig. 1 shows a model of a helix described by these equations, and Table 1 contains the first ten values of δ_j for one of the filaments in Fig. 1.

The recursive relation in (1) is nothing more than a correlated random walk in ψ , and can be parameterized in terms of the first moment and the square root of the second moment of the distribution of δ_j 's:

$$\langle \delta_j \rangle; \langle \delta_j^2 \rangle^{1/2} = \delta_{1,m,n}, \dots$$