

Debye–Waller factors of compounds with the caesium chloride structure

H. X. Gao^a and L.-M. Peng^{b,a*}

Received 13 April 2000

Accepted 22 May 2000

^aBeijing Laboratory of Electron Microscopy, Center for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, PO Box 2724, Beijing 100080, People's Republic of China, and ^bDepartment of Electronics, Peking University, Beijing 100871, People's Republic of China. Correspondence e-mail: lmpeng@implab.blem.ac.cn

The lattice dynamics of five compounds with the caesium chloride structure have been investigated using shell models. Debye–Waller factors for these compounds are calculated over the temperature range from 1 to 1000 K and the results are presented analytically in a polynomial form. When experimental results are available, the calculated results are compared to the experimentally measured Debye–Waller factors and typically the discrepancies between these factors are less than 10%.

© 2000 International Union of Crystallography
Printed in Great Britain – all rights reserved

1. Introduction

The Debye–Waller factor, which describes the effect of the lattice vibrations on diffracted-beam intensities, is among the few parameters that one must know in order to perform dynamical electron diffraction calculations (Peng, 1999). The Debye–Waller factors are, however, not readily available for most crystals. Experimentally, the Debye–Waller factors may be measured using inelastic neutron and X-ray diffraction techniques (Willis & Pryor, 1975). However, the experimental results are normally published for only a few temperatures, such as for room temperature, while in many applications it is desirable to have the Debye–Waller factors at different temperatures. It is the purpose of this paper to obtain temperature-dependent Debye–Waller factors for compounds with the caesium chloride structure. Our evaluations of the Debye–Waller factors are based on the harmonic approximation of the lattice dynamics, assuming that the forces between pairs of atoms in a crystal are proportional to their relative displacements. While this approximation is valid at low temperature, it is well known that a crystal with harmonic interatomic forces would have no thermal expansion, no temperature dependence of the elastic constants and many other properties not possessed by real crystals. We expect that our harmonic results will become less accurate as temperature increases. These results will nevertheless provide a starting point for structural refinements and for assessing, among other things, the anharmonicity and dynamic deformation effects.

In a previous paper (Gao *et al.*, 1999), we have calculated the Debye–Waller factors of 19 compounds with the sodium chloride structure. The present paper is a sequential work to investigate the lattice dynamics of compounds with the caesium chloride structure and to calculate the temperature-dependent Debye–Waller factors of these compounds.

2. Lattice dynamics of the caesium chloride lattice

The caesium chloride lattice is a body-centered cubic lattice, with cations at the corners 000 and anions at the body-centered positions $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ of the simple cubic lattice. Each atom may be viewed as at the center of a cube of atoms of the opposite kind, so that the number of nearest neighbors or coordination number is eight. The caesium chloride lattice differs from the sodium chloride lattice mostly in the second-nearest-neighbor distances. For an ideal caesium chloride lattice, the ratio between the second-nearest-neighbor distance and the first-nearest-neighbor distance is 1.154, which is only about 82% that of an ideal sodium chloride lattice. An important consequence of this structural difference between these two lattices is that in the case of the caesium chloride lattice we need to consider the interactions between second-nearest neighbors for both the cations and the anions, while for the sodium chloride lattice we need only to consider the interactions between the second-nearest neighbors for anions. Shown in Fig. 1 is a schematic diagram of the shell model we used in this paper.

Theoretical treatments of the lattice dynamics of crystals with the caesium chloride structure have been discussed by several authors. In particular, the rigid-ion model was investigated by Ganesan & Srinivasan (1963). The shell model, which was originally introduced by Dick & Overhauser (1958) for alkali halides, was firstly formulated for the CsCl structure by Cowley & Okazaki (1967). This shell model was later modified by Mahler & Engelhardt (1971) to include a breathing term, and dispersion curves of the caesium halide were calculated. Crystals with the caesium chloride structure generally exhibit a complex dielectric behavior resulting from the high polarizability of the constituent ions. A careful analysis of high-frequency dielectric constants assuming additive ionic polarizabilities suggests that the electronic polarizabilities of the positive ion and the negative ion are of

the same order of magnitude. In our theoretical model, we consider, therefore, that both types of ions are polarizable, *i.e.* the spring constants k_1 and k_2 connecting the ions and the outer electronic shells (see Fig. 1) are both finite.

Under the harmonic, adiabatic and electrostatic approximations, the equations of motion for the shell model can be written in a compact matrix form

$$\left. \begin{aligned} \mathbf{M}\omega^2\mathbf{u} &= (\mathbf{R} + \mathbf{ZCZ})\mathbf{u} + (\mathbf{T} + \mathbf{ZCY})\mathbf{w} \\ 0 &= (\mathbf{T}^T + \mathbf{YCZ})\mathbf{u} + (\mathbf{S} + \mathbf{K} + \mathbf{YCY})\mathbf{w}, \end{aligned} \right\} \quad (1)$$

where \mathbf{M} , \mathbf{Z} , \mathbf{Y} and \mathbf{K} are 6×6 diagonal matrices representing the ion masses, the ion charges, the shell charges and the core-shell coupling constants, respectively. The short-range interactions include core-core, core-shell and shell-shell interactions and are given by 6×6 matrices \mathbf{R} , \mathbf{T} , \mathbf{S} , respectively, while \mathbf{C} specifies the long-range Coulomb interactions that may be calculated using the dimensionless coefficients first given by Kellermann (1940) for the sodium chloride lattice, \mathbf{u} is a six-dimensional vector specifying the core displacement components along the x , y , z directions and for the two types of ions (denoted by superscripts 1 and 2), and \mathbf{w} is another six-dimensional vector specifying the relative displacement components of the shells with respect to their corresponding ions along the x , y , z directions and for the two types of ions (also denoted by superscripts 1 and 2). To reduce the number of fitting parameters, we follow Cowley & Okazaki (1967) and assume that the next-nearest-neighbor forces act through the shells and the forces are axially symmetric at all wave vectors. Under these assumptions, elements of the matrices are given, in units of e^2/V , by

$$\begin{aligned} R_{xx}^{11} &= \frac{4}{3}(A_{12} + 2B_{12}) + A_{11} + 2B_{11} - A_{11} \cos 2q_x r_0 \\ &\quad - B_{11}(\cos 2q_y r_0 + \cos 2q_z r_0) \\ R_{xx}^{22} &= \frac{4}{3}(A_{12} + 2B_{12}) + A_{22} + 2B_{22} - A_{22} \cos 2q_x r_0 \\ &\quad - B_{22}(\cos 2q_y r_0 + \cos 2q_z r_0) \\ R_{xx}^{12} &= R_{xx}^{21} = -\frac{4}{3}(A_{12} + 2B_{12}) \cos q_x r_0 \cos q_y r_0 \cos q_z r_0 \\ R_{xy}^{11} &= R_{xy}^{22} = 0 \\ R_{xy}^{12} &= R_{xy}^{21} = \frac{4}{3}(A_{12} - B_{12}) \sin q_x r_0 \sin q_y r_0 \cos q_z r_0 \\ T_{xy}^{12} &= \gamma_T R_{xy}^{12} \\ S_{xx}^{12} &= \alpha_S R_{xx}^{12} \\ S_{xy}^{12} &= \alpha_S \gamma_S R_{xy}^{12}, \end{aligned} \quad (2)$$

where $\mathbf{q} = (q_x, q_y, q_z)$ is the wavevector, e is the electron charge, V is the volume of the cubic unit cell, γ_T , α_S and γ_S are ratios between different force constants, and A_{12} , B_{12} , A_{11} , B_{11} , A_{22} and B_{22} represent short-range force parameters. The indices 1 and 2, referring to cation and anion, respectively, imply that the model includes the effects of short-range interactions between both negative ions and positive ions (second-nearest neighbors) as well as first-nearest neighbours. All other elements of the matrices may be obtained readily by applying symmetry permutations. For example, R_{yy} and R_{zz} may be obtained from the symmetry relation $R_{yy} = R_{zz} = R_{xx}$, and similarly R_{yz} and R_{zx} may be obtained

from the symmetry relation $R_{yz} = R_{zx} = R_{xy}$. It should also be noted that all matrices are symmetric, for example $R_{xy} = R_{yx}$ and $S_{xy} = S_{yx}$.

In this work, we studied two shell models (SMs). In the first SM, we considered the full implementation of the above expressions for the matrices \mathbf{R} , \mathbf{S} and \mathbf{T} , while in the second SM the fitting parameters were reduced by letting $\mathbf{R} = \mathbf{T} = \mathbf{S}$, *i.e.* $\gamma_T = \alpha_S = \gamma_S = 1$ for all wave vectors. Physically, these constraints mean that all short-range forces between ions act entirely through the shell. The first SM amounts to 14 adjustable parameters, while the second amounts to 11 adjustable parameters.

3. Debye-Waller factors of a cubic lattice

For a given set of adjustable model parameters, the equation of motion (1) may be solved, giving six solutions of ω and \mathbf{u} for a given wavevector \mathbf{q} . These solutions are indexed by phonon mode index $\mathbf{q}j$, ($j = 1, 2, 3, 4, 5, 6$). For compounds with the caesium chloride structure, since the crystal lattice is a cubic lattice, the Debye-Waller factors are isotropic under the harmonic approximation. For each atom k ($k = 1, 2$ for cation and anion) in the unit cell, the Debye-Waller factor is presented as $B(k)$ and at a fixed temperature this factor is given by

$$B(k) = \frac{8\pi^2}{3m_k N} \sum_{\mathbf{q}j} \left(\frac{\bar{E}}{\omega^2} \right)_{\mathbf{q}j} |\mathbf{u}_k(\mathbf{q}j)|^2, \quad (3)$$

where $\bar{E}_{\mathbf{q}j}$ is the mean energy of the phonon in the mode ($\mathbf{q}j$):

$$\bar{E}_{\mathbf{q}j} = \hbar\omega_{\mathbf{q}j}(\bar{n}_{\mathbf{q}j} + 1/2),$$

and $\bar{n}_{\mathbf{q}j}$ is the mean occupation number of the mode and is given by the Bose-Einstein distribution

$$\bar{n}_{\mathbf{q}j} = [\exp(\hbar\omega_{\mathbf{q}j}/k_B T) - 1]^{-1},$$

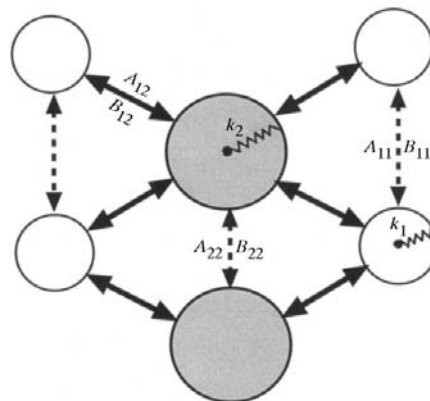


Figure 1 Schematic diagram showing the interactions between cations and anions for a caesium chloride lattice. The solid arrows represent the first-nearest-neighbor interactions A_{12} and B_{12} , where the subscripts 1 and 2 represent cation and anion, respectively, and A and B denote the radial and tangential force constants, respectively. The dashed arrows represent the second-nearest-neighbor interactions A_{11} and B_{11} (between cations), and A_{22} and B_{22} (between anions). k_1 and k_2 are the core-shell coupling constants of cations and anions, respectively.

Table 1
Model parameters.

(a) 11-parameter SM

Crystal	A_{12} (e/V)	B_{12} (e/V)	A_{11} (e/V)	B_{11} (e/V)	A_{22} (e/V)	B_{22} (e/V)	Z (e)	K_1 (e/V)	K_2 (e/V)	Y_1 (e)	Y_2 (e)	σ
CsCl	7.832	-0.258	0.793	-0.165	0.651	-0.154	0.820	302.9	453.1	-2.657	-3.972	0.0016
CsBr	8.135	-0.656	0.994	-0.194	0.951	-0.052	0.786	168.8	424.9	-0.402	-2.682	0.0018
CsI	8.522	-0.528	1.191	-0.265	0.172	0.099	0.921	217.1	148.7	1.930	-2.238	0.0021
TlCl	7.890	-0.879	-0.293	0.055	1.411	-0.060	0.864	52.3	501.6	-1.294	-4.086	0.0037
TlBr	8.006	-0.956	-0.520	0.0004	1.767	-0.132	0.854	52.8	493.5	-1.093	-4.250	0.0021

(b) 14-parameter SM

Crystal	A_{12} (e/V)	B_{12} (e/V)	A_{11} (e/V)	B_{11} (e/V)	A_{22} (e/V)	B_{22} (e/V)	Z (e)	K_1 (e/V)	K_2 (e/V)	Y_1 (e)	Y_2 (e)	γ_T	γ_S	S_0/R_0	σ
CsCl	7.936	-0.384	1.156	-0.146	0.675	-0.186	0.776	153.1	880.6	-1.762	-4.850	0.698	1.210	-4.525	0.0014
CsBr	8.161	-0.667	0.775	-0.157	0.967	-0.066	0.799	181.4	451.9	-0.255	-2.879	1.051	0.748	1.226	0.0017
CsI	8.505	-0.507	1.048	-0.227	0.191	0.082	0.921	195.9	155.6	1.692	-2.302	0.897	1.694	2.520	0.0021
TlCl	8.377	-0.973	-0.436	0.099	1.586	-0.069	0.886	39.4	528.5	-0.990	-4.023	1.014	1.510	2.018	0.0035
TlBr	8.016	-0.981	-0.548	0.005	1.793	-0.135	0.848	52.6	536.3	-1.096	-4.275	0.991	0.997	1.672	0.0020

Table 2
Elastic constants (10^{12} dyn cm $^{-2}$).

Crystal	11-parameter SM			14-parameter SM		
	C_{11}	C_{12}	C_{44}	C_{11}	C_{12}	C_{44}
CsCl	0.4166	0.1042	0.1105	0.4125	0.1373	0.1140
CsBr	0.3391	0.1366	0.0876	0.3362	0.1336	0.0865
CsI	0.2934	0.0681	0.0644	0.2905	0.0659	0.0654
TlCl	0.5038	0.1869	0.1066	0.5253	0.2174	0.1159
TlBr	0.4455	0.1892	0.0893	0.4411	0.1955	0.0897

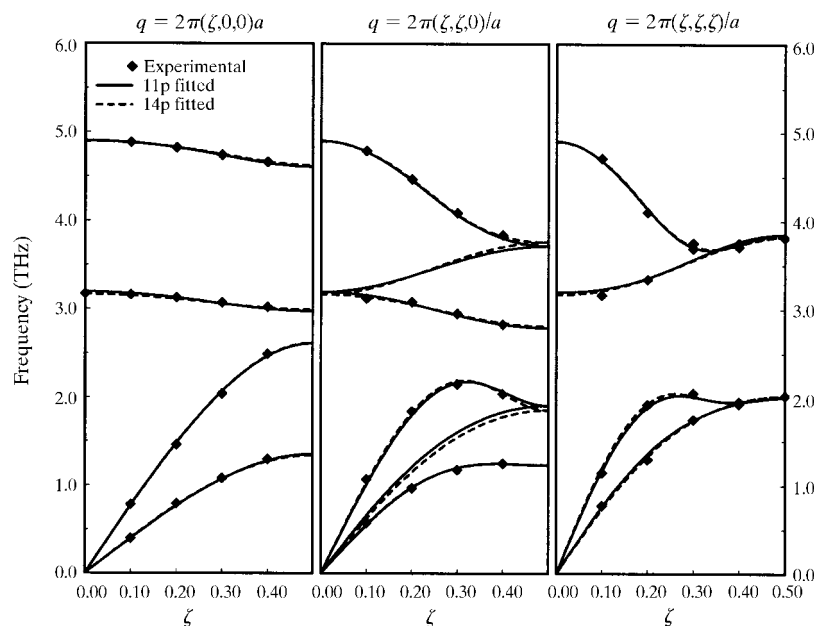


Figure 2
Experimental and calculated phonon-dispersion curves for a CsCl crystal. The calculations were made using the 11-parameter SM (solid curve) and the 14-parameter SM (dotted curve), and the experimental phonon-dispersion curves were measured at 78 K by Ahmad *et al.* (1972).

$\omega_{\mathbf{q}j}$ is the frequency of the phonon, $\mathbf{u}_k(\mathbf{q}j)$ is the complex displacement eigenvector, m_k is the mass of the k th atom and N is the number of wavevectors in the summation over the Brillouin zone. In performing the summation over phonon modes, particular attention should be paid to the so-called ‘zerophonon’ term, as first pointed out by Buyers & Smith (1968), which results from singularities due to phonon branches with $\omega(\mathbf{q} = 0, j) = 0$. In this work, numerical summation is performed using the computer routine developed by Reid (1987).

4. Results and discussion

The two shell models we investigated use 11 parameters ($A_{12}, B_{12}, A_{11}, B_{11}, A_{22}, B_{22}, Z, Y_1, Y_2, k_1, k_2$) and 14 parameters ($A_{12}, B_{12}, A_{11}, B_{11}, A_{22}, B_{22}, Z, Y_1, Y_2, k_1, k_2, \gamma_T, \gamma_S, \alpha_S$), respectively. The adjustable parameters are determined by fitting the measured phonon frequencies in high-symmetry directions with model calculations. In our program, the fitting is performed using the combination of the standard multidimensional downhill simplex method and the simulated-annealing method (Press *et al.*, 1986). The goodness of fit between the measured and calculated phonon-dispersion curves is given by an error indicator σ , which is defined as follows:

$$\sigma = (M - K)^{-1} \sum_{i=1}^M (\omega_{\text{exp}}^i - \omega_{\text{mod}}^i)^2, \quad (4)$$

where M is the number of experimental data, K is the number of adjustable parameters, ω_{exp} is the experimental frequency and ω_{mod} is the model frequency for a particular point on the

Table 3

Polynomial regression form-fitting parameters of the Debye–Waller factors calculated using the 11-parameter shell model.

(a) 0–80 K

Crystal	Atom	a_0	a_1	a_2	a_3	a_4	ME (%)
CsCl	Cs	0.19200	$-9.32891\text{E}-4$	$1.24655\text{E}-4$	$-1.09899\text{E}-6$	$3.72778\text{E}-9$	0.52
	Cl	0.35291	$7.61576\text{E}-5$	$3.20808\text{E}-5$	$1.43255\text{E}-7$	$-1.64323\text{E}-9$	0.04
CsBr	Cs	0.20343	$-9.21443\text{E}-4$	$1.54253\text{E}-4$	$-1.50007\text{E}-6$	$5.67996\text{E}-9$	0.45
	Br	0.24988	$-4.28096\text{E}-4$	$9.70985\text{E}-5$	$-6.16537\text{E}-7$	$1.26817\text{E}-9$	0.19
CsI	Cs	0.21257	$-8.97273\text{E}-4$	$1.76420\text{E}-4$	$-1.79416\text{E}-6$	$7.08823\text{E}-9$	0.39
	I	0.21701	$-8.53885\text{E}-4$	$1.65725\text{E}-4$	$-1.60810\text{E}-6$	$6.06843\text{E}-9$	0.37
TlCl	Tl	0.19770	$-7.60460\text{E}-4$	$3.12840\text{E}-4$	$-3.98796\text{E}-6$	$1.87507\text{E}-8$	0.91
	Cl	0.37889	$1.17940\text{E}-4$	$3.01218\text{E}-5$	$3.55468\text{E}-7$	$-3.20722\text{E}-9$	0.13
TlBr	Tl	0.19771	-0.00111	$2.99872\text{E}-4$	$-3.75750\text{E}-6$	$1.74420\text{E}-8$	0.71
	Br	0.25854	$-4.72016\text{E}-4$	$1.04919\text{E}-4$	$-6.66251\text{E}-7$	$1.32453\text{E}-9$	0.28

(b) 80–1000 K

Crystal	Atom	a_0	a_1	a_2	a_3	a_4	ME (%)
CsCl	Cs	0.04602	0.00567	$7.00518\text{E}-7$	$-7.67034\text{E}-10$	$3.01533\text{E}-13$	0.31
	Cl	0.16333	0.00485	$2.40028\text{E}-6$	$-2.60727\text{E}-9$	$1.01869\text{E}-12$	0.88
CsBr	Cs	0.04348	0.00665	$6.22486\text{E}-7$	$-6.68495\text{E}-10$	$2.58682\text{E}-13$	0.43
	Br	0.07168	0.00615	$1.02629\text{E}-6$	$-1.10544\text{E}-9$	$4.29313\text{E}-13$	0.66
CsI	Cs	0.04607	0.00737	$6.97347\text{E}-7$	$-7.60489\text{E}-10$	$2.97656\text{E}-13$	0.29
	I	0.04834	0.00725	$7.34509\text{E}-7$	$-8.02746\text{E}-10$	$3.14886\text{E}-13$	0.31
TlCl	Tl	0.03024	0.01038	$4.65718\text{E}-7$	$-5.11275\text{E}-10$	$2.01124\text{E}-13$	0.13
	Cl	0.16442	0.00560	$2.42881\text{E}-6$	$-2.64152\text{E}-9$	$1.03301\text{E}-12$	0.83
TlBr	Tl	0.03020	0.00980	$4.61384\text{E}-7$	$-5.04827\text{E}-10$	$1.98156\text{E}-13$	0.17
	Br	0.07582	0.00651	$1.15017\text{E}-6$	$-1.25866\text{E}-9$	$4.94321\text{E}-13$	0.37

phonon-dispersion curves. Given in Tables 1(a) and 1(b) are the model parameters for the two SMs we investigated, *i.e.* the 11-parameter SM and the 14-parameter SM. The model parameters were determined by fitting calculated phonon-

dispersion curves to those experimentally measured curves, and the experimental phonon-dispersion curves used in our fitting were obtained from references for (a) CsCl (Ahmad *et al.*, 1972); (b) CsBr (Rolandson & Raunio, 1971); (c) CsI (Bührer & Hälgl, 1971); (d) TlCl (Fujii *et al.*, 1978) and (e) TlBr (Cowley & Okazaki, 1967). For further comparison, we also list in Table 2 the calculated elastic constants using the two SMs. From the error indicator listed in Table 1, it is seen that for most of the compounds the 14-parameter SM provides a better description of the phonon-dispersion curves than the 11-parameter SM. Shown in Fig. 2 are experimentally measured and calculated phonon-dispersion curves for a CsCl crystal using the 11-parameter SM and the 14-parameter SM. The figure shows that both SMs reproduce excellently most features of the phonon-dispersion curves.

The Debye–Waller factors were calculated numerically using (3) over the temperature range from 1 to 1000 K. For all the compounds, it was found that the temperature dependence of the Debye–Waller factor is rather smooth and the curves of $B(T)$ may be fitted analytically using the polynomial regression form

$$B(T) = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4, \quad (5)$$

where T is measured in kelvin, B is given in Å^2 and a_i are fitting parameters. For all five compounds with the caesium chloride structure, the fitting parameters are given in Tables 3 and 4

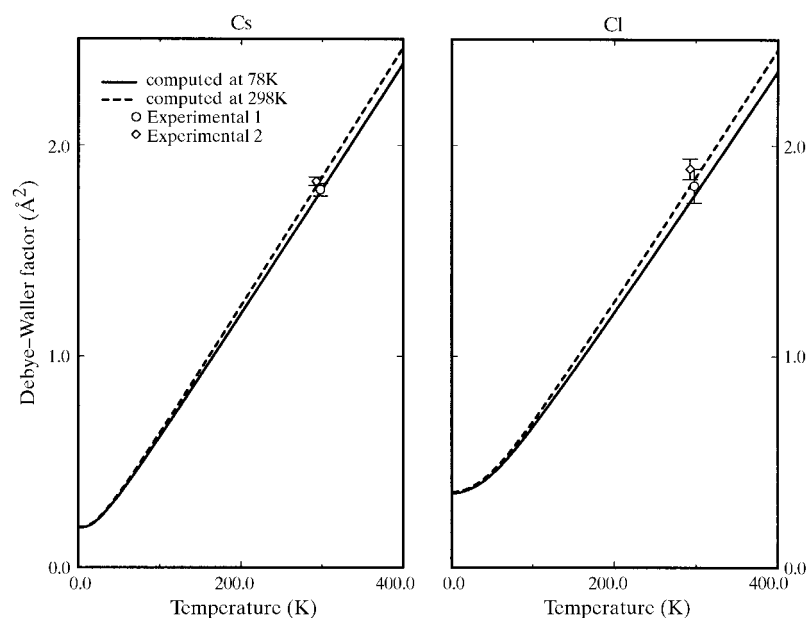


Figure 3

Experimental and calculated Debye–Waller factors for Cs^{1+} and Cl^{1-} ions of a CsCl crystal. The calculated Debye–Waller factors were based on fitting experimental phonon-dispersion curves measured at 78 and 298 K, respectively. The experimental room-temperature Debye–Waller factors denoted by circle error bars were taken from Barnea & Post (1966) and those denoted by diamond error bars were taken from Butt *et al.* (1993).

Table 4

Polynomial regression form-fitting parameters of the Debye–Waller factors calculated using the 14-parameter shell model.

(a) 0–80 K

Crystal	Atom	a_0	a_1	a_2	a_3	a_4	ME (%)
CsCl	Cs	0.19036	−9.10016E−4	1.22707E−4	−1.08235E−6	3.68061E−9	0.50
	Cl	0.35030	6.39211E−5	3.31992E−5	1.17168E−7	−1.50137E−9	0.05
CsBr	Cs	0.20417	−9.20228E−4	1.54877E−4	−1.50202E−6	5.66455E−9	0.46
	Br	0.24995	−4.19446E−4	9.76084E−5	−6.24174E−7	1.30696E−9	0.19
CsI	Cs	0.21434	−9.33589E−4	1.79157E−4	−1.82167E−6	7.18631E−9	0.41
	I	0.21745	−8.76931E−4	1.67403E−4	−1.63431E−6	6.20733E−9	0.39
TlCl	Tl	0.20095	−7.99987E−4	3.24559E−4	−4.15866E−6	1.96232E−8	0.97
	Cl	0.37477	1.09621E−4	2.56619E−5	4.13366E−7	−3.49634E−9	0.14
TlBr	Tl	0.19805	−0.00109	2.99804E−4	−3.75322E−6	1.74123E−8	0.73
	Br	0.25893	−4.81267E−4	1.06923E−4	−6.99310E−7	1.50929E−9	0.26

(b) 80–1000 K

Crystal	Atom	a_0	a_1	a_2	a_3	a_4	ME (%)
CsCl	Cs	0.04587	0.00560	6.93610E−7	−7.57098E−10	2.96719E−13	0.33
	Cl	0.16295	0.00481	2.39007E−6	−2.59405E−9	1.01270E−12	0.82
CsBr	Cs	0.04346	0.00669	6.19356E−7	−6.64832E−10	2.57440E−13	0.43
	Br	0.07132	0.00617	1.00875E−6	−1.08079E−9	4.17783E−13	0.76
CsI	Cs	0.04624	0.00745	7.06922E−7	−7.74571E−10	3.04329E−13	0.23
	I	0.04840	0.00727	7.41666E−7	−8.12946E−10	3.19430E−13	0.29
TlCl	Tl	0.03036	0.01067	4.72673E−7	−5.22856E−10	2.07256E−13	0.13
	Cl	0.16407	0.00541	2.42180E−6	−2.63348E−9	1.02966E−12	0.87
TlBr	Tl	0.03032	0.00983	4.66100E−7	−5.11821E−10	2.01608E−13	0.10
	Br	0.07580	0.00654	1.14901E−6	−1.25640E−9	4.93055E−13	0.49

Table 5

Experimental and calculated Debye–Waller B factors (room temperature).

Crystal	Experimental			11p-SM			14p-SM		
	B^+	B^-	\bar{B}	B^+	B^-	\bar{B}	B^+	B^-	\bar{B}
CsCl	1.83 (2)	1.89 (5)	1.84 (5)	1.71	1.70	1.71	1.73	1.72	1.73
CsBr	2.00 (9)	2.24 (12)	2.09 (15)	2.03	1.94	2.00	2.04	1.94	2.00
CsI	2.17 (11)	2.19 (12)	2.24 (16)	2.25	2.22	2.24	2.27	2.23	2.25
TlBr	—	—	—	2.93	2.05	2.68	2.94	2.07	2.70
TlCl	3.28 (7)	2.00 (7)	3.10 (10)	3.10	1.96	2.93	3.19	1.90	3.00

for different models, together with a maximum-error (ME) indicator for the fit:

$$\text{ME} = \max \left\{ \frac{B^{(i)} - B_{\text{fit}}^{(i)}}{(B^{(i)} + B_{\text{fit}}^{(i)})/2}, i = 1, \dots \right\} \times 100\%. \quad (6)$$

Tables 3 and 4 show that the analytical fit is excellent for all the compounds with ME being less than 1%.

We have also compared our calculated Debye–Waller factors to available experimental room-temperature Debye–Waller factors for compounds with the caesium chloride structure (Butt *et al.*, 1993). For all the compounds (except TlBr), Debye–Waller factors for both the cation and the anion are given in Table 5, together with an average \bar{B} factor, defined by

$$\bar{B} = \frac{m^+ B^+ + m^- B^-}{m^+ + m^-}, \quad (7)$$

where the superscripts + and − denote positive (cation) and negative (anion) ions, respectively, and m refers to the mass of

the corresponding ions. Table 5 shows that, for most of the compounds, the difference between the experiment and calculated mean \bar{B} factors is less than 10%.

It should be noted that our present results are based on a harmonic model, which was utilized in both lattice dynamics calculations and evaluations of Debye–Waller factors. Since we did not consider the anharmonic effects in our model explicitly, our results at high temperatures may only be regarded as extrapolated values from harmonic results, which are known to be accurate only at low temperature. Shown in Fig. 3 are calculated curves of the Debye–Waller factor for CsCl and experimentally measured room-temperature Debye–Waller factors from two sources (Barnea & Post, 1966; Butt *et al.*, 1993). The calculations were based on two sets of experimental phonon-dispersion curves, measured at 78 and 298 K, respectively (Ahmad *et al.*, 1972). For an ideal harmonic situation, the force constants (or our model parameters A_{12} , B_{12} *etc.*) would be independent of the temperature. Fig. 3 shows, however, that the calculated Debye–Waller factors and SM force constants are indeed dependent on the

temperatures at which the phonon-dispersion curves were measured. We expect that this discrepancy between the two calculated curves of Debye–Waller factors results mainly from the anharmonic effects, and that the anharmonic effects will become more important at higher temperatures. Fig. 3 shows, nevertheless, that at room temperature the discrepancy between the two sets of calculated Debye–Waller factors is of the same order of magnitude as the experimental error bars, and that the curve based on phonon-dispersion curves measured at 298 K seems to agree with experimentally measured room-temperature Debye–Waller factors better than that at 78 K. This may suggest that effectively some of the anharmonic effects have been included in our model derived from experimental phonon-dispersion curves measured at 298 K. In any case, the higher-temperature Debye–Waller factors should not be regarded as accurate and should be used only as an estimate of the true anharmonic temperature factor.

5. Concluding remarks

Temperature-dependent Debye–Waller factors have been calculated for several compounds with the caesium chloride structure for the temperature range from 1 to 1000 K and the resulting $B(T)$ functions have been fitted analytically using the polynomial regression form. The room-temperature (293 K) values of the Debye–Waller factors are compared to existing experimental values, and for most of the compounds the

agreement between the experimental and calculated values is better than 10%.

The authors are grateful to Professor B. T. M. Willis for valuable discussions concerning anharmonic effects. This work was supported by the National Science Foundation of China, Chinese Academy of Sciences and Peking University.

References

- Ahmad, A., Smith, H., Wakabayashi, N. & Wilkinson, M. (1972). *Phys. Rev. B*, **6**, 3956–4004.
- Barnea, Z. & Post, B. (1966). *Acta Cryst.* **21**, 181–182.
- Bührer, W. & Hälgl, W. (1971). *Phys. Status Solidi B*, **46**, 679–687.
- Butt, N., Bashir, J. & Khan, M. (1993). *Acta Cryst.*, **A49**, 171–174.
- Buyers, W. & Smith, T. (1968). *J. Phys. Chem. Solids*, pp. 1051–1057.
- Cowley, E. & Okazaki, A. (1967). *Proc. R. Soc. London Ser. A*, **300**, 45–61.
- Dick, B. & Overhauser, A. (1958). *Phys. Rev.* **112**, 90–103.
- Fujii, Y., Sakuma, T., Nakahara, J., Hoshino, S., Kobayashi, K. & Fujii, A. (1978). *J. Phys. Soc. Jpn*, **44**, 1237–1240.
- Ganesan, S. & Srinivasan, R. (1963). *Proc. R. Soc. London Ser. A*, **271**, 154–168.
- Gao, H., Peng, L.-M. & Zuo, J. (1999). *Acta Cryst.* **A55**, 1014–1025.
- Kellermann, E. (1940). *Philos. Trans. R. Soc. London*, **238**, 513–548.
- Mahler, G. & Engelhardt, P. (1971). *Phys. Status Solidi B*, **45**, 543–553.
- Peng, L.-M. (1999). *Micron*, **30**, 625–649.
- Press, W. H., Flannery, B. P., Teukolsky, S. & Vetterling, W. (1986). *Numerical Recipes*. Cambridge University Press.
- Reid, J. (1987). *Comput. Phys. Commun.* **46**, 141–148.
- Rolandson, S. & Raunio, G. (1971). *Phys. Rev. B*, **4**, 4617–4623.
- Willis, B. & Pryor, A. (1975). *Thermal Vibrations in Crystallography*. Cambridge University Press.