Acta Cryst. (1999). A**55**, 1014–1025

Lattice dynamics and Debye–Waller factors of some compounds with the sodium chloride structure

H. X. Gao,[a] L.-M. Peng[a]* and J. M. Zuo[b]

[a]*Beijing Laboratory of Electron Micoscopy, Center for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, PO Box 2724, Beijing 100080, People's Republic of China, and* [b]*Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287-1504, USA. E-mail: lmpeng@lmplab.blem.ac.cn*

(*Received 7 December 1998; accepted 20 May 1999*)

Abstract

The lattice dynamics of 19 compounds with the sodium chloride structure have been investigated using shell models. The models are compared with existing experimentally measured phonon-dispersion curves and refined using a multidimensional downhill simplex method. Debye–Waller factors for these compounds are calculated over the temperature range from 1 to 1000 K where appropriate and the results are fitted analytically using polynomial regression. The results are compared with experimentally measured room-temperature Debye–Waller factors and for most of the compounds the agreement is found to be better than 10%. At lower temperatures, it is expected that these results would be more accurate, since the harmonic approximation, which is crucial to the calculation of the Debye–Waller factors, works better. In choosing the models for particular applications, it is recommended that the model with the smallest standard error σ is used for fitting the experimentally measured phonon-dispersion curves, or the model that shows best agreement with reliable experimental measurements of more relevant physical quantities, such as Debye–Waller factors in crystallography.

1. Introduction

The sodium chloride structure is among the most commonly occurring structure type for AB compounds (Pettifor, 1995). Compounds with the sodium chloride structure include alkali halides (such as LiF and NaF), metal oxides (such as MgO and NiO) and transition-metal compounds (such as TiN and TiC) (Bilz & Kress, 1979). There is tremendous interest in these compounds, and in particular in the transition-metal oxides (Cox, 1995) since many of the high-temperature superconductors are closely related to these compounds. A detailed understanding of the compounds with the simple sodium chloride structure would therefore serve as a gateway to a deeper understanding of the more complicated high-T_c cuprates (Poole *et al.*, 1995).

Until now, much of the structural work on solids involves using either X-ray or electron diffraction and in both cases quantitative investigations require the use of Debye–Waller factors to take into account the effect of lattice vibrations on the diffracted-beam amplitudes (Willis & Pryor, 1975; Cowley, 1993). Unfortunately, for most compounds with the sodium chloride structure, the Debye–Waller factors are either unavailable or measured only at one or a few temperatures while for many applications it is desirable to have the Debye–Waller factors at different temperatures, such as in the case of *in situ* monitoring of the growth of thin films on these compounds (Peng, 1999). It is the purpose of the present paper to investigate the lattice dynamics of compounds with the sodium chloride structure and to calculate the Debye–Waller factors of these compounds. The temperature dependence of the Debye–Waller factors is parameterized using polynomial regression fitting and the Debye–Waller factors for 19 compounds with the sodium chloride structure may therefore be easily calculated for any temperature using the parameters given in this article.

2. Lattice dynamics of the sodium chloride lattice

In this section, we will be concerned with the lattice dynamics of ionic crystals with the sodium chloride structure. The sodium chloride lattice consists of equal numbers of cations, such as Ni^{2+} or Mg^{2+}, and anions, such as O^{2-}, sitting at alternate points of a simple cubic lattice (see Fig. 1*a*), *i.e.* a cation and anion interpenetrating f.c.c. lattice. Each ion in this lattice has six of

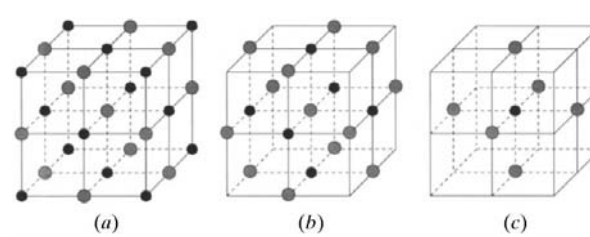

Fig. 1. Schematic digram showing (*a*) the sodium chloride structure; (*b*) the six nearest neighbors and the twelve second-nearest neighbors of the anion (gray ion, such as O^{2-}); (*c*) the six nearest neighbors of the cation (black ion, such as Ni^{2+}).

the other kind of ion as its nearest neighbors (see Fig. 1*c*), and twelve of the same kind of ion as its second-nearest neighbors (see Fig. 1*b*).

The first attempt to calculate the phonon-dispersion curves, *i.e.* the frequency spectrum of the crystal, was made by Born and Karman (for a review, see Born & Huang, 1954). In their original theory, quasielastic forces between neighboring particles were assumed. For ionic lattices, however, the forces are largely of long range and, for many compounds, force constants out to at least fifth neighbors are often required to explain experimental results. It was soon realized that the unrealistically large number of force constants involved is due to the fact that forces of long range in the crystal are acting through the distortion and compression of the valence-electron distribution. A so-called *shell model* (SM) was then proposed (Dick & Overhauser, 1958; Cochran, 1959) in which the atom is represented by a core consisting of the nucleus and the inner electrons and a shell representing the outer electrons (see Fig. 2).

In the original SM (Dick & Overhauser, 1958; Cochran, 1959), the shell of the outer electrons is rigid, *i.e.* the shell is not allowed to distort. The usual SM is therefore also called the *rigid-shell model*. The SM used in the present study follows that developed for alkali halide crystals by the Chalk River group (Woods *et al.*, 1960, 1963; Cowley *et al.*, 1963). Shown in Fig. 2 is a schematic representation of the shell model. The shells have the charges Y_1 and Y_2 and are coupled to the cores of the positive (labeled 1) and negative (labeled 2) ions by the force constants k_1 and k_2, respectively. For positive ions (such as Ni^{2+}), only force constants to first-nearest neighbors (A_{12}, B_{12}; see Fig. 1*c*) are considered, while for negative ions (such as O^{2-}) up to second-nearest-neighbor force constants (A_{22} and B_{22}; see Fig. 1*b*) are included. The equations of motion are then, in matrix notation (Woods *et al.*, 1960),

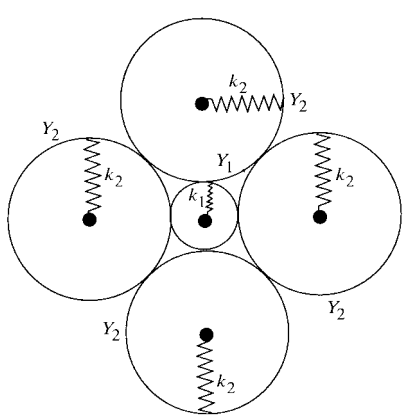

Fig. 2. Schematic representation of the shell model and relevant parameters.

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

where **R**, **T** and **S** describe short-range ion–ion, ion–shell and shell–shell interactions; **u** and **w** are the core displacement vector and the displacement vector of the shells relative to their own cores, respectively; **M**, **Z**, **Y** and **K** have as their diagonal elements the ion masses, the ionic charges, shell charges and shell-core force constants linking the shells with their own cores; **C** is the matrix of Coulomb coefficients which may be calculated using the dimensionless coefficients given by Kellermann (1940).

Normally, we assume that all short-range forces between ions act through the shell. This assumption leads to the condition $\mathbf{R}=\mathbf{T}=\mathbf{S}$, reducing the number of short-range interactions to one.

The short-range-interaction matrix **R** depends on **q**, *i.e.* the phonon wavevector, and components of this matrix are, for the sodium chloride structure,

$$\begin{aligned}R_{xx}^{12} &= -(e^2/V)\{A_{12}\cos q_x r_0 + B_{12}(\cos q_y r_0+\cos q_z r_0)\}\\ R_{xx}^{11} &= (e^2/V)(A_{12}+2B_{12})\\ R_{xx}^{22} &= (e^2/V)\{A_{12}+2B_{12}+2A_{22}+4B_{22}\\ &\quad -(A_{22}+B_{22})\cos q_x r_0(\cos q_y r_0+\cos q_z r_0)\\ &\quad -2B_{22}\cos q_y r_0\cos q_z r_0\}\\ R_{xy}^{11} &= R_{xy}^{12}=0\\ R_{xy}^{22} &= (e^2/V)(A_{22}-B_{22})\sin q_x r_0\sin q_y r_0,\end{aligned}\tag{2}$$

where e is the eletronic charge, V is the volume of the unit cell ($=2r_0^3$ with r_0 the interionic distance) and A_{12}, B_{12}, A_{22}, 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 negative ions (second neighbors) as well as first nearest neighbors.

For certain ionic lattices, it was found that an improvement over the usual SM may be achieved by allowing spherically symmetric distortions of the ion shells, and this is the so-called *breathing-shell model* (BSM) first introduced by Schröder (Schröder, 1966; Nüsslein & Schröder, 1967). In this model, the equations of motion are

$$\begin{aligned}\mathbf{M}\omega^2\mathbf{u} &= (\mathbf{R}+\mathbf{ZCZ})\mathbf{u}+\mathbf{Q}\mathbf{v}+(\mathbf{R}+\mathbf{ZCY})\mathbf{w}\\ 0 &= \mathbf{Q}^+(\mathbf{u}+\mathbf{w})+\mathbf{H}\mathbf{v}\\ 0 &= (\mathbf{R}+\mathbf{YCZ})\mathbf{u}+\mathbf{Q}\mathbf{v}+(\mathbf{R}+\mathbf{K}+\mathbf{YCY})\mathbf{w},\end{aligned}\tag{3}$$

where **v** is the vector giving the isotropic deformation of the shells. The matrices **Q** and **H** represent the short-range shell–breathing interaction and the breathing–breathing interaction, respectively, and $\mathbf{Q}^+$ denotes the conjugate matrix of **Q**. Explicitly, **Q** and **H** are given by the expressions

Table 1. *Model parameters of the eight-parameter BSM*

Crystal	A_{12} ($e/2V$)	B_{12} ($e/2V$)	A_{22} ($e/2V$)	B_{22} ($e/2V$)	Z (e)	K_2 (e/V)	G_2 (e/V)	Y_2 (e)	σ	Reference
KF	11.896	−1.378	−0.589	0.084	1.027	63.10	31858.21	−1.575	0.115	Buhrer (1970)
KCl	12.055	−0.968	−0.038	0.057	0.916	245.82	4852.03	−3.402	0.004	Raunio & Rolandson (1970*a*)
KBr	12.041	−0.997	−0.037	0.116	0.860	296.35	32019.81	−3.459	0.002	Woods *et al.* (1963)
KI	12.206	−0.767	0.146	0.052	0.825	311.35	6727.60	−4.232	0.002	Dolling *et al.* (1966)
NaF	8.992	−0.814	0.390	−0.021	0.883	84.07	21022.27	−1.281	0.063	Ruyers (1967)
NaCl	9.729	−0.820	0.859	−0.055	0.886	161.23	20412.90	−3.115	0.005	Raunio & Rolandson (1970*a*)
NaBr	8.468	−0.558	0.565	0.022	0.789	624.05	4372.84	−5.824	0.004	Reid & Smith (1970)
NaI	8.981	−0.750	0.630	0.177	0.772	391.94	29016.39	−4.822	0.006	Woods *et al.* (1963)
RbF	11.609	−1.296	−0.939	0.132	0.990	214.51	20888.52	−2.021	0.087	Raunio & Rolandson (1970*a*)
RbCl	12.101	−0.700	0.172	0.072	0.756	57.83	43262.02	−0.227	0.010	Raunio & Rolandson (1970*a*)
RbBr	12.711	−0.770	0.182	0.196	0.713	84.84	435.35	0.414	0.005	Rolanason & Raunio (1971)
RbI	14.323	−1.403	0.107	0.247	0.909	328.75	29317.34	−4.298	0.022	Raunio & Rolandson (1970*b*)
LiF	6.360	−0.626	0.886	0.044	0.847	395.97	48656.51	−3.496	0.060	Dolling *et al.* (1968)
CaO	36.721	−5.373	−3.003	0.914	2.094	62.42	6032.76	−2.866	0.195	Reider *et al.* (1973)
FeO	19.760	−2.596	1.112	−0.351	1.409	82.81	14846.78.	−2.748	0.087	Kugel *et al.* (1977)
MnO	20.124	−2.862	0.556	−0.128	1.498	114.20	23514.59	−2.721	0.161	Wagner *et al.* (1976)
SrO	28.922	−4.333	−0.155	0.329	1.703	44.98	34089.59	−1.393	0.294	Rieder & Migoni (1975)
MgO	23.782	−2.202	2.171	−0.355	1.662	84.61	3517.45	−2.628	0.104	Sangster *et al.* (1970)
NiO	22.719	−2.213	0.419	−0.304	1.482	70.584	27796.68	−2.412	0.108	Reichardt *et al.* (1975)

$$\mathbf{Q} = \begin{pmatrix} 0 & D_0 \\ D_0 & D_2 \end{pmatrix}, \quad \mathbf{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \tag{4}$$

with

$$D_0 = (e^2/V) i A_{12} \begin{pmatrix} \sin q_x r_0 \\ \sin q_y r_0 \\ \sin q_z r_0 \end{pmatrix}$$

$$D_2 = (e^2/V) i\, 2^{1/2} A_{22} \begin{pmatrix} \sin q_x r_0 (\cos q_y r_0 + \cos q_z r_0) \\ \sin q_y r_0 (\cos q_z r_0 + \cos q_x r_0) \\ \sin q_z r_0 (\cos q_x r_0 + \cos q_y r_0) \end{pmatrix}$$

$$H_{11} = (e^2/V)(G_1 + 3A_{12})$$

$$H_{12} = H_{21} = (e^2/V) A_{12} (\cos q_x r_0 + \cos q_y r_0 + \cos q_z r_0)$$

$$H_{22} = (e^2/V)\{G_2 + 3A_{12} + 2A_{22}(3 + \cos q_x r_0 \cos q_y r_0 + \cos q_y r_0 \cos q_z r_0 + \cos q_z r_0 \cos q_x r_0)\}, \tag{5}$$

and $G1$ and $G2$ are the breathing force constants for the positive and negative ions, respectively. In the present study, we examined two versions of the BSM. The first is the eight-parameter BSM, assuming that the positive-ion shells do not deform such that the corresponding force constants k_1 and G_1 are effectively infinite and the value of the shell charge Y_1 has no influence on the equations of motion. In the second model, this assumption on the positive-ion shells is relaxed, and a total of eleven parameters is used.

3. Debye–Waller factors of cubic lattice

For compounds with the sodium chloride structure, since the lattice is a cubic lattice, the Debye–Waller factors are isotropic. For each atom k ($k = 1, 2$ for cation and anion, respectively) in the unit cell, the Debye–Waller factor is given by B_k at a given temperature T:

$$B_k = \frac{8\pi^2}{3 m_k N} \sum_{\mathbf{q}j} \left(\frac{\overline{E}}{\omega^2} \right)_{\mathbf{q}j} \left| U_k(\mathbf{q}j) \right|^2, \tag{6}$$

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

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

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

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

$\omega_{\mathbf{q}j}$ is the frequency of the phonon, $U_k(\mathbf{q}j)$ is the complex displacement eigenvector, m_k the mass of the kth atom and N the number of wavevectors in the summation over the Brillouin zone. By solving the eigenvalue equations (1) or (2), we can obtain eigenvalues $\omega_{\mathbf{q}j}$ and eigenvectors $U_k(\mathbf{q}j)$, for all modes and atoms. The Debye–Waller B factors may therefore be calculated for any temperature using equation (6). What deserves extra attention is the 'zero-phonon' term resulting from the singularity caused by phonon branches where $\omega(\mathbf{q} = 0, j) = 0$, and this point has been discussed in some detail by Reid (1987).

4. Results

Our present BSMs use eight parameters (A_{12}, B_{12}, A_{22}, B_{22}, Z, Y_2, k_2, G_2) and eleven parameters (A_{12}, B_{12}, A_{22}, B_{22}, Z, Y_1, k_1, G_1, Y_2, k_2, G_2), respectively. These parameters are obtained by refining calculated phonon-dispersion curves so that these curves fit to that of the experimentally measured ones optimally. In our

Table 2. *Model parameters of the eleven-parameter BSM*

Crystal	A_{12} $(e/2V)$	B_{12} $(e/2V)$	A_{22} $(e/2V)$	B_{22} $(e/2V)$	Z (e)	K_1 (e/V)	G_1 (e/V)	Y_1 (e)	K_2 (e/V)	G_2 (e/V)	Y_2 (e)	σ
KF	11.927	−1.386	−0.595	0.088	1.028	−1.21E+18	−2.80E+20	3.444	63.02	8253.57	−1.583	0.125
KCl	11.625	−0.943	−0.060	0.170	0.877	−2.64E+18	1.77E+20	1.930	468.88	4138.07	−4.188	0.004
KBr	12.247	−1.103	0.025	0.137	0.873	1.45E+19	−7.71E+19	12.234	239.82	4182.00	−3.339	0.002
KI	12.160	−0.784	0.068	0.124	0.812	−5.61E+17	4.32E+19	1.976	408.42	5143.08	−4.693	0.002
NaF	8.786	−0.726	−0.108	0.182	0.878	7.36E+17	1.23E+19	4.151	460.20	3411.48	−3.889	0.055
NaCl	9.708	−0.826	0.869	−0.052	0.884	6.13E+18	1.85E+20	6.081	164.21	8115.17	−3.127	0.006
NaBr	8.461	−0.544	0.575	0.004	0.792	9.92E+17	2.41E+20	3.963	556.19	4495.12	−5.546	0.005
NaI	8.881	−0.737	1.062	0.034	0.754	8.96E+18	6.01E+20	7.480	552.23	3086.97	−5.585	0.005
RbF	11.902	−1.195	−1.053	0.196	0.951	−8.63E+18	2.11E+20	3.826	58.48	5828.39	−0.484	0.089
RbCl	13.180	−1.240	−0.321	0.104	0.949	−2.56E+17	3.41E+20	6.151	136.41	6322.22	−2.488	0.010
RbBr	12.902	−0.878	−0.002	−0.028	0.885	−4.46E+18	−4.29E+20	−0.772	417.78	7675.84	−4.498	0.001
RbI	13.937	−1.226	0.261	0.091	0.885	3.15E+18	4.81E+20	5.948	380.47	4892.21	−4.448	0.024
LiF	6.677	−0.660	0.999	−0.017	0.891	−1.45E+19	1.86E+21	0.549	117.03	7780.14	−2.232	0.020
CaO	37.720	−6.178	−3.563	1.0748	2.109	−2.19E+18	−3.37E+20	−0.838	62.27	6074.08	−2.858	0.198
FeO	18.649	−2.227	1.344	−0.453	1.361	1.60E+19	2.18E+21	29.672	88.17	3505.12	−2.710	0.096
MnO	20.273	−3.076	0.578	0.010	1.501	−8.56E+16	1.40E+21	13.679	105.94	5117.09	−2.555	0.190
SrO	32.349	−5.603	−3.073	0.942	1.883	−3.11E+18	−2.16E+20	0.732	65.29	5678.56	−2.145	0.236
MgO	24.038	−2.054	1.445	−0.405	1.669	1.50E+19	2.44E+21	24.297	83.78	4986.52	−2.613	0.158
NiO	21.280	−1.961	1.344	−0.313	1.414	1.06E+19	2.35E+21	20.263	65.14	5673.53	−2.123	0.112

Table 3. *Model parameters of the SM*

Crystal	A_{12} $(e/2V)$	B_{12} $(e/2V)$	A_{22} $(e/2V)$	B_{22} $(e/2V)$	Z (e)	K_1 (e/V)	K_2 $(e/2)$	Y_1 (e)	Y_2 (e)	σ
KF	9.492	−0.864	−0.450	0.097	0.851	−1.58E+07	−6.94E+06	8.283	−13.241	0.182
KCl	10.352	−0.796	0.193	0.191	0.745	−2.16E+07	−8.13+06	10.999	−14.534	0.014
KBr	10.567	−0.745	−0.066	0.218	0.712	−7.62E+06	5.68+E06	5.351	−6.418	0.009
KI	11.402	−0.487	0.298	−0.096	0.745	−2.17E+06	1391.82	−0.090	−7.948	0.004
NaF	7.731	−0.587	0.104	0.147	0.778	5.80E+07	1.42E+06	−6.098	−0.769	0.077
NaCl	8.050	−0.584	0.756	0.057	0.715	−9.58E+06	−5.51E+06	4.444	−9.712	0.059
NaBr	7.045	−0.327	0.804	−0.051	0.680	−2.35E+06	−3.84E+06	1.255	−8.760	0.047
NaI	7.156	−0.359	1.083	−0.035	0.626	−3.32E+06	−2.67E+06	1.580	−8.968	0.034
RbF	10.450	−1.050	−0.871	0.153	0.904	7.97E+08	8.36E+06	−135.497	−11.204	0.094
RbCl	10.568	−0.620	−0.110	0.109	0.747	−7.40E+06	−2.06E+06	1.601	−9.609	0.018
RbBr	10.795	−0.351	0.624	−0.243	0.685	1.40E+06	−3.88E+05	−0.145	−7.302	0.007
LiF	5.753	−0.692	0.888	0.136	0.765	−4.99E+06	−3.64E+06	1.896	2.760	0.510
CaO	29.090	−3.172	−0.126	0.338	1.707	396.21	72.26	−1.699	−2.124	0.052
FeO	12.798	−0.778	1.164	−0.298	1.012	−9.11E+06	1798.02	−0.763	−6.728	0.311
MnO	14.076	−1.708	1.287	−0.169	1.143	7644.20	1.89E+07	−9.276	−4.979	0.236
SrO	31.869	−4.224	0.092	0.057	1.785	314.41	67.89	−1.450	−2.130	0.026
MgO	30.933	−3.810	−0.269	0.095	1.934	246.92	103.77	3.149	−3.251	0.071
NiO	35.264	−4.956	−2.529	0.109	1.986	110.33	81.92	3.167	−3.231	0.031

program, the fitting is performed using the standard multidimensional downhill simplex method, for details see Press *et al.* (1986). Our rigid SM uses nine parameters, A_{12}, B_{12}, A_{22}, B_{22}, Z, K_1, K_2, Y_1, Y_2, and the parameters are obtained *via* the same numerical procedure as in the BSM.

The goodness of fit between the measured and calculated phonon-dispersion curves is given by the standard error indicator σ, which is defined as follows:

$$\sigma = (N - K)^{-1} \sum_{i=1}^{N} (\omega^i_{\text{expt}} - \omega^i_{\text{mod}})^2, \qquad (7)$$

where N is the number of experimental data, K is the number of adjustable parameters, ω_{expt} is the experimental frequency and ω_{mod} is the model frequency for a particular point on the phonon-dispersion curves.

Given in Table 1 and Table 2 are the model parameters of the eight-parameter BSM and eleven-parameter BSM, respectively, for 19 compounds with the sodium chloride structure, Table 3 gives SM parameters of the same compounds and Table 4 gives the elastic constants calculated using these models. An indicator σ, defined in equation (7), has also been given of the fitting error. From this error indicator, it is seen that for most of the compounds the BSM provides a better description of the phonon-dispersion curves than the SM. For a few compounds, the rigid SM gives smaller fitting error. It should be noted, however, that this fact does not imply that for these compounds the rigid SM provides a better description of lattice vibrations than the BSM. This is

Table 4. *Calculated elastic constants (10^{11} Pa) using the shell models*

Crystal	Eight-parameter BSM			Eleven-parameter BSM			SM		
	C_{11}	C_{12}	C_{44}	C_{11}	C_{12}	C_{44}	C_{11}	C_{12}	C_{44}
KF	0.679	0.125	0.130	0.679	0.124	0.130	0.615	0.063	0.103
KCl	0.456	0.057	0.073	0.457	0.037	0.073	0.465	0.032	0.059
KBr	0.406	0.041	0.051	0.412	0.044	0.052	0.396	0.014	0.041
KI	0.330	0.031	0.042	0.331	0.023	0.041	0.324	0.037	0.035
NaF	1.088	0.250	0.272	0.991	0.075	0.297	0.990	0.082	0.250
NaCl	0.594	0.142	0.140	0.594	0.141	0.139	0.570	0.085	0.108
NaBr	0.424	0.066	0.098	0.422	0.068	0.098	0.394	0.070	0.086
NaI	0.366	0.041	0.074	0.382	0.069	0.070	0.337	0.058	0.061
RbF	0.523	0.064	0.085	0.580	0.033	0.080	0.502	0.038	0.075
RbCl	0.464	0.036	0.047	0.410	0.049	0.052	0.380	0.020	0.045
RbBr	0.414	0.005	0.037	0.362	0.045	0.044	0.359	0.056	0.033
RbI	0.332	0.032	0.036	0.326	0.040	0.033	0.304	0.047	0.023
LiF	1.280	0.395	0.607	1.267	0.484	0.652	1.337	0.328	0.513
CaO	2.084	0.484	0.921	2.133	0.446	0.865	2.483	0.504	0.814
FeO	2.725	1.170	0.660	2.615	1.135	0.660	2.220	0.616	0.521
MgO	3.292	1.334	1.587	3.138	1.278	1.533	3.412	1.256	1.689
MnO	2.141	0.933	0.701	2.188	0.889	0.706	2.013	0.726	0.479
SrO	1.884	0.538	0.463	1.587	0.319	0.441	2.080	0.641	0.536
NiO	3.516	1.111	0.957	3.634	1.141	1.019	3.850	1.308	1.221

because there is no guarantee from the numerical minimization routine that the global minimum has been achieved by adjusting the fitting parameters. The difference in the fitting errors may result from the numerical fitting procedure rather than the difference in the physical models and definite conclusions cannot therefore be drawn as to which model is better based on the very small difference in the fitting error.

Shown in Fig. 3 are experimentally measured (Reichardt *et al.*, 1975) and calculated phonon-dispersion curves, *i.e.* $\omega(q)$ curves, for an NiO single crystal using the rigid-shell model, and in Table 5 numerical values of the phonon frequencies measured in THz are given for certain points of the Brillouin zone. In both Fig. 3 and Table 5, the notations LO, TO, LA and TA refer to the longitudinal optic, transverse optic, longitudinal acoustic and transverse acoustic modes of lattice vibrations, respectively. Fig. 3 and Table 5 show that the simple SM reproduces excellently most features of the phonon-dispersion surfaces.

The Debye–Waller factors were calculated numerically using equation (7) over the temperature range from 1 to 1000 K. For all compounds, it was found that the temperature dependence of the Debye–Waller B

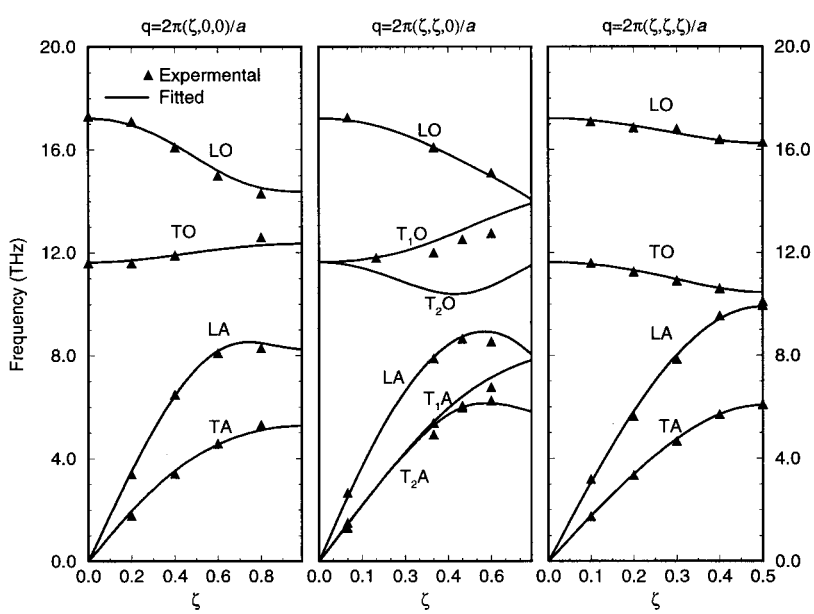

Fig. 3. Experimental and calculated phonon-dispersion curves for an NiO single crystal. The calculations are based on the rigid-shell model. Experimental data were measured at room temperature ($T = 293$ K).

Table 5. *Experimental and fitted phonon frequencies (THz) for NiO*

q	LO		TO_1		TO_2		LA		TA_1		TA_2	
$(2\pi/a)$	Exp.	Fitted	Exp.	Fitted	Exp.	Fitted	Exp.	Fitted	Exp.	Fitted	Exp.	Fitted
(0, 0, 0)	17.3	17.22	11.60	11.63	11.60	11.63	–	–	–	–	–	–
(0.2, 0, 0)	17.1	16.96	11.60	11.72	11.60	11.72	3.39	3.53	1.77	1.97	1.77	1.97
(0.4, 0, 0)	16.1	16.20	11.90	11.91	11.90	11.91	6.49	6.44	3.41	3.53	3.41	3.53
(0.6, 0, 0)	15.0	15.19	–	–	–	–	8.1	8.20	4.59	4.56	4.59	4.56
(0.8, 0, 0)	14.3	14.53	12.60	12.29	12.60	12.29	8.29	8.49	5.30	5.11	5.30	5.11
(1.0, 0, 0)	14.3	14.36	12.90	12.35	12.90	12.35	8.25	8.26	5.44	5.28	5.44	5.28
(0.1, 0.1, 0)	17.25	17.15	–	–	–	–	2.66	2.51	1.30	1.45	1.50	1.46
(0.2, 0.2, 0)	–	–	11.80	11.82	–	–	–	–	–	–	–	–
(0.4, 0.4, 0)	16.1	16.10	12.0	12.43	–	–	7.88	7.95	4.93	5.29	5.39	5.43
(0.5, 0.5, 0)	–	–	12.5	12.88	–	–	8.66	8.74	6.05	6.40	5.97	5.98
(0.6, 0.6, 0)	15.1	14.97	12.75	13.35	–	–	8.54	8.91	6.77	7.14	6.24	6.15
(0.7, 0.7, 0)	–	–	13.4	13.77	–	–	7.96	8.42	7.38	7.66	6.09	5.94
(0.1, 0.1, 0.1)	17.1	17.15	11.6	11.55	11.6	11.55	3.19	3.07	1.74	1.77	1.74	1.77
(0.2, 0.2, 0.2)	16.85	16.93	11.25	11.31	11.25	11.31	5.63	5.83	3.34	3.40	3.34	3.40
(0.3, 0.3, 0.3)	16.8	16.64	10.9	10.96	10.9	10.96	7.86	8.01	4.67	4.76	4.67	4.76
(0.4, 0.4, 0.4)	16.4	16.37	10.6	10.62	10.6	10.62	9.55	9.42	5.71	5.71	5.71	5.71
(0.5, 0.5, 0.5)	16.3	16.25	10.1	10.46	10.1	10.46	9.95	9.90	6.10	6.07	6.10	6.07

Table 6. *Polynomial regression form fitting parameters of the Debye–Waller factors using the 8-parameter breathing-shell model (0–80 K)*

Crystal	Atom	a_0	a_1	a_2	a_3	a_4	ME (%)
KF	K	0.27571	−3.32494E−5	1.87421E−5	1.49770E−7	−1.39061E−9	0.07
	F	0.41479	−6.04705E−6	1.86464E−5	4.82217E−8	−4.98724E−10	0.02
KCl	K	0.33940	−2.44397E−4	5.12860E−5	−2.23415E−8	−1.26439E−9	0.11
	Cl	0.34563	−1.72910E−4	4.70577E−5	−4.10598E−8	−9.28645E−10	0.07
KBr	K	0.35949	−2.77972E−4	9.14532E−5	−5.59495E−7	1.33742E−9	0.08
	Br	0.25581	−6.49310E−4	1.21039E−4	−9.37167E−7	2.78053E−9	0.24
KI	K	0.38445	−1.76176E−4	1.24495E−4	−9.73957E−7	3.32067E−9	0.08
	I	0.22203	−9.08631E−4	1.95526E−4	−2.05856E−6	8.39699E−9	0.39
NaF	Na	0.30602	3.98147E−5	4.06721E−6	1.15835E−7	−6.40539E−10	0.02
	F	0.33108	1.20411E−5	6.64791E−6	4.31929E−8	−2.12535E−10	0.01
NaCl	Na	0.41222	−1.29800E−6	1.49828E−5	2.53630E−7	−1.82398E−9	0.03
	Cl	0.30328	−3.03046E−5	1.73283E−5	1.99679E−7	−1.66904E−9	0.06
NaBr	Na	0.46862	−7.19006E−5	4.11032E−5	4.90356E−8	−1.11530E−9	0.02
	Br	0.23187	−4.87177E−4	7.23054E−5	−3.30670E−7	1.36840E−11	0.26
NaI	Na	0.51167	−1.25096E−4	7.11282E−5	−2.36401E−7	1.37852E−11	0.02
	I	0.19961	−8.26779E−4	1.32175E−4	−1.19357E−6	4.18518E−9	0.44
RbF	Rb	0.21025	−3.66053E−4	6.77139E−5	−3.53794E−7	3.52939E−10	0.23
	F	0.44432	−1.92120E−5	4.48371E−5	−2.81705E−7	1.09771E−9	0.05
RbCl	Rb	0.24292	−5.90523E−4	1.16908E−4	−9.10778E−7	2.72001E−9	0.26
	Cl	0.36178	−6.37367E−5	7.42361E−5	−4.23158E−7	1.02239E−9	0.03
RbBr	Rb	0.26003	−5.95074E−4	1.58170E−4	−1.46482E−6	5.40178E−9	0.22
	Br	0.25390	−3.49864E−4	1.33065E−4	−1.16858E−6	4.13048E−9	0.10
RbI	Rb	0.27978	−6.31814E−4	2.06460E−4	−2.10848E−6	8.49324E−9	0.17
	I	0.21837	−5.81927E−4	2.00630E−4	−2.18855E−6	9.23484E−9	0.18
LiF	Li	0.56720	8.85194E−7	3.67756E−6	−4.43257E−9	1.11086E−10	0.01
	F	0.28219	5.78456E−7	3.29258E−6	1.31150E−8	2.42208E−11	0.02
FeO	Fe	0.14083	2.13216E−5	8.28893E−7	8.89083E−8	−4.94667E−10	0.06
	O	0.25050	3.28858E−6	3.21280E−6	8.01388E−9	−8.39598E−11	0.02
MnO	Mn	0.14761	2.75093E−5	5.37885E−7	1.06174E−7	−5.95965E−10	0.05
	O	0.25942	−6.66539E−6	4.04046E−6	−9.45446E−9	2.41369E−11	0.02
MgO	Mg	0.16879	−1.03456E−6	1.02703E−6	2.75699E−9	1.24392E−11	0.02
	O	0.20230	−5.45783E−6	1.39472E−6	−4.98346E−9	3.35819E−11	0.03
CaO	Ca	0.15046	1.12126E−5	8.80019E−7	3.20880E−8	−1.00173E−10	0.03
	O	0.25041	−1.22639E−5	2.50437E−6	−8.44724E−9	5.78345E−11	0.01
SrO	Sr	0.11770	6.10637E−6	2.73220E−6	1.24080E−7	−8.50367E−10	0.08
	O	0.29331	−9.38276E−6	5.91716E−6	−3.73093E−8	2.21618E−10	0.02
NiO	Ni	0.11058	1.23089E−5	1.14084E−6	2.54305E−8	−9.47985E−11	0.04
	O	0.21920	−7.05146E−6	2.35555E−6	−3.15099E−9	7.03740E−12	0.02

Table 7. *Polynomial regression form fitting parameters of the Debye–Waller factors using the 8-parameter breathing-shell model (80–1000 K)*

Crystal	Atom	a_0	a_1	a_2	a_3	a_4	ME (%)
KF	K	0.14210	0.00319	2.03723E−6	−2.20260E−9	8.57938E−13	0.80
	F	0.27183	0.00298	3.70077E−6	−3.95915E−9	1.53186E−12	1.02
KCl	K	0.14740	0.00526	2.16231E−6	−2.34850E−9	9.17431E−13	0.56
	Cl	0.16072	0.00494	2.33990E−6	−2.53646E−9	9.89405E−13	0.64
KBr	K	0.14849	0.00656	2.18595E−6	−2.37469E−9	9.27544E−13	0.40
	Br	0.07532	0.00660	1.13566E−6	−1.23924E−9	4.85350E−13	0.22
KI	K	0.15007	0.00796	2.22428E−6	−2.41914E−9	9.45619E−13	0.41
	I	0.04830	0.00795	7.38449E−7	−8.09286E−10	3.18149E−13	0.10
NaF	Na	0.21556	0.00164	2.84859E−6	−3.02750E−9	1.16617E−12	0.98
	F	0.25013	0.00143	3.20245E−6	−3.38124E−9	1.29694E−12	1.11
NaCl	Na	0.23656	0.00376	3.33781E−6	−3.59699E−9	1.39831E−12	0.83
	Cl	0.15744	0.00338	2.26084E−6	−2.44465E−9	9.52303E−13	0.64
NaBr	Na	0.24414	0.00542	3.51576E−6	−3.80300E−9	1.48166E−12	0.67
	Br	0.07487	0.00504	1.12278E−6	−1.22375E−9	4.78931E−13	0.33
NaI	Na	0.24812	0.00700	3.61528E−6	−3.92067E−9	1.53000E−12	0.62
	I	0.04818	0.00607	7.35329E−7	−8.05465E−10	3.16371E−13	0.17
RbF	Rb	0.06957	0.00462	1.04105E−6	−1.13525E−9	4.44639E−13	0.24
	F	0.27762	0.00405	3.83450E−6	−4.11339E−9	1.59415E−12	0.91
RbCl	Rb	0.07057	0.00637	1.06963E−6	−1.17101E−9	4.60064E−13	0.18
	Cl	0.16240	0.00595	2.38107E−6	−2.58558E−9	1.00982E−12	0.53
RbBr	Rb	0.07078	0.00771	1.07013E−6	−1.16882E−9	4.58208E−13	0.24
	Br	0.07526	0.00705	1.13211E−6	−1.23530E−9	4.84010E−13	0.23
RbI	Rb	0.07104	0.00924	1.07828E−6	−1.17986E−9	4.63130E−13	0.19
	I	0.04819	0.00824	7.34566E−7	−8.04322E−10	3.15715E−13	0.14
LiF	Li	0.53285	2.89093E−4	5.51183E−6	−5.55348E−9	2.06668E−12	0.99
	F	0.23275	7.26051E−4	2.81718E−6	−2.93924E−9	1.11884E−12	1.19
FeO	Fe	0.09213	8.93933E−4	1.25371E−6	−1.34072E−9	5.18502E−13	1.03
	O	0.23088	3.15684E−4	2.36871E−6	−2.38009E−9	8.84014E−13	0.85
MnO	Mn	0.09451	9.85963E−4	1.29258E−6	−1.38372E−9	5.35530E−13	1.01
	O	0.23738	3.31997E−4	2.51014E−6	−2.54116E−9	9.48559E−13	0.95
MgO	Mg	0.15572	1.28564E−4	1.64443E−6	−1.66358E−9	6.20501E−13	1.02
	O	0.19891	−5.75138E−6	1.74277E−6	−1.68302E−9	6.08490E−13	0.60
CaO	Ca	0.11592	5.33863E−4	1.46472E−6	−1.54394E−9	5.91822E−13	1.19
	O	0.23539	1.45381E−4	2.45394E−6	−2.47339E−9	9.20443E−13	0.97
SrO	Sr	0.06305	0.00118	9.00958E−7	−9.73898E−10	3.79380E−13	0.79
	O	0.25948	5.03334E−4	2.96681E−6	−3.05531E−9	1.15312E−12	1.13
NiO	Ni	0.08204	4.75869E−4	1.06656E−6	−1.13098E−9	4.35211E−13	1.17
	O	0.21062	1.13101E−4	1.96029E−6	−1.92248E−9	7.02603E−13	0.66

factor is rather smooth, and all curves of $B(T)$ were then fitted analytically using the polynomial regression form:

$$B(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4, \qquad (8)$$

where T is measured in Kelvin, B is given in Å^2 and a_i are fitting parameters. For all the 19 compounds with the sodium chloride structure investigated, the fitting parameters are given in Tables 6 and 7, Tables 8 and 9, and Tables 10 and 11 for the eight-parameter BSM, eleven-parameter BSM and the SM, respectively, together with the maximum error (ME) of all data points:

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

Tables 6–11 show that the analytical fit is excellent for all compounds, with ME being less than 1% for all but a few compounds.

To visualize how good the polynomial regression fitting of the temperature dependence of the Debye–Waller factors is, we plotted in Fig. 4 the $B(T)$ curves for two oxides MgO and CaO. This figure shows that the analytical fitting using the polynomial regression form is excellent for all atoms in the crystal. It should also be noted that the Debye–Waller B factors for the positive ions, *i.e.* Mg^{2+} and Ca^{2+}, are larger than that of the negative oxygen ions, O^{2-}, and that the Debye–Waller factors for O^{2-} may differ significantly in MgO from that in CaO, *i.e.* the Debye–Waller factor of an atom may depend sensitively on its environment in the crystal.

5. Comparison with experiments

A compilation of the isotropic Debye–Waller B factors for diatomic cubic compounds was recently given by Butt *et al.* (1993). Of the 52 compounds included in that compilation, 14 compounds with the sodium chloride structure have been investigated in this paper. In

Table 8. *Polynomial regression form fitting parameters of the Debye–Waller factors using the 11-parameter breathing-shell model (0–80 K)*

Crystal	Atom	a_0	a_1	a_2	a_3	a_4	ME (%)
KF	K	0.27569	−3.97001E−5	1.90082E−5	1.45132E−7	−1.36815E−9	0.07
	F	0.41449	−1.32321E−5	1.90294E−5	3.95364E−8	−4.43675E−10	0.01
KCl	K	0.34407	−2.71951E−4	5.20042E−5	−7.64989E−9	−1.40092E−9	0.11
	Cl	0.33970	−1.59544E−4	4.57814E−5	−5.53940E−8	−7.72741E−10	0.05
KBr	K	0.36082	−3.06273E−4	9.25366E−5	−5.74224E−7	1.42586E−9	0.07
	Br	0.25412	−6.33280E−4	1.18614E−4	−9.10515E−7	2.66978E−9	0.27
KI	K	0.38640	−2.04061E−4	1.26784E−4	−1.00081E−6	3.44973E−9	0.07
	I	0.22061	−8.82914E−4	1.92263E−4	−2.01719E−6	8.20798E−9	0.38
NaF	Na	0.31824	3.36863E−5	3.28677E−6	1.30257E−7	−6.58199E−10	0.01
	F	0.32146	5.17396E−6	6.33234E−6	3.29345E−8	−1.57649E−10	0.01
NaCl	Na	0.41303	−5.80361E−6	1.52557E−5	2.51515E−7	−1.81479E−9	0.03
	Cl	0.30318	−3.03046E−5	1.73283E−5	1.99679E−7	−1.66904E−9	0.06
NaBr	Na	0.46778	−5.23749E−5	4.03194E−5	5.83251E−8	−1.16063E−9	0.02
	Br	0.23260	−4.85717E−4	7.24684E−5	−3.24320E−7	−4.86362E−11	0.27
NaI	Na	0.51388	−9.52548E−5	7.31870E−5	−2.61936E−7	1.43879E−10	0.08
	I	0.19861	−7.92322E−4	1.32936E−4	−1.21423E−6	4.31378E−9	0.39
RbF	Rb	0.20574	−3.25100E−4	6.34232E−5	−3.20302E−7	2.71684E−10	0.19
	F	0.44368	3.77853E−6	4.20515E−5	−2.49335E−7	9.64524E−10	0.04
RbCl	Rb	0.24532	−6.61109E−4	1.22166E−4	−9.70945E−7	2.96674E−9	0.27
	Cl	0.36621	−1.50104E−4	8.05590E−5	−4.90654E−7	1.29254E−9	0.02
RbBr	Rb	0.25697	−6.16459E−4	1.52916E−4	−1.39827E−6	5.08502E−9	0.22
	Br	0.25998	−5.05979E−4	1.41578E−4	−1.26004E−6	4.50533E−9	0.18
RbI	Rb	0.27878	−5.25372E−4	2.07079E−4	−2.13499E−6	8.69368E−9	0.12
	I	0.22175	−5.39958E−4	2.10075E−4	−2.31512E−6	9.83668E−9	0.17
LiF	Li	0.55882	−4.51204E−6	4.05664E−6	−1.12501E−8	1.42384E−10	0.01
	F	0.28529	4.69857E−6	2.88026E−6	2.42906E−8	−4.19277E−11	0.02
FeO	Fe	0.14086	2.18745E−5	9.05213E−7	8.72665E−8	−4.85494E−10	0.04
	O	0.25160	−3.94824E−6	3.75333E−6	−1.88399E−9	−2.04531E−11	0.01
MnO	Mn	0.14816	2.53320E−5	3.21022E−7	1.11325E−7	−6.20955E−10	0.03
	O	0.25571	−2.31760E−6	3.87375E−6	−1.28513E−8	5.75966E−11	0.02
MgO	Mg	0.16642	−2.21183E−6	1.38712E−6	−5.48783E−9	6.78861E−11	0.03
	O	0.20771	−9.49815E−6	1.57687E−6	−5.95688E−9	3.92882E−11	0.02
CaO	Ca	0.15039	1.30475E−5	7.74278E−7	3.62603E−8	−1.30679E−10	0.03
	O	0.25202	−3.40839E−6	2.42189E−6	−1.14017E−8	1.02351E−10	0.02
SrO	Sr	0.11954	−1.11103E−5	4.27707E−6	1.11528E−7	−8.02252E−10	0.09
	O	0.29511	−1.53269E−5	6.92256E−6	−4.85607E−8	2.77940E−10	0.01
NiO	Ni	0.11079	1.07347E−5	8.56104E−7	2.94718E−8	−1.15121E−10	0.03
	O	0.21440	−2.63667E−6	1.91857E−6	2.36603E−9	−2.88934E−11	0.02

Table 12, we list the experimental Debye–Waller B factors for these compounds [with two additions for NaBr and NaI taken from Gopi & Sirdeshmukh (1998)] and calculated values using SM, eight-parameter (8p) and eleven-parameter (11p) BSMs. For most of the compounds, Debye–Waller B factors for both the cation and the anion are given, together with an average $\overline{B}$, defined by

$$\overline{B} = \frac{m^+B^+ + m^-B^-}{m^+ + m^-},$$

where the superscripts + and − denote cation (positive ion) and anion (negative ion), respectively, and m refers to the mass of the relevant ion. Table 12 shows that, for most of the compounds, the difference between the experimental and calculated mean $\overline{B}$ factors is less than 10% (the exceptions being MgO, 15%; SrO, 30%; KCl, 17%; KI, 16%; NaBr, 35%; RbI, 18%). For most of the compounds, the consistency among different shell

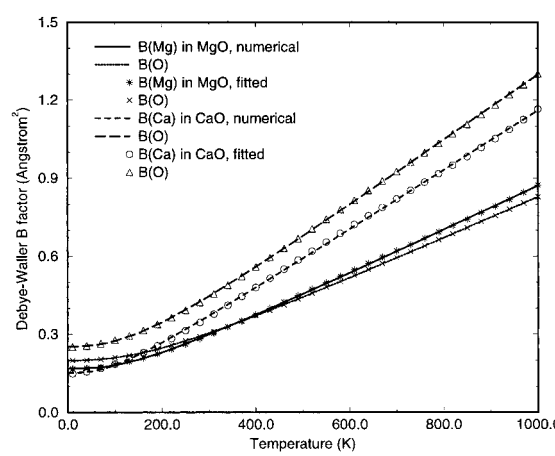

Fig. 4. Numerical and fitted Debye–Waller B factors for temperature range from 1 to 1000 K for MgO and CaO oxides (eight-parameter BSM).

Table 9. *Polynomial regression form fitting parameters of the Debye–Waller factors using the 11-parameter breathing-shell model (80–1000 K)*

Crystal	Atom	a_0	a_1	a_2	a_3	a_4	ME (%)
KF	K	0.14194	0.00318	2.02989E−6	−2.19253E−9	8.53360E−13	0.59
	F	0.27178	0.00297	3.69801E−6	−3.95570E−9	1.53053E−12	0.96
KCl	K	0.14761	0.00537	2.16668E−6	−2.35307E−9	9.19088E−13	0.58
	Cl	0.16026	0.00477	2.32750E−6	−2.52224E−9	9.83875E−13	0.61
KBr	K	0.14868	0.00659	2.19080E−6	−2.38050E−9	9.30057E−13	0.48
	Br	0.07524	0.00652	1.13348E−6	−1.23774E−9	4.85304E−13	0.27
KI	K	0.15024	0.00803	2.23466E−6	−2.43511E−9	9.53368E−13	0.39
	I	0.04829	0.00787	7.37853E−7	−8.08101E−10	3.17417E−13	0.16
NaF	Na	0.21945	0.00175	2.93528E−6	−3.12712E−9	1.20651E−12	1.00
	F	0.24767	0.00128	3.14520E−6	−3.31513E−9	1.27028E−12	1.20
NaCl	Na	0.23672	0.00378	3.34096E−6	−3.60005E−9	1.39937E−12	0.89
	Cl	0.15733	0.00338	2.25586E−6	−2.43726E−9	9.48641E−13	0.64
NaBr	Na	0.24414	0.00540	3.51803E−6	−3.80606E−9	1.48289E−12	0.64
	Br	0.07509	0.00507	1.13152E−6	−1.23607E−9	4.84749E−13	0.33
NaI	Na	0.24823	0.00712	3.61419E−6	−3.91746E−9	1.52803E−12	0.59
	I	0.04800	0.00609	7.30330E−7	−7.99154E−10	3.13594E−13	0.18
RbF	Rb	0.06966	0.00444	1.04785E−6	−1.14546E−9	4.49484E−13	0.41
	F	0.27795	0.00397	3.83827E−6	−4.11514E−9	1.59392E−12	0.83
RbCl	Rb	0.07044	0.00650	1.06161E−6	−1.15833E−9	4.53694E−13	0.27
	Cl	0.16240	0.00613	2.37878E−6	−2.58312E−9	1.00912E−12	0.51
RbBr	Rb	0.07064	0.00749	1.06457E−6	−1.16088E−9	4.54347E−13	0.17
	Br	0.07548	0.00725	1.13991E−6	−1.24437E−9	4.87347E−13	0.18
RbI	Rb	0.07118	0.00931	1.08335E−6	−1.18566E−9	4.65529E−13	0.15
	I	0.04818	0.00858	7.36715E−7	−8.07694E−10	3.17577E−13	0.16
LiF	Li	0.52670	2.69660E−4	5.38908E−6	−5.41633E−9	2.01237E−12	0.96
	F	0.23424	7.51248E−4	2.85120E−6	−2.97887E−9	1.13506E−12	1.20
FeO	Fe	0.09225	8.93403E−4	1.25697E−6	−1.34554E−9	5.20857E−13	1.03
	O	0.23132	3.27612E−4	2.37755E−6	−2.38946E−9	8.87476E−13	0.87
MnO	Mn	0.09459	9.91526E−4	1.29568E−6	−1.38792E−9	5.37390E−13	1.00
	O	0.23554	2.98103E−4	2.47013E−6	−2.49509E−9	9.29894E−13	0.94
MgO	Mg	0.15411	1.26015E−4	1.61232E−6	−1.62822E−9	6.06784E−13	0.95
	O	0.20298	1.11489E−5	1.81777E−6	−1.76510E−9	6.40742E−13	0.64
CaO	Ca	0.11567	5.40657E−4	1.46108E−6	−1.53965E−9	5.89934E−13	1.18
	O	0.23641	1.56284E−4	2.47508E−6	−2.49681E−9	9.29524E−13	0.98
SrO	Sr	0.06287	0.00126	8.94448E−7	−9.65280E−10	3.75579E−13	1.02
	O	0.26031	5.45236E−4	2.98862E−6	−3.08222E−9	1.16459E−12	1.11
NiO	Ni	0.08230	4.66033E−4	1.07087E−6	−1.13581E−9	4.37201E−13	1.16
	O	0.20747	8.48242E−5	1.89257E−6	−1.84447E−9	6.70888E−13	0.62

models is better than that between theory and experiments and the relative error between different modes is less than 10% for all but one compound (RbI).

It should be noted that the recommended Debye–Waller B factors (Butt *et al.*, 1988, 1993; Gopi & Sirdeshmukh, 1998) by the Neutron Diffraction Commission of the International Union of Crystallography were derived from results published by different research groups using different samples of different origins and different methods of measurement. These values are therefore not necessarily the most reliable and accurate values available. For example, for MgO, the recommended value for Mg is 0.37 Å^2 and for O it is 0.33 Å^2 at room temperature (293 K) (Butt *et al.*, 1993). But these values are rather peculiar since all models of lattice dynamics result in $B(\mathrm{O}) > B(\mathrm{Mg})$ rather than the other way round as for the recommended values. A careful convergent-beam electron diffraction (CBED) study (Zuo *et al.*, 1997) recently confirmed that for MgO the Debye–Waller B factor given by Lawrence (1973) is rather accurate, and our eleven-parameter BSM reproduces excellently the values of Lawrence (1973) and Zuo *et al.* (1997) (see Fig. 5).

Shown in Fig. 5 are calculated Debye–Waller B-factor curves for MgO using eight-parameter BSM, eleven-parameter BSM and SM, respectively, and these factors are compared with two experimental measurements of the same quantity at room temperature (Barron, 1977; Lawrence, 1973). The figure shows that for this ionic crystal the BSM gives a better agreement with experimental values than the SM and that the eleven-parameter BSM is better than the eight-parameter BSM, indicating that, although the deformation of magnesium ion shells is very small compared with that of the oxygen ion shells, it affects the Debye–Waller factors noticeably. We have also checked the twelve-parameter BSM, which does not assume axial symmetry for the second-neighbor forces (Sangster *et al.*, 1970), but no significant improvement was obtained.

Table 10. *Polynomial regression form fitting parameters of the Debye–Waller factors using the rigid-shell model (0–80 K)*

Crystal	Atom	a_0	a_1	a_2	a_3	a_4	ME (%)
KF	K	0.29458	−6.81010E−5	2.64123E−5	1.20713E−7	−1.43214E−9	0.06
	F	0.41724	−2.56411E−5	2.61628E−5	−3.08070E−8	−1.97007E−10	0.01
KCl	K	0.35108	−2.86697E−4	6.24034E−5	−1.29029E−7	−8.64591E−10	0.11
	Cl	0.34226	−1.68140E−4	5.53387E−5	−1.85447E−7	−1.44140E−10	0.05
KBr	K	0.36653	−2.23787E−4	1.03665E−4	−7.15246E−7	2.07526E−9	0.05
	Br	0.25778	−5.44187E−4	1.29513E−4	−1.05939E−6	3.39108E−9	0.21
KI	K	0.38928	−4.97566E−5	1.36475E−4	−1.14227E−6	4.16604E−9	0.11
	I	0.22718	−8.14654E−4	2.12569E−4	−2.29871E−6	9.58498E−9	0.33
NaF	Na	0.32010	4.95832E−5	3.85285E−6	1.41749E−7	−7.78417E−10	0.02
	F	0.32736	−3.34682E−8	7.85151E−6	2.87214E−8	−1.70971E−10	0.02
NaCl	Na	0.41685	−2.66635E−5	2.19180E−5	1.69976E−7	−1.44695E−9	0.03
	Cl	0.30699	−4.52679E−5	2.33341E−5	1.34282E−7	−1.40670E−9	0.04
NaBr	Na	0.45731	2.12619E−7	4.46367E−5	−7.03737E−8	−3.43032E−10	0.02
	Br	0.23772	−4.97386E−4	8.15193E−5	−4.33123E−7	4.35132E−10	0.26
NaI	Na	0.50260	9.41895E−5	6.88601E−5	−2.76363E−7	4.30295E−10	0.07
	I	0.20527	−7.84506E−4	1.47559E−4	−1.40239E−6	5.19718E−9	0.41
RbF	Rb	0.21613	−3.91131E−4	7.54848E−5	−4.36069E−7	6.85672E−10	0.21
	F	0.44723	−3.39465E−5	5.13454E−5	−3.69282E−7	1.52615E−9	0.04
RbCl	Rb	0.25434	−6.82927E−4	1.36797E−4	−1.14361E−6	3.73328E−9	0.27
	Cl	0.36564	−7.46912E−5	8.71707E−5	−5.99161E−7	1.87169E−9	0.05
RbBr	Rb	0.25918	−3.86128E−4	1.65083E−4	−1.58939E−6	6.10337E−9	0.12
	Br	0.26561	−3.31655E−4	1.61214E−4	−1.54179E−6	5.92304E−9	0.11
RbI	Rb	0.27622	8.91225E−5	2.09362E−4	−2.20366E−6	9.15598E−9	0.18
	I	0.23266	−1.64386E−4	2.44972E−4	−2.81388E−6	1.23540E−8	0.29
LiF	Li	0.57061	−4.53029E−6	3.94434E−6	−6.23556E−10	8.34746E−11	0.01
	F	0.28196	1.85037E−5	2.55475E−6	3.07542E−8	−9.33475E−11	0.01
FeO	Fe	0.14924	3.30161E−5	1.21304E−6	9.99419E−8	−5.66510E−10	0.03
	O	0.25382	−1.23076E−5	5.08206E−6	−1.02169E−8	−8.59823E−12	0.02
MnO	Mn	0.15975	2.64513E−5	1.51414E−6	1.29972E−7	−7.86383E−10	0.02
	O	0.27091	−8.80652E−6	5.81373E−6	−2.31632E−8	9.13059E−11	0.01
MgO	Mg	0.16669	1.77125E−6	8.98604E−7	6.39641E−11	4.37938E−11	0.01
	O	0.20122	2.03980E−6	8.56483E−7	2.33811E−9	−1.81980E−12	0.03
CaO	Ca	0.15127	1.05237E−5	6.96057E−7	3.61086E−8	−1.30389E−10	0.03
	O	0.25298	2.09390E−7	1.94372E−6	−1.15640E−9	2.81140E−11	0.02
SrO	Sr	0.11543	8.97031E−7	1.98280E−6	1.27050E−7	−8.46248E−10	0.07
	O	0.29201	−9.64426E−6	5.05839E−6	−3.20953E−8	2.10576E−10	0.01
NiO	Ni	0.10637	2.21722E−5	−7.15042E−8	3.92623E−8	−1.77838E−10	0.03
	O	0.21800	−8.29782E−6	1.93034E−6	−3.43445E−9	2.11463E−11	0.01

A good physical model uses as few fitting parameters as possible. In this sense, we prefer to use the SM and the eight-parameter BSM. But, for some compounds, the introduction of more parameters improves the agreement between the experimental and calculated values of the Debye–Waller *B* factors significantly, such as for the case of MgO. It should be noted that the shell models of lattice vibrations are only phenomenological descriptions of the lattice dynamics, and are desired to describe only certain aspects of the problem, *i.e.* the phonon-dispersion curves. It is therefore not surprising that our models of lattice dynamics cannot provide any better agreement between the calculated and experimentally measured values of the Debye–Waller *B* factors. It is also true that the correctness of a particular shell model cannot be judged from a single parameter, such as the Debye–Waller factor. For this reason, we have calculated the elastic constants C_{11}, C_{12} and C_{44} for different models and the results are listed in Table 4. These values may also be measured experimentally (Bruüesch, 1982),

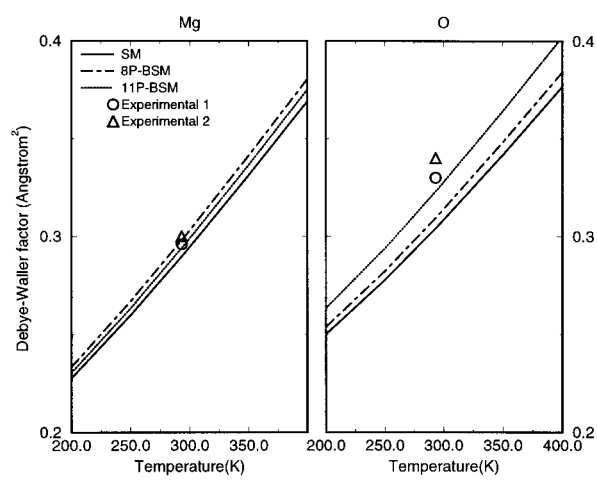

Fig. 5. Experimental and calculated Debye–Waller *B* factors for Mg^{2+} and O^{2-} ions in an MgO single crystal. In the figure, the experimentally measured data denoted by a circle was taken from Barron (1977) and that denoted by a triangle was taken from Lawrence (1973).

Table 11. *Polynomial regression form fitting parameters of the Debye–Waller factors using the rigid-shell model (80–1000 K)*

Crystal	Atom	a_0	a_1	a_2	a_3	a_4	ME (%)
KF	K	0.14377	0.00377	2.07709E−6	−2.24904E−9	8.76878E−13	0.69
	F	0.27078	0.00325	3.67564E−6	−3.92956E−9	1.51966E−12	0.85
KCl	K	0.14785	0.00576	2.17114E−6	−2.35821E−9	9.21219E−13	0.42
	Cl	0.16024	0.00505	2.32908E−6	−2.52463E−9	9.84989E−13	0.62
KBr	K	0.14886	0.00706	2.19775E−6	−2.39050E−9	9.34897E−13	0.44
	Br	0.07515	0.00694	1.12781E−6	−1.22937E−9	4.81227E−13	0.20
KI	K	0.15016	0.00846	2.22731E−6	−2.42420E−9	9.48418E−13	0.40
	I	0.04816	0.00855	7.30773E−7	−7.97959E−10	3.12625E−13	0.15
NaF	Na	0.21939	0.00185	2.94001E−6	−3.13550E−9	1.21078E−12	1.07
	F	0.24851	0.00142	3.16320E−6	−3.33552E−9	1.27845E−12	1.05
NaCl	Na	0.23697	0.00400	3.34701E−6	−3.60739E−9	1.40241E−12	0.80
	Cl	0.15738	0.00361	2.26025E−6	−2.44443E−9	9.52279E−13	0.66
NaBr	Na	0.24314	0.00528	3.49047E−6	−3.77211E−9	1.46856E−12	0.69
	Br	0.07503	0.00540	1.12691E−6	−1.22911E−9	4.81379E−13	0.34
NaI	Na	0.24787	0.00688	3.60939E−6	−3.91441E−9	1.52774E−12	0.57
	I	0.04801	0.00660	7.25951E−7	−7.92457E−10	3.10521E−13	0.20
RbF	Rb	0.06986	0.00493	1.05063E−6	−1.14791E−9	4.50367E−13	0.25
	F	0.27778	0.00424	3.83895E−6	−4.11836E−9	1.59598E−12	0.76
RbCl	Rb	0.07062	0.00704	1.06674E−6	−1.16663E−9	4.58178E−13	0.18
	Cl	0.16234	0.00633	2.37979E−6	−2.58448E−9	1.00955E−12	0.49
RbBr	Rb	0.07063	0.00802	1.06417E−6	−1.16142E−9	4.55122E−13	0.18
	Br	0.07543	0.00799	1.13864E−6	−1.24374E−9	4.87645E−13	0.19
RbI	Rb	0.07091	0.00988	1.07251E−6	−1.17207E−9	4.59833E−13	0.19
	I	0.04827	0.00998	7.37060E−7	−8.08304E−10	3.18073E−13	0.15
LiF	Li	0.53259	3.60678E−4	5.50697E−6	−5.54807E−9	2.06450E−12	0.97
	F	0.23269	7.34771E−4	2.83465E−6	−2.97266E−9	1.13748E−12	1.17
FeO	Fe	0.09430	0.00104	1.30465E−6	−1.40055E−9	5.43031E−13	0.88
	O	0.23128	4.06971E−4	2.37757E−6	−2.38960E−9	8.87672E−13	0.83
MnO	Mn	0.09671	0.00124	1.34224E−6	−1.44045E−9	5.58300E−13	1.12
	O	0.24239	4.87180E−4	2.61756E−6	−2.66264E−9	9.96897E−13	0.96
MgO	Mg	0.15477	1.07588E−4	1.62470E−6	−1.64208E−9	6.12347E−13	1.01
	O	0.19852	−2.02943E−5	1.72993E−6	−1.66655E−9	6.01300E−13	0.60
CaO	Ca	0.11673	5.27306E−4	1.48061E−6	−1.56131E−9	5.98580E−13	1.20
	O	0.23739	1.47667E−4	2.49606E−6	−2.52047E−9	9.38933E−13	1.00
SrO	Sr	0.06274	0.00111	8.94016E−7	−9.65292E−10	3.75626E−13	0.69
	O	0.25973	4.42280E−4	2.97163E−6	−3.06043E−9	1.15513E−12	1.15
NiO	Ni	0.08100	3.98311E−4	1.03962E−6	−1.09865E−9	4.21692E−13	1.22
	O	0.21013	7.52839E−5	1.94944E−6	−1.90952E−9	6.97203E−13	0.69

providing additional indicators for judging the goodness of the models of lattice vibrations. For general applications, we recommend the use of the model with the smallest standard error σ for fitting the experimentally measured phonon-dispersion curves. For more specific applications, the model may be chosen based on its agreement with experimental measurements of more relevant physical quantities, such as measured Debye–Waller factors in crystallography applications.

6. Concluding remarks

Both the rigid- and breathing-shell models have been used to investigate the lattice dynamics of ionic compounds with the sodium chloride structure and the model parameters are obtained by refining the calculated phonon frequencies against the experimentally measured phonon-dispersion curves using the technique of inelastic neutron scattering. Based on these models, Debye–Waller factors for these compounds are calculated for the temperature range 1 to 1000 K, where appropriate, and fitted analytically using polynomial regression form. The room-temperature (293 K) values of the Debye–Waller factors are compared with existing experimental values, and for most of the compounds studied the agreement between the experimental and calculated values of the room-temperature Debye–Waller factors is better than 10%. At lower temperatures, we would expect that the general agreement between the experimental measured and calculated Debye–Waller factors is better since the harmonic approximation works better at lower temperatures.

The authors are grateful to Professor J. C. H. Spence for advice and many useful discussions on electron diffraction, and to Professor J. B. Page for many useful discussions on lattice dynamics and for providing the original rigid-shell-model program. This work was

Table 12. *Experimental and calculated Debye–Waller B factors*

	Experimental			11p-BSM			8p-BSM			SM		
Crystal	B^+	B^-	$\overline{B}$	B^+	B^-	$\overline{B}$	B^+	B^-	$\overline{B}$	B^+	B^-	$\overline{B}$
CaO	0.35 (1)	0.44 (1)	0.38 (1)	0.368	0.442	0.389	0.367	0.436	0.387	0.366	0.442	0.388
MgO	0.37 (1)	0.33 (1)	0.35 (1)	0.295	0.325	0.307	0.299	0.311	0.304	0.291	0.305	0.296
SrO	0.43 (2)	1.93 (6)	0.66 (6)	0.490	0.612	0.509	0.468	0.598	0.488	0.447	0.580	0.468
KF	–	–	1.21 (2)	1.210	1.382	1.266	1.210	1.384	1.267	1.386	1.463	1.411
KCl	2.17 (1)	2.16 (1)	2.17 (1)	1.867	1.714	1.794	1.834	1.764	1.801	1.985	1.796	1.895
KBr	2.36 (4)	2.38 (4)	2.37 (6)	2.230	2.070	2.122	2.222	2.095	2.137	2.370	2.194	2.252
KI	3.52 (22)	2.80 (15)	2.97 (27)	2.660	2.416	2.473	2.638	2.441	2.487	2.785	2.616	2.656
LiF	1.05 (1)	0.65 (1)	0.76 (1)	0.954	0.638	0.722	0.973	0.627	0.720	0.994	0.630	0.727
NaF	0.91 (1)	0.91 (1)	0.91 (1)	0.923	0.825	0.879	0.881	0.876	0.879	0.952	0.869	0.914
NaCl	1.72 (2)	1.41 (1)	1.53 (2)	1.562	1.298	1.402	1.557	1.298	1.400	1.629	1.366	1.469
NaBr	1.55 (15)	1.14 (10)	1.23	2.061	1.642	1.736	2.066	1.632	1.729	2.022	1.738	1.801
NaI	2.63 (25)	1.81 (15)	1.94	2.577	1.891	1.996	2.541	1.885	1.986	2.506	2.040	2.111
RbF	–	–	1.40 (25)	1.444	1.693	1.489	1.499	1.714	1.538	1.591	1.772	1.624
RbCl	2.14 (7)	2.27 (7)	2.18 (10)	2.054	2.120	2.073	2.018	2.067	2.032	2.216	2.180	2.205
RbBr	–	–	2.34 (16)	2.348	2.287	2.318	2.412	2.226	2.322	2.504	2.505	2.504
RbI	–	–	3.36 (40)	2.886	2.625	2.730	2.864	2.525	2.661	3.052	3.038	3.044

supported by the Chinese Academy of Sciences, National Science Foundation of China, and NSF (grant 19425006).

References

Barron, T. (1977). *Acta Cryst.* A**33**, 602–604.

Bilz, H. & Kress, W. (1979). *Phonon Dispersion Relations in Insulators*. Berlin: Springer-Verlag.

Born, M. & Huang, K. (1954). *Dynamical Theory of Crystal Lattice*. Oxford University Press.

Bruüesch, P. (1982). *Phonons: Theory and Experiments I – Lattice Dynamics and Models of Interatomic Forces*. Berlin: Springer-Verlag.

Buhrer, W. (1970). *Phys. Status Solidi*, **41**, 789–795.

Butt, N., Bashir, J. & Khan, M. (1993). *Acta Cryst.* A**49**, 171–174.

Butt, N., Bashir, J. & Willis, B. (1988). *Acta Cryst.* A**44**, 396–398.

Cochran, W. (1959). *Proc. R. Soc. London Ser. A*, **253**, 260–276.

Cowley, J. (1993). *Electron Diffraction Techniques.* Oxford University Press.

Cowley, R., Cochran, W., Brockouse, B. & Woods, A. (1963). *Phys. Rev.* **131**, 1030–1039.

Cox, P. (1995). *Transition Metal OxiDesign*. Oxford: Clarendon Press.

Dick, B. & Overhauser, A. (1958). *Phys. Rev.* **112**, 90–103.

Dolling, G., Cowley, R., Schittenhelm, C. & Thorson, I. (1966). *Phys. Rev*. **147**, 577–582.

Dolling, G., Smith, H., Nicklow, R., Vijayarachavan, P. & Wilkinson, M. (1968). *Phys. Rev. B*, **168**, 970–979.

Gopi, N. & Sirdeshmukh, D. (1998). *Acta Cryst.* A**54**, 513–514.

Kellermann, E. (1940). *Philos. Trans. R. Soc. London*, **238**, 513–548.

Kugel, G., Carabatos, C., Hennion, B., Revcolevschi, A. & Tocchetti, D. (1977). *Phys. Rev. B*, **16**, 378–385.

Lawrence, J. (1973). *Acta Cryst.* A**29**, 94–95.

Nüsslein, V. & Schröder, U. (1967). *Phys. Status Solidi*, **21**, 309–314.

Peng, L.-M. (1999). In *Topics in Electron Diffraction and Microscopy of Materials*, edited by P. B. Hirsch. London: Institute of Physics.

Pettifor, D. (1995). *Bonding and Structures of Molecules and Solids*. Oxford University Press.

Poole, C. P., Farach, H. A. & Creswick, R. J. (1995). *Superconductivity*. New York: Academic Press.

Press, W. H., Flannery, B. P., Teukolsky, S. & Vetterling, W. (1986). *Numerical Recipes*. Cambridge University Press.

Raunio, G. & Rolandson, S. (1970*a*). *Phys. Rev. B*, **2**, 2098–2103.

Raunio, G. & Rolandson, S. (1970*b*). *Phys. Status Solidi*, **40**, 749–757.

Reichardt, W., Wagner, V. & Kress, W. (1975). *J. Phys. C*, **8**, 3955–3962.

Reid, J. (1987). *Comput. Phys. Commun.* **46**, 141–148.

Reid, J. & Smith, T. (1970). *Phys. Rev. B*, **1**, 1833–1844.

Rieder, K. & Migoni, R. (1975). *Phys. Rev. B*, **12**, 3374–3379.

Reider, K., Weinstein, B., Cardona, M. & Bilz, H. (1973). *Phys. Rev. B*, **8**, 4780–4786.

Rolanason, S. & Raunio, G. (1971). *J. Phys. C*, **4**, 958–965.

Ruyers, W. (1967). *Phys. Rev. B*, **153**, 923–930.

Sangster, M., Peckham, G. & Saunderson, D. (1970). *J. Phys. C*, **3**, 1026–1036.

Schröder, U. (1966). *Solid State Commun.* **4**, 347–349.

Wagner, V., Reichardt, W. & Kress, W. (1976). *Neutron Scattering*, **1**, 175–180.

Willis, B. & Pryor, A. (1975). *Thermal Vibrations in Crystallography*. Cambridge University Press.

Woods, A., Brockouse, B. & Cowley, R. (1963). *Phys. Rev*. **131**, 1025–1029.

Woods, A., Cochran, W. & Brockouse, B. (1960). *Phys. Rev.* **119**, 980–999.

Zuo, J., O'Keeffe, M., Rez, P. & Spence, J. (1997). *Phys. Rev. Lett.* **78**, 4777–4780.