References

GOLDBERG, S. Z., DUESLER, E. N. & RAYMOND, K. N. (1971). *Chem. Commun.* p. 826.
GOLDBERG, S. Z., DUESLER, E. N. & RAYMOND, K. N. (1971). *Inorg. Chem.* In the press.
HAMILTON, W. (1964). *Statistics in Physical Science*. New York: Ronald Press.
IBERS, J. A. (1971). *Acta Cryst.* **B27**, 250.
LEVY, H. A. (1956). *Acta Cryst.* **9**, 679.
LA PLACA, S. J. & IBERS, J. A. (1965). *Acta Cryst.* **18**, 511.
RAYMOND, K. N. & WENK, H. R. (1971). *Contr. Miner. Petrol.* **30**, 135.
SCHERINGER, C. (1963). *Acta Cryst.* **16**, 546.
STROUSE, C. E. (1970). *Acta Cryst.* **A26**, 604.
WENK, H. R. & RAYMOND, K. N. (1972). To be published.

Acta Cryst. (1972). **A28**, 164

Debye–Waller *B* Values of Some NaCl-Type Structures and Interionic Interaction

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Debye–Waller *B* values of NaCl, KCl, MgO and AgCl are calculated from lattice dynamics based on a a simple, rigid-ion type, interaction model. The parameters introduced in the model have intelligible significance. The present approach compares favourably with experimental evidence and previous physical calculations.

Introduction

The determination of Debye–Waller *B* values from X-ray and neutron-diffraction data is a problem not yet completely solved. Table 1 shows, chronologically, experimental room-temperature *B* values of NaCl. Large deviations, even between values determined most recently, indicate that these data are probably not the final ones. Various problems connected with experiment and data analysis have been amply discussed by several authors (Abrahams & Bernstein, 1965; Maslen, 1967; Göttlicher, 1968; Linkoaho, 1969). It seems that, at this moment, the most serious problem is evaluating the thermal diffuse scattering (TDS) contribution to observed intensities at the Bragg reflexions. Different authors use different simplified models to deduce the magnitude of the TDS corrections. The resulting change in average room-temperature NaCl Debye–Waller *B* values ranges from 0·04 to 0·20 Å^2 for single-crystal measurements and from 0·03 to 0·06 Å^2 for powder measurements, depending on experimental set-up and model used for calculations (Nilsson, 1957; Pryor, 1966; Suortti, 1967; Göttlicher, 1968).

Theoretical calculations of Debye–Waller *B* values for NaCl-type structures have been made for most of the interaction models in current use for lattice dynamical calculations. In the following, Debye–Waller *B* values of NaCl, KCl, MgO and AgCl are calculated from lattice dynamics employing a simple rigid-ion type interaction model. The results compare favourably with experimental evidence and previous calculations based on more complicated interaction models.

Interaction model

The interaction model, used for the present calculations, is essentially Kellerman's (1940) rigid-ion model but extended with second nearest-neighbour short-range interactions. The lattice dynamical calculations have been done using the Born von Kármán theory as presented by Maradudin, Montroll & Weiss (1963).

Like other models, the model is semi-empirical in in the sense that, lacking sufficient knowledge of interatomic forces, parameters need to be scaled with the aid of experimental information. The interaction is assumed to be pair-wise additive and is split into a long-range Coulomb part and a short-range part, not necessarily repulsive. The parameters of the model are:

1. The effective electric charge of the ions, *se*, where *e* is the elementary charge, determining the Coulomb interaction. Values of *se*, required for lattice dynamics, are closely comparable with Szigeti's (1950) effective charge used in his theory of dielectric constants.

2. First and second derivatives of the short-range pair-potentials, with respect to interionic distance, taken at equilibrium separation. Considering only first- and second-neighbour short-range interactions, then, for NaCl type structures, one is dealing with three different short-range interactions and, thus, six short-range parameters. These parameters, or force constants, are denoted by $\varphi'_{++}, \varphi''_{++}, \varphi'_{+-}, \varphi''_{+-}, \varphi'_{--}, \varphi''_{--}$, ($\varphi'_{++}$ being the first derivative of the potential between

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positive ions when all ions are in their equilibrium positions, and so on).

The above parameters are derived from the following experimental quantities: The frequencies of the transverse and longitudinal optical phonons for zero wave-vector, the three elastic constants C_{11}, C_{12}, C_{44} and the lattice constant. All data refer to the temperature at which predicted properties are required. For the atomic masses, the average isotopic masses of the elements in their natural isotopic abundances have been taken. Further, it has been assumed, from a consideration of the magnitudes of the ion radii (Pauling, 1960) and from quantum chemical calculations for NaCl and MgO carried out by Petterson, Vallin, Calais & Mansikka (1967) and Calais, Mansikka, Petterson & Vallin (1967), that owing to the relative smallness of the positive ions the short-range interaction between these ions may be neglected, *i.e.*, φ'_{++} and φ''_{++} both equal zero. In this approximation, the present model is essentially a five-parameter model.

Calculation specifications

Experimental data and the derived model parameters are given in Table 2. Among the experimental data, values of the longitudinal optical phonons are probably the least reliable. The inelastic neutron-scattering data for NaCl at 300°K of Schmunk & Winder (1970) exhibit considerable irregularities in the region of zero-wave-vector, where ω_{LO} has to be determined.

The value of ω_{LO} for zero-wave-vector $\mathbf{k}$ of MgO has not been measured but has been derived from ω_{TO}, the frequency of the transverse optical phonon at zero-wave-vector and dielectric data employing the Lyddane Sachs–Teller relation.

The model parameters were obtained by substituting experimental data in the solution of the dynamical equation around zerowave-vector. This solution can be obtained analytically; hence, the scaling procedure introduces no rounding or convergence errors. The parameters, obtained in this way, are shown in the right-hand part of Table 2.

Lattice dynamical calculations return the data used for their scaling within the precision of the calculations. It is noticed that the positive signs of φ'_{+-} for MgO and of φ'_{--} for KCl indicate short-range attraction instead of short-range repulsion between neighbouring Mg^{2+} and O^{2-} ions in MgO and Cl^- ions in KCl. We are tempted to interpret the short-range attraction of Mg^{2+} and O^{2-} as an indication that the lattice constant is determined by $O^{2-}-O^{2-}$ repulsion rather than the $Mg^{2+}-O^{2-}$ short-range repulsion, in agreement with considerations based on ionic radii. For KCl, the apparent $Cl^- - Cl^-$ short-range attraction may be due to neglect of short-range interaction between the positive ions.

In the other cases, the short-range interactions between negative ions are repulsive, in addition to their Coulomb repulsion. This agrees qualitatively with quantum-chemical calculations (Petterson *et al.*, 1967; Calais *et al.*, 1967).

Debye–Waller *B* values

Debye–Waller *B* values of NaCl, KCl, MgO and AgCl calculated according to the specifications given above, together with experimental and previous theoretical values, are shown in Table 3. Experimental Debye–Waller *B* values of NaCl at room temperature are given in Table 1.

A total number of 262 wave-vectors in the irreducible part of the Brillouin zone is included in the summations, while near the origin ($\mathbf{k}=0$) a finer mesh is employed. Estimated convergence errors, remaining after this procedure, range from 0·01 Å^2 for NaCl at 80°K to 0·04 Å^2 for AgCl at 300°K. Convergence errors increase with temperature (*cf.* in this connexion, Reid & Smith, 1970). Theoretical values of Buyers & Smith (1968) and Reid & Smith (1970) were obtained by interpolating their data. Models used by Buyers & Smith and Reid & Smith are versions of Karo & Hardy's (1963) deformation dipole model. Pryor (1966) and Sanger (1969) used a shell model of Woods, Cochran & Brockhouse (1960).

As far as comparison is possible, present values agree at least as well with experiment as do previously calculated ones. In this connexion, it should be realized that the model performs well for a variety of NaCl-type structures since MgO and AgCl are not alkali halides. The improvement is striking, if one compares the difference $B_+ - B_-$ of the individual Debye–Waller *B* values of the atoms. Most earlier calculations give too small a value for the difference between the Debye–Waller *B* values of the two atoms. In some cases, even

Table 1. *Experimental room-temperature B values of* NaCl

B_{Na}	B_{Cl}	Method	References
1·54 Å^2	1·25 Å^2	X-ray, single crystal	Waller & James (1927)
1·82	1·60	X-ray, single crystal	Brindley (1930)
1·25	1·12	X-ray, single crystal	von Renninger (1952)
1·25	1·00	X-ray, single crystal	Witte & Wölfel (1958)
1·29	1·15	X-ray, powder	Vihinen (1960)
1·63	1·42	Neutron, single crystal	Levy, Agron & Busing (1963)
1·639 ± 0·037	1·326 ± 0·023	X-ray, single crystal	Abrahams & Bernstein (1965)
1·84	1·44	X-ray, powder	Merisalo & Paakkari (1967)
1·89	1·61	X-ray, single crystal	Göttlicher (1968)
1·81 ± 0·03	1·49 ± 0·03	X-ray, powder	Linkoaho (1969)

the wrong sign of this quantity is found as compared with experiment. As has been realized by Cowley & Cowley (1966), this is due to the fact that only nearest-neighbour short-range interaction has been taken into account. In an accompanying paper (Huiszoon & Groenewegen, 1972), it is shown that at temperatures above the Debye temperature of the lattice, Debye–Waller B values no longer depend on the atomic masses and are determined solely by the interatomic forces. As a consequence, it follows for NaCl-type structures that if only nearest-neighbour interaction is taken into account, both types of atoms become equivalent from the lattice dynamical point of view and calculated Debye–Waller B values become equal, at $T \geq T_D$, a result already stated by Waller (1925). From the above it follows that interaction models including short-range interaction between nearest neighbours only will fail to account properly for the difference $B_+ - B_-$. When the atomic masses have become irrelevant for the B values, the heavier atoms do not necessarily have the smaller B values. Experiment indicates that this is indeed the case for MgO, KCl and AgCl. From the present calculations, this also follows for MgO and KCl. The result for AgCl, though slightly out of balance with experiment, is still considered quite encouraging.

Conclusion

The rigid-ion model, in combination with the present method of determining model parameters, appears to include sufficient essential features to predict Debye–Waller B values. The number and accessibility of the experimental data needed to scale the model may prove an asset to the model's applicability.*

Table 2. *Experimental quantities and derived model parameters*

Crystal	Temperature	Lattice constant	Reference	Frequencies of optical phonons (10^{13} rad.sec^{-1})		Reference	Elastic constants (10^{11} dyne.cm^{-1})			Reference	Short-range interaction force constants (10^2 dyne.cm^{-1})				
	(°K)	(Å)		ω_{LO}	ω_{TO}		C_{11}	C_{12}	C_{44}		s	φ'_{+-}/r_{+-}	φ''_{+-}	φ'_{--}/r_{--}	φ''_{--}
NaCl	80	5·598	1	4·98	3·25	5	5·744	1·200	1·335	10	0·706	−9·87	197	−1·76	32·7
NaCl	300	5·6411	1	4·93	3·08	6	4·947	1·288	1·287	10	0·730	−7·89	183	−4·02	30·6
KCl	115	6·24	2	4·01	2·76	2	4·60	0·58	0·653	2	0·742	−12·5	186	0·72	10·1
MgO	300	4·212	3	13·56	7·42	7,8	28·917	8·796	15·461	11	1·153	4·21	777	−14·9	267
AgCl	300	5·556	4	3·69	2·00	9	5·965	3·646	0·618	12	0·795	−28·0	216	−17·0	54·2

1. Pautamo (1963)
2. Copley, Macpherson & Timusk (1969)
3. Skinner (1957)
4. Donnay (1963)
5. Raunio, Almqvist & Stedman (1969)
6. Schmunk & Winder (1970)
7. Peckham (1967)
8. Buckland & Saunderson (1967)
9. Bottger & Geddes (1967)
10. Fugate & Schuele (1966)
11. Chung (1963)
12. Hinshaw, Lewis & Briscoe (1967)

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* Details of parameter calculations and FORTRAN lattice dynamical programs, both in unpolished form, are available on request.

References

ABRAHAMS, S. C. & BERNSTEIN, J. L. (1965). *Acta Cryst.* **18**, 926.

BOTTGER, G. L. & GEDDES, A. L. (1967). *J. Chem. Phys.* **46**, 3000.

BRINDLEY, G. W. (1930). *Phil. Mag.* **9**, 193.

BUCKLAND, R. J. & SAUNDERSON, D. H. (1967). Report AERE-R-5467. Atomic Energy Research Establishment, Harwell, Didcot, Berks. England.

BUYERS, W. J. L. & SMITH, T. (1968). *J. Phys. Chem. Solids*, **29**, 1051.

CALAIS, J. L., MANSIKKA, K., PETTERSON, G., VALLIN, J. (1967). *Preprint No.* 185, Quantum Chemistry Group, Uppsala, Sweden.

CHUNG, D. H. (1963). *Phil. Mag.* **8**, 833.

COPLEY, J. R. D., MACPHERSON, R. W. & TIMUSK, T. (1969). *Phys. Rev.* **182**, 965.

COWLEY, E. R. & COWLEY, R. A. (1966). *Proc. Roy. Soc.* **A292**, 209.

DONNAY, J. D. H. (1963). *Crystal Data*, ACA Monograph.

FUGATE, R. Q. & SCHUELE, D. E. (1966). *J. Phys. Chem. Solids*, **27**, 493.

Table 3. *Experimental and theoretical Debye–Waller B values*

Crystal	Temperature (°K)	Experimental B_+(Å^2)	B_-(Å^2)	Reference	Theoretical B_+(Å^2)	B_-(Å^2)	Reference
NaCl	80	0·62±0·06	0·41±0·06	1	0·55	0·43	Present work
		0·58±0·05	0·51±0·05	2	0·546	0·492	10
					0·536	0·437	11
NaCl	300	For experimental data see Table 1.			1·63	1·39	Present work
					1·643	1·602	10
					1·578	1·367	11
					1·63	1·59	12
					1·45	1·48	13
KCl	86	0·592		3	0·602*	0·561*	Present work
					0·824	0·853	14
	290	1·64		3	1·91*	1·73*	Present work
	293	1·92	1·78	4	2·62	2·68	14
	300	2·08	2·06	5			
	298	2·15	2·15	6			
MgO	300	0·35±0·01	0·31^5±0·01	7	0·355	0·28	Present work
		0·46±0·03	0·33^5±0·05	8	0·29	0·35	7
AgCl	300	2·20	2·09	9	2·13	2·15	Present work

* These data have been obtained from the model scaled with the aid of 115°K experimental quantities.

1. Merisalo & Paakkari (1967)
2. Linkoaho (1969)
3. James & Brindley (1928)
4. Wasastjerna (1946)
5. Patomäki & Linkoaho (1969)
6. Jayalakshmi & Viswamitra (1970)
7. Sanger (1969)
8. Raccah & Arnott (1967)
9. Korhonen & Linkoaho (1966)
10. Buyers & Smith (1968)
11. Reid & Smith (1970)
12. Pryor (1966)
13. Ratner (1958)
14. Copley *et al.* (1969)

GÖTTLICHER, S. (1968). *Acta Cryst.* **324**, 122.

HINSHAW, W., LEWIS, J. T. & BRISCOE, C. V. (1967). *Phys. Rev.* **163**, 876.

HUISZOON, C. & GROENEWEGEN, P. P. M. (1972). *Acta Cryst.* A**28**, 170.

JAMES, R. W. & BRINDLEY, G. W. (1928). *Proc. Roy. Soc.* A**122**, 155.

JAYALAKSHMI, K. & VISWAMITRA, M. A. (1970). *Phys. Letters*, **32**A, 83.

KARO, A. M. & HARDY, J. R. (1963). *Phys. Rev.* **129**, 2024.

KELLERMAN, E. W. (1940). *Phil. Trans.* A**238**, 513.

KORHONEN, U. & LINKOAHO, M. (1966). *Ann. Acad. Sci. Fenn.* A**VI**, No. 195.

LEVY, H. A., AGRON, P. A. & BUSING, W. R. (1963). Paper E-7, ACA Meeting, Cambridge, Mass.

LINKOAHO, M. V. (1969). *Acta Cryst.* A**25**, 450.

MARADUDIN, A. A., MONTROLL, E. W. & WEISS, G. (1963). *Theory of Lattice Dynamics in the Harmonic Approximation.* New York: Academic Press.

MASLEN, V. W. (1967). *Acta Cryst.* **23**, 907.

MERISALO, M. & PAAKKARI, T. (1967). *Acta Cryst.* **23**, 1107.

NILSSON, N. (1957). *Ark. Fysik*, **12**, 247.

PAULING, L. (1960). *The Nature of the Chemical Bond.* New York: Cornell Univ. Press.

PATOMÄKI, L. K. & LINKOAHO, M. V. (1969). *Acta Cryst.* A**25**, 304.

PAUTAMO, Y. (1963) *Ann. Acad. Sci. Fenn.* A**VI**, No. 129.

PECKHAM, G. (1967). *Proc. Phys. Soc.* **90**, 657.

PETTERSON, G. J., VALLIN, J., CALAIS, J. L. & MANSIKKA, K. (1967). *Ark. Fysik*, **34**, 371.

PRYOR, A. W. (1966). *Acta Cryst.* **20**, 138.

RACCAH, P. M. & ARNOTT, R. J. (1967). *Phys. Rev.* **153**, 1028.

RATNER, A. M. (1958). *Kristallografia*, **3**, 740.

RAUNIO, G., ALMQVIST, L. & STEDMAN, R. (1969). *Phys. Rev.* **178**, 1469.

REID, J. S. & SMITH, T. (1970). *J. Phys. Chem. Solids*, **31**, 2689.

RENNINGER, M. VON (1952). *Acta Cryst.* **5**, 711.

SANGER, P. L. (1969). *Acta Cryst.* A**25**, 694.

SCHMUNK, R. E. & WINDER, D. E. (1970), *J. Phys. Chem. Solids*, **31**, 131.

SKINNER, B. J. (1957). *Amer. Miner.* **42**, 39.

SUORTTI, P. (1967). *Ann. Acad. Sci. Fenn.* A**VI**, No. 240.

SZIGETI, B. (1950). *Proc. Roy. Soc.* A**204**, 51.

VIHINEN, S. (1960). *Ann. Acad. Sci. Fenn.* A**VI**, No. 51.

WALLER, I. (1925). Dissertation, p. 31. Uppsala.

WALLER, I. & JAMES, R. W. (1927). *Proc. Roy. Soc.* A**117**, 214.

WASASTJERNA, J. A. (1946). *Soc. Sci. Fenn. Comm. Phys. Math.* **13**, 1.

WITTE, H. & WÖLFEL, E. (1958). *Rev. Mod. Phys.* **30**, 51.

WOODS, A. D. B., COCHRAN, W. & BROCKHOUSE, B. N. (1960). *Phys. Rev.* **119**, 980.