

Table 3. *Observed and calculated temperature factors of NaCl*  
(Standard deviations are given in parentheses)

Temperature (°K)	$B_{\text{Na}}$ (Å <sup>2</sup> )	$B_{\text{Cl}}$ (Å <sup>2</sup> )	$\gamma/x^2$
4.2 Experiment	0.35 (0.08)	0.27 (0.04)	$\alpha$
Reid & Smith	0.40	0.30	$\gamma$
295 Experiment-TDS corr.	1.70 (0.10)	1.44 (0.03)	$\gamma^*$
Reid & Smith	1.56	1.35	

### Discussion

The observed  $B$  factors at 4.2°K are in approximate agreement with the theoretical values of Reid & Smith; on the other hand, at room temperature the observed values are higher than those given by the calculations but in better agreement with recent X-ray determinations (Table 1). Linkoaho (1969) has suggested that the discrepancy between observed and calculated  $B$  values is due to the difficulty in making a reliable correction for thermal diffuse scattering (the correction increases the values of the observed  $B$  factors). A further possibility is that the discrepancy between experimental and calculated  $B$  values stems from the neglect of anharmonicity in the lattice dynamical calculations. Third-order and fourth-order anharmonic terms are ignored in the theory, although experimental evidence for a fourth-order (quartic) term in the Debye-Waller factors of both NaCl (Butt & Sölt, 1971) and KCl (Sölt, Butt & O'Connor, 1973) has been obtained by using Mössbauer  $\gamma$ -ray diffraction.

If we examine the present results in the light of the anharmonic treatment of Willis (1969), the quartic anharmonic coefficient in the potential expansion

$$V = V_0 + \frac{1}{2}\alpha r^2 + \gamma r^4$$

[Willis, 1969, equation (4.8)] is as given in Table 4. The Table also includes corresponding values for KCl deduced by Willis (1969) and the anharmonic parameters for NaCl and KCl obtained by Viswamitra & Jayalakshmi (1972) from single-crystal X-ray diffraction measurements close to the melting points.

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### On the interpretation of anisotropic temperature factors. II. By C. SCHERINGER, *Institut für Kristallographie der Universität Karlsruhe, Germany (BRD)*\*

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A discussion of how the interatomic thermal coupling is expressed in the anisotropic temperature factors was given in a preceding paper. Here a further aspect of this question is treated.

In a preceding paper (Scheringer, 1972) we discussed how the interatomic thermal coupling is expressed in the anisotropic temperature factors although these factors do not contain explicit coupling terms. We gave a lattice-dynamical formulation of the anisotropic temperature factors which showed that the mean-square amplitude matrix of the atoms of the unit cell is proportional to the sum of the inverse dynamical matrices of the crystal. On inversion of

Table 4. *Potential parameters for NaCl and KCl*

	NaCl	KCl
$\gamma/x^2$	$-0.11 \cdot 10^{12} \text{ erg}^{-1}$	$-0.14 \cdot 10^{12} \text{ erg}^{-1}$
$\alpha$	$2.25 \cdot 10^{-12} \text{ erg Å}^{-2}$	$1.64 \cdot 10^{-12} \text{ erg Å}^{-2}$
$\gamma$	$-0.56 \cdot 10^{-12} \text{ erg Å}^{-4}$	$-0.38 \cdot 10^{-12} \text{ erg Å}^{-4}$
$\gamma^*$	$-0.99 \cdot 10^{-12} \text{ erg Å}^{-4}$	$-0.215 \cdot 10^{-12} \text{ erg Å}^{-4}$

\* Taken from Viswamitra & Jayalakshmi (1972).

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the dynamical matrices, the information which is contained in the off-diagonal blocks of these matrices is transferred into the diagonal blocks of the mean-square amplitude matrix. In the quoted paper, however, we did not take into account the fact that information on the interatomic coupling is also transferred into the mean-square amplitude matrix from the so-called 'self terms', which occur in the diagonal blocks of the dynamical matrices. The self terms also contain information on the interatomic interactions, and it is the purpose of this note to show how the self terms contribute to the anisotropic temperature factors.

The elements of the dynamical matrix of wave vector  $\mathbf{q}$

are given by

$$L_{ik}(\mathbf{q}, rr') = \sum_{l'} \varphi_{ik}(lr, l'r') \exp \{-i\mathbf{q} \cdot [\mathbf{X}(lr) - \mathbf{X}(l'r')]\}, \quad (1)$$

cf. e.g. Cochran & Cowley (1967).  $l, l'$  denote the cells in the crystal;  $r, r'$  the atoms in the cell; and  $i, k = 1, 2, 3$  the directions of space.  $\mathbf{X}(lr)$  is the position vector of the atom  $lr$  in the crystal.  $\varphi_{ik}(lr, l'r')$  are the interatomic force constants. They describe the force which is exerted on the atom  $lr$  in the direction  $i$  when the atom  $l'r'$  is displaced by unit length in the direction  $k$ . Since the interatomic forces imply 'interactions' among the atoms we regard non-zero values of the force constants as expressing interactions between the two respective atoms. The  $3 \times 3$  diagonal blocks of the dynamical matrices represent the elements for the case  $r' = r$ . The force constants in these elements usually refer to the cases  $l' \neq l$ , i.e. to interactions of different atoms within a Bravais array. However, once a term arises in the sum of equation (1) for which  $l' = l$  then this is called the 'self term'. The constant  $\varphi_{ik}(lr, lr)$  describes the force which the atom  $lr$  exerts on itself in the direction  $i$  when it is displaced by unit length in the direction  $k$ . This force is established by the fact that, in the crystal at rest, all atoms  $l'r'$  exert counter forces on the atom  $lr$  when this is displaced in the crystal. Hence the expression for the self terms can be derived from the condition of translation invariance of the crystal. According to Martin (1971) we obtain

$$\frac{1}{2}[\varphi_{ik}(lr, lr) + \varphi_{ki}(lr, lr)] = - \sum_{l'r'}' \varphi_{ik}(lr, l'r'). \quad (2)$$

The summation contains only terms with  $l'r' \neq lr$ . Obviously the left-hand side of equation (2) is symmetric in  $i$  and  $k$  and hence the right-hand side must also be symmetric. When the self terms are calculated from equation (2) only those constants  $\varphi_{ik}(lr, lr)$  are physically acceptable which are symmetric in  $i$  and  $k$ . This guarantees that the dynamical matrices are hermitian. Since in equation (2) the sum is taken over all interactions with indices  $l'r'$  the self terms  $\varphi_{ik}(lr, lr)$  can be regarded as representing interactions of the atom  $lr$  with all other atoms in the crystal.

Now, how much weight do the self terms have in the elements of the dynamical matrices? In order to see this we write down the diagonal elements of the dynamical matrices, insert equation (2) into equation (1) and thus obtain

$$L_{ik}(\mathbf{q}, rr) = \sum_{l'}' \varphi_{ik}(lr, l'r) \{ \exp(-i\mathbf{q} \cdot [\mathbf{X}(lr) - \mathbf{X}(l'r)]) - 1 \} - \sum_{r' \neq r} \sum_{l'}' \varphi_{ik}(lr, l'r'). \quad (3)$$

The first sum in equation (3) arises from the self term and the other terms for which  $l' \neq l$ , whereas the second sum is due only to the self term. The role of the self term in equation (3) depends on the magnitude  $|\mathbf{q}| = q$  of the wave vector and on the dimensions of the unit cell. For small values of  $q$  the exponential factor is nearly unity and thus the first sum nearly vanishes so that the diagonal blocks  $L_{ik}(\mathbf{q}, rr)$  are almost exclusively determined by the self terms. The magnitude of the unit cell enters into equation (3) in the following way. The terms in the first sum refer only to interactions of atoms which belong to the same Bravais array. The magnitudes of the interatomic force constants decrease with increasing distance between the respective atoms; hence the terms in the first sum of equation (3) decrease with growing cell dimensions. The second sum of equation (3), on the other hand, contains terms which refer to interactions of different atoms within one unit cell. Large cells contain many atoms and thus there will be several terms with larger magnitudes of the force constants. Thus for long waves and large unit cells the second sum in equation (3), which arises only from the self term, will govern the diagonal blocks of the dynamical matrices. The influence of the self terms on the atomic vibration tensors follows from the fact that the diagonal elements of the dynamical matrices play an important part in the calculation of the elements of the inverse dynamical matrices and thus, with equations (10) and (15) of Scheringer (1972), contribute to the atomic vibration tensors in the corresponding manner.

We conclude that the interatomic thermal coupling enters into the atomic vibration tensors in two ways. On the one hand, the interactions, which are expressed in the off-diagonal elements of the dynamical matrices, are transferred into the diagonal blocks of the inverse dynamical matrices by the mechanism of the matrix inversion; on the other hand, the interactions, which are expressed by the self terms and are contained in the diagonal blocks of the dynamical matrices, are also transferred into the diagonal blocks of the inverse dynamical matrices.

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