

## SHORT COMMUNICATIONS

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*Acta Cryst.* (1981). A37, 264–266

**On the X-ray or neutron diffraction determination of atomic position parameters.** By S. L. MAIR and S. W. WILKINS, *CSIRO Division of Chemical Physics, PO Box 160, Clayton, Victoria, Australia 3168*

(Received 18 January 1980; accepted 16 September 1980)

### Abstract

It is shown that, unless the atomic position parameters in a crystal are completely determined by symmetry, the position parameters corresponding to the minimum of the potential in the thermally strained lattice differ from those corresponding to thermodynamic equilibrium. By appropriate refinement of X-ray or neutron diffraction data, it is possible to obtain both sets of position parameters as well as the linear and higher-order coefficients of one-particle potentials expanded about the equilibrium positions.

In the conventional analysis of crystal structure factors obtained from elastic X-ray or neutron scattering data, the time-averaged distribution of scattering material is represented as a superposition of independent atom-like distributions referred to certain nuclear positions. There appears to be some confusion in the literature as to what these positions represent. They are frequently assumed to be the thermodynamic equilibrium positions,  $\mathbf{r}_j^{(e)}(T)$ , of the  $J$ th atom (where  $J = l\kappa$  refers to the  $\kappa$ th atom in the  $l$ th unit cell) at the temperature of measurement,  $T$  (see, for example, Born, 1942–3).

For a finite system, the thermodynamic equilibrium positions,  $\mathbf{r}_j^{(e)}(T)$ , are defined (see, for example, Liebfried & Ludwig, 1961) as the values of  $\mathbf{r}_j$  which minimize the Helmholtz energy,  $A$ , viz

$$\frac{\partial A(\{\mathbf{r}_j\}; T)}{\partial r_{j\alpha}} = 0 \quad \text{for all } J, \alpha, \quad (1)$$

where  $r_{j\alpha}$  is the  $\alpha$ th Cartesian component of  $\mathbf{r}_j$ . It may be shown (e.g. Liebfried & Ludwig, 1961, p. 316) that the  $\mathbf{r}_j^{(e)}$  determined by (1) are in fact the ensemble-averaged positions of the atoms, i.e.

$$\mathbf{r}_j^{(e)} = \langle \mathbf{r}_j \rangle = \text{tr}(\mathbf{r}_j \rho) / \text{tr}(\rho), \quad (2)$$

where  $\rho$  is the appropriate statistical mechanical density operator. By the ergodic hypothesis, one may also assume the  $\langle \mathbf{r}_j \rangle$  to equal the time-averaged position of the  $J$ th atom in the unit cell.

For a crystal with  $s$  atoms in the unit cell, the conditions (1) may be written in equivalent form as

$$\frac{\partial A(\{\mathbf{r}_\kappa\}; \mathbf{g}, T)}{\partial r_{\kappa\alpha}} = 0 \quad \text{for } \kappa = 1, \dots, (s-1) \text{ and all } \alpha, \quad (3a)$$

together with the condition

$$\frac{\partial A(\{\mathbf{r}_\kappa\}; \mathbf{g}, T)}{\partial g_{\alpha\beta}} = 0 \quad \text{for all } \alpha, \beta, \quad (3b)$$

which determines the unit cell of the thermally strained lattice with metrical coefficients  $g_{\alpha\beta} = \mathbf{a}_\alpha \cdot \mathbf{a}_\beta$ . For a general strain a maximum of six components of  $\mathbf{g}$  must be considered (see Freese & Döring, 1979; Segmüller, 1964).

The equilibrium or time-averaged positions,  $\mathbf{r}_\kappa^{(e)}(T)$ , are, in general, different from the corresponding positions,  $\mathbf{r}_\kappa^{(m)}(T)$ , defining the minimum potential energy configuration in the thermally strained lattice, viz the solutions for  $\{\mathbf{r}_\kappa\}$  such that

$$\frac{\partial \Phi(\{\mathbf{r}_\kappa\}; \mathbf{g})}{\partial r_{\kappa\alpha}} = 0, \quad \text{for } \kappa = 1, \dots, (s-1) \text{ and all } \alpha, \quad (4)$$

where  $\Phi(\{\mathbf{r}_\kappa\}; \mathbf{g})$  is the potential energy of the strained crystal.

That  $\mathbf{r}_\kappa^{(e)}$  and  $\mathbf{r}_\kappa^{(m)}$  need not necessarily be equal may be inferred from the standard statistical mechanical relation

$$A(\{\mathbf{r}_\kappa\}; \mathbf{g}, T) = \Phi(\{\mathbf{r}_\kappa\}; \mathbf{g}) + U_v(\{\mathbf{r}_\kappa\}; \mathbf{g}, T) - TS(\{\mathbf{r}_\kappa\}; \mathbf{g}, T), \quad (5)$$

where  $S$  is the vibrational entropy of the crystal and  $U_v(\{\mathbf{r}_\kappa\}; \mathbf{g}, T)$  is the vibrational energy which, in general, does not go to zero at 0 K. However,  $\mathbf{r}_\kappa^{(e)}$  necessarily equals  $\mathbf{r}_\kappa^{(m)}$  when atoms are on sites for which the position parameters are completely determined by symmetry (type I sites), because then the condition

$$\left( \frac{J}{\alpha} \right) \equiv \frac{\partial \Phi}{\partial r_{J\alpha}} \Big|_{\mathbf{r}_j = \mathbf{r}_j^{(e)}} = 0 \quad (6)$$

is enforced by symmetry (see Liebfried & Ludwig, 1961), and  $\mathbf{r}_j^{(e)} = \mathbf{r}_j^{(m)}$ . For all other sites (type II),  $\mathbf{r}_j^{(e)} \neq \mathbf{r}_j^{(m)}$  in general,

and it transpires that such sites necessarily belong to one of 10 point-group symmetries, namely:

$$1, m, 2, mm2, 3, 3m, 4, 4mm, 6, 6mm.$$

They are the symmetries listed by Stewart (1976) as possessing non-vanishing atomic dipole components. That these are the only point groups possessed by type II sites may be verified by inspection of *International Tables for X-ray Crystallography* (1952), or by arguments used by Lax (1974) to define the crystal classes which can exhibit ferro-electricity.

To understand which positions one obtains from an analysis of X-ray or neutron diffraction data, it is helpful to write the Debye-Waller factor (DWF) in terms of the potential energy  $\Phi$ . We begin by making a Taylor expansion of  $\Phi$  about the  $\mathbf{r}_J^{(e)}(T)$  (Born & Huang, 1954), *viz*

$$\begin{aligned} \Phi(\{\mathbf{u}\}) = & \Phi_0 + \sum_{\alpha} \Phi \left( \begin{matrix} J \\ \alpha \end{matrix} \right) u_{J\alpha} + \frac{1}{2} \sum_{\alpha\beta} \Phi \left( \begin{matrix} JJ' \\ \alpha\beta \end{matrix} \right) u_{J\alpha} u_{J'\beta} \\ & + \frac{1}{6} \sum_{\alpha\beta\gamma} \Phi \left( \begin{matrix} JJ' J'' \\ \alpha\beta\gamma \end{matrix} \right) u_{J\alpha} u_{J'\beta} u_{J''\gamma} + \dots, \end{aligned} \quad (7)$$

where  $\mathbf{u}_J = \mathbf{r}_J - \mathbf{r}_J^{(e)}$  are small nuclear displacements from the reference positions,  $\mathbf{r}_J^{(e)}$  (see Fig. 1). The full anharmonic DWF for the  $J$ th atom in this coordinate system is then

$$\begin{aligned} e^{-M_J} = & \langle e^{i\mathbf{k}\cdot\mathbf{u}_J} \rangle \\ = & \text{tr}(e^{-\beta\Phi(\{\mathbf{u}\})} e^{i\mathbf{k}\cdot\mathbf{u}_J}) / \text{tr} e^{-\beta\Phi(\{\mathbf{u}\})}, \end{aligned} \quad (8)$$

where  $\beta = 1/(k_B T)$ , with  $k_B$  the Boltzmann constant and  $\mathbf{k}$  the scattering vector.

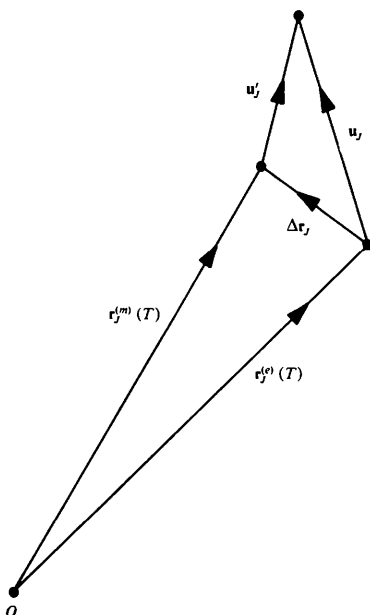


Fig. 1. Vector diagram illustrating  $\mathbf{r}_J^{(e)}$ ,  $\mathbf{r}_J^{(m)}$  and displacements  $\mathbf{u}_J$ ,  $\mathbf{u}_J'$  for atom  $J$ .

By a shift  $\Delta\mathbf{r}_J = \mathbf{r}_J^{(e)} - \mathbf{r}_J^{(m)}$  in the reference position, (7) can be re-written as an expansion about the  $\mathbf{r}_J^{(m)}$ , *viz*

$$\begin{aligned} \Phi'(\{\mathbf{u}'\}) = & \Phi'_0 + \frac{1}{2} \sum_{\alpha\beta} \Phi' \left( \begin{matrix} JJ' \\ \alpha\beta \end{matrix} \right) u'_{J\alpha} u'_{J'\beta} \\ & + \frac{1}{6} \sum_{\alpha\beta\gamma} \Phi' \left( \begin{matrix} JJ' J'' \\ \alpha\beta\gamma \end{matrix} \right) u'_{J\alpha} u'_{J'\beta} u'_{J''\gamma} + \dots, \end{aligned} \quad (9)$$

where  $\mathbf{u}'_J = \mathbf{r}_J - \mathbf{r}_J^{(m)} = \mathbf{u}_J + \Delta\mathbf{r}_J$ . Unlike (7), (9) has no linear term in the displacements. The original coefficients

$$\left[ \Phi_0, \Phi \left( \begin{matrix} J \\ \alpha \end{matrix} \right), \Phi \left( \begin{matrix} JJ' \\ \alpha\beta \end{matrix} \right), \Phi \left( \begin{matrix} JJ' J'' \\ \alpha\beta\gamma \end{matrix} \right), \dots \right]$$

may be expressed in terms of the new coefficients

$$\left[ \Phi'_0, \Phi' \left( \begin{matrix} JJ' \\ \alpha\beta \end{matrix} \right), \Phi' \left( \begin{matrix} JJ' J'' \\ \alpha\beta\gamma \end{matrix} \right), \dots \right]$$

as polynomials in  $\Delta\mathbf{r}_{J\alpha}$ . Substitution of (9) in (8) gives the DWF as

$$e^{-M_J} = e^{-i\mathbf{k}\cdot\Delta\mathbf{r}_J} \text{tr}[e^{-\beta\Phi'(\{\mathbf{u}'\})} e^{i\mathbf{k}\cdot\mathbf{u}'_J}] / \text{tr} e^{-\beta\Phi'(\{\mathbf{u}'\})}. \quad (10)$$

Examination of (7) to (10) shows that it is not possible to refine simultaneously both for the effect of the linear coefficient  $\Phi \left( \begin{matrix} J \\ \alpha \end{matrix} \right)$  in the DWF and for the equilibrium

position, since one can always apply the transformation leading from (7) to (9) and hence reduce the number of parameters (*cf.* Whiteley, Moss & Barnea, 1978, where the number of parameters considered for a wurtzite structure could have been reduced by two). It follows that a refinement using a full anharmonic DWF (assuming exact knowledge of the atomic scattering factor) leads to positions  $\mathbf{r}_J^{(m)}$  defining the minimum of the full many-body potential for the thermally strained lattice.

If, on the other hand, the DWF is omitted in a refinement of the data, the phase factor  $e^{-i\mathbf{k}\cdot\Delta\mathbf{r}_J}$  does not occur and one might expect the refined positions to approximate closely the equilibrium or mean positions,  $\mathbf{r}_J^{(e)}$ , of the atoms. (The same effect would be obtained if the terms odd in the displacements were omitted from the DWF.)

Because the DWF cannot reveal information on correlations between the motions of the various atoms, it is not possible to obtain separately the coefficients of the full many-body potential; however (see, for example, Dawson, Hurley & Maslen, 1967; Mair, 1980), the individual coefficients of effective one-particle potentials (OPP's) may be obtained

$$\left[ \text{i.e. } \Phi'_{\text{OPP}} \left( \begin{matrix} J \\ \alpha\beta \end{matrix} \right), \Phi'_{\text{OPP}} \left( \begin{matrix} J \\ \alpha\beta\gamma \end{matrix} \right), \text{ etc.} \right].$$

To relate these coefficients to those of corresponding OPP's expanded about the equilibrium positions

$$\left[ \text{i.e. } \Phi_{\text{OPP}} \left( \begin{matrix} J \\ \alpha \end{matrix} \right), \Phi_{\text{OPP}} \left( \begin{matrix} J \\ \alpha\beta \end{matrix} \right), \Phi_{\text{OPP}} \left( \begin{matrix} J \\ \alpha\beta\gamma \end{matrix} \right), \dots \right],$$

the only additional information required is the  $\Delta\mathbf{r}_J$ , which may be obtained by calculating  $\mathbf{r}_J^{(e)}$  from the  $\Phi'_{\text{OPP}}$  coefficients using (2).

The magnitude of the  $\Delta r_j$  for a particular system will depend on the anharmonicity present and on the symmetry at the atomic sites concerned. For example, in CdS, which has the rather highly symmetric wurtzite structure, the sum of the  $\Delta r_j$  for adjacent Cd and S atoms, as measured by the change in the structural parameter for the equilibrium and minimum energy configurations, is 0.0019 Å at room temperature (Barnea & Stevenson, 1980). This represents a significant change in the structural parameter, of magnitude three times its standard deviation. In a less highly symmetric system undergoing large thermal vibrations the  $\Delta r_j$  will be correspondingly higher.

An important consequence of the measurability of  $r_j^{(e)}$  for ionic crystals is that a series of measurements as a function of temperature will provide the temperature-dependence of the rigid-ion contribution to the primary pyro-electric coefficient,  $p_a^{(1)}$  (see, for example, Mair & Barnea, 1975), which is given by

$$p_a^{(1)} = \frac{1}{V} \sum_{\kappa=1}^s q_{\kappa} \frac{\partial r_{\kappa a}^{(e)}}{\partial T} - p_a^{(2)}. \quad (11)$$

Here  $q_{\kappa}$  is the charge associated with the  $\kappa$ th ion (assumed to be independent of  $T$ ),  $V$  is the volume of the unit cell, and  $p_a^{(2)}$  is the secondary pyro-electric coefficient, which can be calculated from thermal expansion data.

We conclude that, if the full Debye–Waller factor is used, the reference positions obtained from an X-ray or neutron diffraction analysis are the positions  $r_j^{(m)}$  defining the minimum of the potential energy in the deformed lattice. If no Debye–Waller factor, or a conventional harmonic Debye–Waller factor, is used, one might expect the positions obtained to correspond closely to the equilibrium or mean positions of the atoms,  $\langle r_j \rangle = r_j^{(e)}$ . For sites fully determined by symmetry, we have the further condition that  $r_j^{(m)} = r_j^{(e)}$ .

If a refinement with the full Debye–Waller factor is made,

both  $r_j^{(m)}$  and  $r_j^{(e)}$  can be obtained, and the linear and higher-order coefficients of the one-particle potentials, expanded about the equilibrium positions, may then be deduced. If the crystal is ionic, measurements of  $r_j^{(m)}$  and  $r_j^{(e)}$  against temperature enable one to obtain the pyro-electric coefficient in the rigid-ion approximation.

We are grateful to Drs A. Hurley, V. Maslen and J. Tibballs for helpful comments, and to Drs Z. Barnea and A. Stevenson for their results on CdS before publication.

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*Acta Cryst.* (1981). **A37**, 266

**A new structural principle in anion-excess fluorite-related superlattices: erratum.** By D. J. M. BEVAN, *School of Physical Sciences, Flinders University, Bedford Park, South Australia 5042*, O. GREIS, *Mineralogisch-Petrographisches Institut der Universität, D-6900 Heidelberg, Federal Republic of Germany* and J. STRÄHLE, *Institut für Anorganische Chemie der Universität, D-7400 Tübingen, Federal Republic of Germany*

(Received 16 December 1980)

#### Abstract

Fig. 1 of Bevan, Greis & Strähle [*Acta Cryst.* (1980), **A36**, 889–890] has been printed upside-down. The legend is correct.

All information is given in the *Abstract*.