ture by use of a neutron powder diffraction data set is in progress.

The structure of Li_2WO_4(iii) (Wilhelmi, Waltersson & Löfgren, 1977) was derived from single-crystal X-ray diffraction data. The Li positions (16 in the unit cell) were not determined. There are three minima in the maps giving altogether 16 locations in the unit cell (see Table 1).

The three minima result in short Li—Li separations (*e.g.* *B–B* 2·15 Å). Therefore, the influence on the minimum positions of the symmetry function described above was examined. The new positions thus obtained all result in acceptable Li—O coordinations and Li—Li distances (*e.g.* *B–B* 2·57 Å) (see also Table 1). Therefore, the 16 atoms in the unit cell are assumed to be situated in:

		x	*y*	*z*
A	4(*e*)	0	0	0·17
B	4(*f*)	0	$\frac{1}{2}$	0·39
C	8(*h*)	0·00	0·24	0·29.

This method gives information about all the potential LiO_4 and LiO_6 polyhedra in a given oxygen matrix. The most probable Li sites may be indicated by the Li—O and Li—Li separations among alternative suggestions. No other types of Li coordinations than LiO_4 and LiO_6 polyhedra have been tested.

The conclusion is that this method may be useful as a tool for determining Li positions in the presence of heavy atoms in crystal structures derived from X-ray diffraction data sets. The accuracy in the Li coordinates is comparable to that obtained by locating atomic positions from Fourier maps.

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References

BAUR, W. H. (1972). *Acta Cryst.* B**28**, 1456–1465.

BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* A**29**, 266–282.

DONNAY, G. (1972). *Acta Cryst.* A**28**, S108.

DONNAY, G. & ALLMAN, R. (1970). *Am. Mineral.* **55**, 1003–1015.

ÉMIRALIEV, A., KOCHAROV, A. G., YAMZIN, I. I. & LYUBIMTSEV, V. A. (1973). *Kristallografiya*, **18**, 1177–1181.

HÜLLEN, A. (1966). *Ber. Bunsenges. Phys. Chem.* **70**, 598–606.

JACOBSON, A. J., COLLINS, B. M. & FENDER, B. E. F. (1974). *Acta Cryst.* B**30**, 1705–1711.

LUNDBERG, M. (1971). *Acta Chem. Scand.* **25**, 3337–3346.

PAULING, L. (1927). *J. Am. Chem. Soc.* **49**, 765–790.

PAULING, L. (1947). *J. Am. Chem. Soc.* **69**, 542–553.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 548. Ithaca: Cornell Univ. Press.

SEQUEIRA, A., BERNAL, I., BROWN, I. D. & FAGGIANI, R. (1975). *Acta Cryst.* B**31**, 1735–1739.

SHANNON, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

TELLGREN, R. & LIMINGA, R. (1972). *J. Solid State Chem.* **4**, 255–261.

THOMAS, J., TELLGREN, R. & ALMLÖF, J. (1975). *Acta Cryst.* B**31**, 1946–1955.

WALTERSSON, K., WERNER, P.-E., & WILHELMI, K.-A. (1977*a*). *Cryst. Struct. Commun.* **6**, 225–230.

WALTERSSON, K., WERNER, P.-E., & WILHELMI, K.-A. (1977*b*). *Cryst. Struct. Commun.* **6**, 231–235.

WILHELMI, K.-A., WALTERSSON, K. & LÖFGREN, P. (1977). *Cryst. Struct. Commun.* **6**, 219–223.

ZACHARIASEN, W. H. & PLETTINGER, H. A. (1961). *Acta Cryst.* **14**, 229–230.

Acta Cryst. (1978). A**34**, 905–908

Dynamic Density and Structure Factors for Rigid Molecules with Large Librations

BY C. SCHERINGER

Institut für Mineralogie der Universität Marburg, D 3550 *Marburg/Lahn, Federal Republic of Germany*

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For rigid molecules which undergo large librations, the dynamic density and the dynamic molecular scattering factor are derived. The general case is treated where translations and librations of the molecule are coupled (no site symmetry). The dynamic molecular scattering factor is an integral which cannot generally be solved, and temperature factors generally do not appear. For the special case of statistically independent translations and librations, a temperature factor for the translations of the molecule is obtained. Moreover, temperature factors are obtained for density units which are spherically symmetric, since the motions of these density units can be described by translations only. The possible cases for which spherically symmetric density units can be assumed and, hence, temperature factors can be applied, are discussed.

Introduction

With the study of electron density distributions in molecular crystals by means of diffraction methods, an accurate description of the thermal vibrations of the molecules is important. Difficulties are primarily presented by large librations, since, with them, the nuclei cannot be considered to move along a straight line, and thus the harmonic approximation of the nuclear motions cannot be applied. The effects of large librations on the density distribution in molecules and possible ways of calculating structure factors are discussed (along with other problems) by Ruysink & Vos (1974), Bats & Feil (1977) and Stevens, Rys & Coppens (1977) (hereafter referred to as SRC). The structure factors were calculated from the dynamic density of the molecule (by Fourier transformation); the dynamic density is obtained by convolution of the static density and the thermal smearing function for rigid-body motions. In the cited papers, the convolution integral for large librations was not correctly established. Furthermore, it was assumed that translations and librations of the molecule are statistically independent; but this does not hold for molecules without site symmetry $\bar{1}$. In this paper we first establish the convolution integral for the general case of coupled translations and librations, and then derive the dynamic scattering factor for the molecule and, hence, the structure factor. It will be seen that temperature factors generally do not appear. We shall show that temperature factors are obtained if the density distribution in the molecule is (at least partially) expressed by density units of spherical symmetry. The possible applications of temperature factors for large librations of molecules will be discussed at the end of the paper.

Dynamic density and dynamic molecular scattering factor

The dynamic density is the average of all instantaneous densities which arise with the thermal motions of the molecules in the crystal. This average is normally described by the convolution integral

$$\rho(\mathbf{x})_{\text{dyn}} = \int_{-\infty}^{+\infty} \rho(\mathbf{x}-\mathbf{u})_{\text{stat}} P(\mathbf{u})\, d\mathbf{u}, \qquad (1)$$

where $\mathbf{u}$ is the thermal-displacement vector at the position $\mathbf{x}$, and $P(\mathbf{u})$ the probability density function (p.d.f.) of $\mathbf{u}$. The Fourier transform of $P(\mathbf{u})$ is the temperature factor for the static density $\rho(\mathbf{x})_{\text{stat}}$. (1) means geometrically that, with a displacement of ρ_{stat} by $\mathbf{u}$, the point at $\mathbf{x}-\mathbf{u}$ comes to lie on the position $\mathbf{x}$, *i.e.* ρ_{stat} is only translated and not rotated. This situation is also assumed in the standard lattice-dynamical derivations of the temperature factor. The thermal average is formed over the displacement vectors of the scattering units. The Fourier transforms of the scattering units (*i.e.* normally the scattering factors of the atoms) are not contained in the thermal average; this means that their orientation is considered to be the same for all thermal configurations. Thus, it is obvious that (1) is not suitable for treating the case of large librations, since the inherent assumption that ρ_{stat} is not rotated will no longer be valid.*

For the case of large librations, the formation of the thermal average has to be rethought. Firstly, we choose a fixed origin in the molecule and consider the displacement vector $\mathbf{u}_{\text{lib}}$ at the position $\mathbf{x}$ (see Fig. 1). Then we have, as usual (Schomaker & Trueblood, 1968; SRC; Scheringer, 1978),

$$\mathbf{u}_{\text{lib}} = \mathbf{D}\mathbf{x} \qquad (2)$$

and further, with SRC

$$\mathbf{R} = \mathbf{E} + \mathbf{D}, \quad \mathbf{R}\mathbf{x} = \mathbf{x} + \mathbf{u}_{\text{lib}}, \quad \mathbf{R}^{-1} = \mathbf{R}^{T}, \qquad (3)$$

where $\mathbf{E}$ is the unit matrix and $\mathbf{D}$ and $\mathbf{R}$ are functions of the librations $\boldsymbol{\omega}$. We must now establish which point of the molecule coincides with point $\mathbf{x}$ for a rotation $\boldsymbol{\omega}$ and a translation $\mathbf{t}$ of the molecule. This point then contributes $P(\mathbf{t},\boldsymbol{\omega})\, d\mathbf{t}\, d\boldsymbol{\omega}$ to the thermal average. As can be seen from Fig. 1, this point is located at position $Q = \mathbf{R}^{-1}(\mathbf{x}-\mathbf{t})$, and the original point $\mathbf{x}$ is transferred to position $P = \mathbf{R}\mathbf{x} + \mathbf{t}$. Thus we obtain for the average density, *i.e.* for the dynamic density with rigid-body motions,

$$\rho(\mathbf{x})_{\text{dyn}} = \iint_{-\infty}^{\infty} \rho[\mathbf{R}^{-1}(\mathbf{x}-\mathbf{t})]_{\text{stat}} P(\mathbf{t},\boldsymbol{\omega})\, d\mathbf{t}\, d\boldsymbol{\omega}. \qquad (4)$$

Note that the real integration limits for $\boldsymbol{\omega}$ are $-\pi$ and π; but this does not matter in practice. In a general crystal metric, $\mathbf{R}$ is not orthogonal and the formulation with $\mathbf{R}^{-1}$ in (4) (instead of $\mathbf{R}^{T}$) is then relevant.

The errors which were made in the quoted papers can easily be detected by means of Fig. 1. Ruysink & Vos [1974, equation (18)]† and Bats & Feil [1977, equation (3)] used (1) with $\mathbf{u} = \mathbf{t} + \mathbf{u}_{\text{lib}} = \mathbf{t} + \mathbf{D}\mathbf{x}$. This would mean that, with a rotation $\boldsymbol{\omega}$, the point $Q'' = -\mathbf{D}\mathbf{x}$ in Fig. 1 would coincide with position $\mathbf{x}$. This is obviously impossible. It is rather the point $Q' = \mathbf{R}^{-1}\mathbf{x}$ in Fig. 1, which is rotated into the position $\mathbf{x}$. SRC assume the point $P' = \mathbf{R}\mathbf{x}$ in Fig. 1 instead of Q'; this would mean that, with the rotation $\boldsymbol{\omega}$, the points $\mathbf{x}$ and

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* The treatment of librations in the harmonic approximation of the nuclear motions can still be performed by applying (1): With a rotation $\boldsymbol{\omega}$, a nucleus is now assumed to move along the tangent of a circle (and not along the circle itself). Thus the nuclei perform translations (and not the intended librations), and then $P(\mathbf{u})$ is a Gaussian distribution whose covariance matrix is formed from the rigid-body vibrations tensors **TLS** (Schomaker & Trueblood, 1968; Scheringer, 1977).

† A referee has pointed out that a positive sign of $\mathbf{Lr}$ (in this paper $\mathbf{D}\mathbf{x}$) was used in the calculation of their examples by Ruysink & Vos (1974). With $+\mathbf{Lr}$, instead of $-\mathbf{Lr}$ which was printed, Ruysink & Vos's equation (18) corresponds to SRC (4), and gives a correct result with a symmetric p.d.f. which is given by a Gaussian distribution of the librations.

$P' = \mathbf{Rx}$ in Fig. 1 would be interchanged. However, with SRC (5) which implies the symmetry of the p.d.f., SRC (4) and (9) can still be considered as correct in a Cartesian coordinate system. With $P(-\boldsymbol{\omega}) = P(\boldsymbol{\omega})$ inserted in SRC (4), and the substitution $\boldsymbol{\omega}' = -\boldsymbol{\omega}$, SRC (4) can be converted to a form that corresponds to (4) without translations. But the error which is inherent in SRC (4) and (9) becomes evident in SRC (14) and (20) and, now, cannot be corrected by application of the symmetry $P(-\boldsymbol{\omega}) = P(\boldsymbol{\omega})$. SRC (14) contains $-\mathbf{Rh}$ instead of $\mathbf{h}$. The first term of SRC (20) is stated to be the same as SRC (14), but it does not contain $-\mathbf{Rh}$, as it should in the line of SRC's derivation. The other two terms in SRC (20) have incorrect signs because $\mathbf{Rh}$ was used in SRC (18) instead of $\mathbf{R}^T\mathbf{h}$. Obviously, neither can the signs be reversed nor $-\mathbf{Rh}$ be removed by application of $P(-\boldsymbol{\omega}) = P(\boldsymbol{\omega})$.

To derive the scattering factor of the dynamic density (4), we first make the substitution $\mathbf{x} - \mathbf{t} = \mathbf{y}$, $d\mathbf{x} = d\mathbf{y}$, then perform a calculation similar to SRC (4–9), but with the substitution $\mathbf{R}^{-1}\mathbf{y} = \mathbf{y}'$, $d\mathbf{y} = d\mathbf{y}'$, and obtain

$$f(\mathbf{h})_{\rm dyn} = \iint_{-\infty}^{+\infty} f(\mathbf{R}^T\mathbf{h})_{\rm stat} \exp(2\pi i \mathbf{h}^T \mathbf{t})\, P(\mathbf{t}, \boldsymbol{\omega})\, d\mathbf{t}\, d\boldsymbol{\omega}. \quad (5)$$

(5) holds in a general crystal metric, but then note $\mathbf{R}^T \neq \mathbf{R}^{-1}$. Since in (5) $\mathbf{R}^T$ arises, and not $\mathbf{R}^{-1}$ as in (4), we do not consider (5) to be a 'convolution integral' with respect to the librations. [From their calculation SRC (4–9), SRC were led to believe that the operations in direct and reciprocal space were fully identical, and hence, they denoted the operation in reciprocal space also by 'convolution'.] The dynamic density (4) and the dynamic molecular scattering factor (5) cannot generally be split up into translations and librations because the p.d.f. $P(\mathbf{t},\boldsymbol{\omega})$ cannot generally be factored into pure translation and rotation parts. Furthermore, (5) contains the remarkable result that temperature factors do not appear.

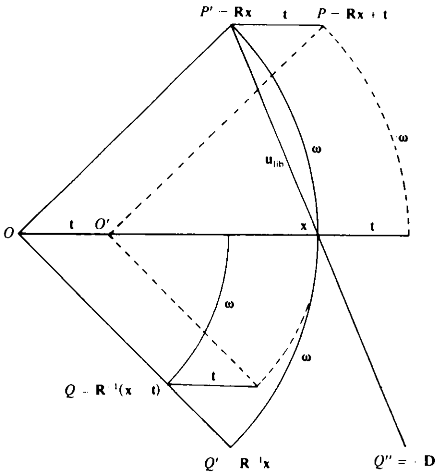

Fig. 1. Convolution for rigid-body motion. After a rotation $\boldsymbol{\omega}$ about the origin O and a translation $\mathbf{t}$, the end-point of the vector $\mathbf{x}$ is shifted into the position $P = \mathbf{Rx} + \mathbf{t}$. At the same time, the point Q, initially located at $\mathbf{R}^{-1}(\mathbf{x} - \mathbf{t})$, is shifted into the position $\mathbf{x}$. The same points P and Q are arrived at if the translation $\mathbf{t}$ is performed first and then the rotation $\boldsymbol{\omega}$ about the shifted molecular origin at O'. For a pure rotation $\boldsymbol{\omega}$ about O neither the point $Q'' = -\mathbf{Dx}$ nor the point $P' = \mathbf{Rx}$ is shifted into the position $\mathbf{x}$ but the point $Q' = \mathbf{R}^{-1}\mathbf{x}$. Solid arcs refer to the origin O, dashed arcs to the origin O' which is obtained after the translation $\mathbf{t}$.

Temperature factors

There are, however, two cases where temperature factors arise in (5). One of these is the case of statistical independence of $\mathbf{t}$ and $\boldsymbol{\omega}$, the other is the case of density units with spherical symmetry. If the translations $\mathbf{t}$ and the librations $\boldsymbol{\omega}$ are statistically independent (for example, if $\mathbf{t}$ and $\boldsymbol{\omega}$ are Gaussian distributed and the correlation tensor $\mathbf{S}$ is zero), we have $P(\mathbf{t},\boldsymbol{\omega}) = P_{\rm tr}(\mathbf{t})\, P_{\rm lib}(\boldsymbol{\omega})$ and can now integrate over $\mathbf{t}$, and obtain from (5)

$$f(\mathbf{h})_{\rm dyn} = T_{\rm tr}(\mathbf{h}) \int_{-\infty}^{\infty} f(\mathbf{R}^T\mathbf{h})_{\rm stat}\, P_{\rm lib}(\boldsymbol{\omega})\, d\boldsymbol{\omega}. \quad (6)$$

$T_{\rm tr}(\mathbf{h})$ is the temperature factor for the translations of the molecule. The remaining integral in (6) cannot generally be expressed by temperature factors, except for the case which we shall now consider.

For charge distributions of spherical symmetry, (5) and (6) can be simplified: $f(\mathbf{h})_{\rm dyn}$ can be expressed by $f(\mathbf{h})_{\rm stat}$ and temperature factors which have to be calculated for the centres of the charge distributions.* We show this for the general case of coupled translations and librations. The basic idea of our proof is to show that, after an appropriate shift of the origin, a density unit of spherical symmetry is rotated into itself, and thus the thermal average for this density unit can be fully described by considering translations only. Let the density unit be centered at $\mathbf{x}_0$ with respect to an arbitrary origin, and let the translations of the molecule be $\mathbf{t}$ with respect to this origin. Then the translations $\mathbf{t}_0$ with respect to the origin $\mathbf{x}_0$ are $\mathbf{t}_0 = \mathbf{t} + \mathbf{Dx}_0$, whereas the librations remain unaltered, *i.e.* $\boldsymbol{\omega}_0 = \boldsymbol{\omega}$ [Scheringer, 1978, equations (6.1)–(6.3)]. This situation was described geometrically by Johnson (1970). We now denote the spherically symmetric density unit by $\rho(\mathbf{x})_{\rm stat}$, and, in a Cartesian coordinate system with origin $\mathbf{x}_0$, we have $|\mathbf{R}^{-1}\mathbf{x}| = |\mathbf{x}|$. Hence, $\rho[\mathbf{R}^{-1}(\mathbf{x} - \mathbf{t}_0)]$

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* SRC have shown this for the case of statistically independent translations and librations; but their proof is only correct with $\mathbf{R}^T\mathbf{h}$ instead of $\mathbf{Rh}$ in SRC (9), which then leads to the identity of SRC (14) and (15) which is asserted but not present.

is independent of $\boldsymbol{\omega}$, and (4) can now be integrated over $\boldsymbol{\omega}$,

$$\rho(\mathbf{x})_{\text{dyn}} = \int_{-\infty}^{\infty} \rho(\mathbf{x}-\mathbf{t}_0)_{\text{stat}}\, q(\mathbf{t}_0)\, \mathrm{d}\mathbf{t}_0. \qquad (7)$$

By definition, $q(\mathbf{t}_0)$ is the marginal p.d.f. of $P(\mathbf{t}_0,\boldsymbol{\omega})$. The appearance of $q(\mathbf{t}_0)$ in (7) means that a given rotational state of ρ_{stat} does not matter in the description of the translations. Obviously this is because the rotations around $\mathbf{x}_0$ transform the density unit into itself. (7) is a convolution integral of the standard form (1) and, hence, the Fourier transform of $q(\mathbf{t}_0)$ is the temperature factor $T(\mathbf{h})$ for the density unit ρ_{stat} and has to be calculated for the present origin, $\mathbf{x}_0$. Finally, we have to remove the restriction of having the origin at the centre of the density unit. Transformation to the initial arbitrary origin introduces a phase factor in the structure factor but leaves the temperature factor unaltered. Hence, the Fourier transform of the dynamic density of a spherically symmetric density unit located at $\mathbf{x}_0$ is given by

$$f(\mathbf{h})_{\text{dyn}} = f(\mathbf{h})_{\text{stat}}\, T(\mathbf{h}) \exp(2\pi i \mathbf{h}^T \mathbf{x}_0), \qquad (8)$$

where the temperature factor $T(\mathbf{h})$ has to be evaluated for the point $\mathbf{x}_0$. (8) can also be derived if one starts from (5). Then one also obtains the temperature factor as the Fourier transform of the marginal p.d.f. $q(\mathbf{t}_0)$.

Temperature factors for the centres of spherically symmetric density units can be calculated from the **TLS ρ** model (Scheringer, 1978). We had assumed that the librations were Gaussian distributed, and had calculated the cumulants which describe the temperature factor up to and including the fourth moments of $\mathbf{t}$ and ω. These temperature factors are independent of choice of origin; they depend on the coordinates $\mathbf{x}$, on the vibration tensors **TLS**, and on the coordinates of a special point $-\boldsymbol{\rho}$ in the molecule for which, when chosen as origin, the translations of the molecule are assumed to be harmonic (Gaussian distributed). Internal motions are neglected.

For calculating temperature factors in practice, the **TLS ρ** model for large librations can be applied in the following cases:

(1) to the spherical atoms in a refinement with X-ray data,

(2) to the nuclei of the atoms in a refinement with neutron data,

(3) to the spherical atoms in *X–N* and related maps,

(4) to the spherically symmetric atomic cores in the refinement of empirical density models, such as were described by Hellner (1977) and Dietrich & Scheringer (1978),

(5) to the one-centre ns^2 orbital products ($n = 1, 2\ldots$) and other spherically symmetric atomic cores in the calculation of dynamic difference densities from theoretical static difference densities, *cf.* SRC.

Unfortunately, the programming of the **TLS ρ** model requires some effort. But in case (3) the large librations of molecules should be treated correctly, since small errors in the temperature factors give rise to large errors in *X–N* maps (Scheringer, Kutoglu & Mullen, 1978). In the refinement of empirical density models [case (4)] an improvement is to be expected, since the components of **TLS ρ** will be less correlated than the temperature factors of the individual atomic cores to the density parameters of the model. The least important application appears to be case (5), since the same temperature factors are used for both contributors to the difference density, and, thus, the errors in the temperature factors cancel each other out to some extent. This is confirmed by actual calculations of dynamic difference densities, *cf.* Hase, Reitz & Schweig (1976), SRC, and Hase, Schulte & Schweig (1978).

If the librations are statistically independent and the density units in a molecule are not spherically symmetric, then the calculation of the dynamic scattering factors is cumbersome and can only be approximated (see SRC for orbital products). If translations and librations are coupled, then the evaluation of (4) and (5) appears to be insoluble. A first approximation in this case is to calculate the temperature factor for the centroid of the density unit and to use it for the whole unit, unless in special cases a better solution is found.

References

BATS, J. W. & FEIL, D. (1977). *Chem. Phys.* **22**, 175–181.

DIETRICH, H. & SCHERINGER, C. (1978). *Acta Cryst.* B**34**, 54–63.

HASE, H. L., REITZ, H. & SCHWEIG, A. (1976). *Chem. Phys. Lett.* **39**, 157–159.

HASE, H. L., SCHULTE, K. W. & SCHWEIG, A. (1978). Private communication.

HELLNER, E. (1977). *Acta Cryst.* B**33**, 3813–3816.

JOHNSON, C. K. (1970). *Crystallographic Computing*, pp. 220–226. Copenhagen: Munksgaard.

RUYSINK, A. F. J. & VOS, A. (1974). *Acta Cryst.* A**30**, 497–502.

SCHERINGER, C. (1977). *Acta Cryst.* A**33**, 426–429.

SCHERINGER, C. (1978). *Acta Cryst.* A**34**, 702–709.

SCHERINGER, C., KUTOGLU, A. & MULLEN, D. (1978). *Acta Cryst.* A**34**, 481–483.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

STEVENS, E. D., RYS, J. & COPPENS, P. (1977). *Acta Cryst.* A**33**, 333–338.