$$\begin{aligned}
\circlearrowright\ \Omega_1 &= G_2G_3(G_1-E_2-E_3)+E_1M_1 \\
\circlearrowright\ 4\Omega_1 &= H_1N_1+G_2N_2+G_3N_3-2\Theta_1 \\
\circlearrowright\ W^2 &= G_1G_2G_3+2E_1E_2E_3-\sum_{123} G_1E_1^2 \\
4W^2 &= \sum_{123}[(G_1+H_1)N_1-\Theta_1]-H_1H_2H_3 \\
\Delta &= G_1G_2G_3\sum_{123}(G_1-2E_1)+\sum_{123} M_2M_3 \\
4\Delta &= \sum_{123} N_2N_3
\end{aligned}$$

*Angles*

| | |
|---|---|
| Angles between planes | $\varphi$ |
| Bragg angle | $\theta$ |
| Angles between wave-vectors | $\psi$ |
| $\Psi=2\sin\psi/2$ | |

*Physical parameters*

| | |
|---|---|
| Wavelength in space | $\lambda_c$ |
| Wavelength in crystal | $\lambda$ |

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# Tensor Analysis of the Harmonic Vibrations of Atoms in Crystals

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It is shown how the tensor algebra of general affine systems gives a useful and natural representation of the harmonic vibration tensor **U**. Formulae given by Cruickshank for the 'smearing function' $t(\mathbf{x})$ and its Fourier transform $q(\mathbf{h})$ are proved to be generally valid, provided the upper and lower suffix notation is used for the vector and tensor components. It is also shown how representing the tensor **U** in a system whose basis vectors are unit vectors and parallel to the crystal axes has many advantages. Finally a simple formalism for the determination of metric quatities of **U**, introducing its mixed components $U^i_j$, is suggested.

## Introduction

The purpose of the present note is to treat the problem of describing the thermal motion of atoms as one of tensor analysis in affine systems.

Assuming an anisotropic harmonic potential field, the thermal motion of atoms in crystals is normally described for every atom in terms of the well-known symmetric tensor **U** (Cruickshank, 1956). The crystallographic system in which this tensor is defined is an affine system (*i.e.* a system whose axes and interaxial angles are in general $\mathbf{a}_1 \neq \mathbf{a}_2 \neq \mathbf{a}_3$, $\gamma_1 \neq \gamma_2 \neq \gamma_3$, $\gamma_i \neq \pi/2$).

The problem of describing the thermal motion of atoms has therefore a more logical and natural formulation if for any general affine system $\mathbf{a}^i$ we introduce its own reciprocal system $\mathbf{a}^i$ defined by $\mathbf{a}_i . \mathbf{a}^j = \delta^j_i$, and use these dual bases throughout the vector and tensor analysis of the thermal motion.

Three main conclusions are reached:

i) Cruickshank's (1956) original formulae (1·6) and (1·7) for the 'smearing function' $t(\mathbf{x})$ and its Fourier transform $q(\mathbf{h})$ are valid in any non-orthogonal crystal system provided contravariant components of **U** and covariant components of **l**, with respect to crystal axes, are used in formula (1·5) of the same paper;

ii) it is useful to refer the tensor **U** to a coordinate system whose basis vectors are unit vectors parallel to the crystal axes, in order to give an expression for tensor **U**, which is independent of the length of the crystal axes and therefore dependent only on the intermolecular and intramolecular forces acting on the atom;

iii) it is especially convenient to use the mixed components $U^i_j$ in the calculation of any metric quantity of the tensor **U**, *e.g.* the length of the principal axes and their orientation with respect to the crystal axes, because the formalism in any affine system is then the same as for Cartesian tensors.

The notation used in this note is similar to that in standard texts of tensor calculus [for example see Gerresten (1962) or Patterson (1959)] except for the frames, for which the notation $(\mathbf{a}_i, \mathbf{a}^i)$, $(\mathbf{b}_i, \mathbf{b}^i)$, $(\mathbf{e}_i, \mathbf{e}^i)$ is preferred, in order to denote explicitly in every case the vectors of the direct and reciprocal bases. The superscripts and subscripts $i, j, k, l, m, n = 1, 2, 3$ are used to specify contravariant and covariant components, respectively. The subscript $r$ denotes the serial number of any quantity.

### Validity of Cruickshank's formulae

In a recent paper, Scheringer (1966) claims that Cruickshank's (1956) formulae (1·6) and (1·7) are not valid in an oblique crystal system. However it is possible to prove, in a more explicit way than does Cruickshank, that they maintain their validity in the affine system defined by the crystal axes.

In the frame $(\mathbf{a}_i, \mathbf{a}^i)$ defined by the direct and reciprocal crystal axes, the symmetric tensor **U**, which represents in a harmonic potential field the mean square amplitude of vibration of any atom, is described either by the contravariant components $U^{ij}$ or the covariant components $U_{ij}$, so that the mean-square displacement $\overline{u^2}$ from the equilibrium position, in the direction of a unit vector **l**, is $\overline{u^2} = U^{ij}l_il_j = U_{ij}l^il^j$, where $l^i$ and $l_i$ are the contravariant and covariant components of **l** respectively.

Let us suppose that the tensor **U** is described, in the frame $(\mathbf{a}_i, \mathbf{a}^i)$, by the contravariant components* $U^{ij}$, so that

$$\overline{u^2} = U^{ij}l_il_j\,. \qquad (1)$$

It is then possible to show (Cramèr, 1961) that the probability density, *i.e.* Cruickshank's 'smearing function', in the direct crystal system is

$$t(\mathbf{x}) = (2\pi)^{-3/2}\,(\det V_{ij})^{1/2} \exp\{-\tfrac{1}{2}V_{ij}x^ix^j\} \qquad (2)$$

where $x^i$ are the contravariant components of the vector **x** and

$$[V_{ij}] = [U^{ij}]^{-1}\,. \qquad (3)$$

The Fourier transform of (2) is

$$q(\mathbf{h}) = (2\pi)^{-3/2}\,(\det V_{jk})^{1/2}\iiint \exp\{-i2\pi h_ix^i - \tfrac{1}{2}V_{jk}x^jx^k\}\mathrm{d}\mathbf{x} \qquad (4)$$

in which $\mathbf{h} = (h_1, h_2, h_3)$ is a Fourier transform vector space.

This is shown in the Appendix to reduce to

$$q(\mathbf{h}) = \exp\{-2\pi^2U^{ij}h_ih_j\}\,. \qquad (5)$$

The expressions (2) and (5) are precisely the formulae given by Cruickshank for the 'smearing function' $t(\mathbf{x})$ and the Fourier transform $q(\mathbf{h})$ provided it is remembered he did not explicitly use the upper and lower suffix notation for contravariant and covariant components, so that his '$U_{ij}$' must be interpreted as our $U^{ij}$ and his '$x_i$' as $x^i$. The components $U^{ij}$ in (5), which are the same as those used in (1), are the contravariant components of the tensor **U** in the frame $(\mathbf{a}_i, \mathbf{a}^i)$ defined by direct and reciprocal axes.

### The components of $U$ in the new $(\mathbf{e}_i, \mathbf{e}^i)$reference frame

As it is well known, the anisotropic temperature factor has the form $\exp(-M)$, where $M = B^{ij}h_ih_j$, and $h_i$ are the covariant components of **h**, the coordinates of a reciprocal-lattice point. From experimental data, generally by least-squares refinement, we obtain the coefficients $B^{ij}$ and the components

$$U^{ij} = B^{ij}/2\pi^2 \qquad (6)$$

Thus the tensor **U** in the frame $(\mathbf{a}_i, \mathbf{a}^i)$ is described by contravariant components $U^{ij}$ defined by (6) and by covariant components defined by

$$U_{ij} = U^{kl}\varepsilon_{ki}\varepsilon_{lj} \qquad (7)$$

where $\boldsymbol{\varepsilon}$ is the metric tensor of the basis $(\mathbf{a}_i)$, whose components are $\varepsilon_{ij} = \mathbf{a}_i\,.\,\mathbf{a}_j$.

Any metric quantity of the tensor **U** can then be determined either from the components $U^{ij}$ or the components $U_{ij}$, provided the metric tensors $\varepsilon_{ij} = \mathbf{a}_i\,.\,\mathbf{a}_j$ and $\varepsilon^{ij} = \mathbf{a}^i\,.\,\mathbf{a}^j$ of the frame $(\mathbf{a}_i, \mathbf{a}^i)$ are taken into account (Busing & Levy, 1958). It is also well known that the components $U^{ij}$ (or $U_{ij}$) defined in that frame do not have an immediate physical interpretation; nor are the several components directly comparable.

It is physically more significant to refer the tensor **U** to a direct oblique system with unit vectors defined as

$$\mathbf{e}_i = \mathbf{a}_i/(a_i)\,.$$

No summation is implied hereafter by the indices of quantities in brackets.

For the change from basis $(\mathbf{a}_i)$ to basis $(\mathbf{e}_i)$,

$$\mathbf{e}_i = t_i^j\mathbf{a}_j\,,$$

---

* The following demonstration may be carried out also for the covariant components $U_{ij}$ with similar results.

the transformation matrix is

$$[t^j_i] = \begin{bmatrix} 1/a_1 & 0 & 0 \\ 0 & 1/a_2 & 0 \\ 0 & 0 & 1/a_3 \end{bmatrix} = [\delta^j_i/(a_i)]$$

where $\delta^j_i$ is the Kronecker symbol.

For the reciprocal basis, we have

$$\mathbf{e}^i = r^i_j \mathbf{a}^j$$

where

$$[r^i_j] = [t^j_i]^{-1} = \begin{bmatrix} a_1 & 0 & 0 \\ 0 & a_2 & 0 \\ 0 & 0 & a_3 \end{bmatrix} = [\delta^i_j(a_j)] .$$

Clearly, the vectors $\mathbf{e}_i$ defining the new direct basis are parallel to the crystal axes $\mathbf{a}_i$, but are $a_i$ times shorter, so that $|\mathbf{e}_i| = 1$. Similarly, the vectors $\mathbf{e}^i$ defining the new reciprocal basis are parallel to the reciprocal crystal axes $\mathbf{a}^i$, but $a_i$ times longer, so that $|\mathbf{e}^i| = 1/\cos\theta_i$, where $\theta_i$ are the angles between the direct and reciprocal axes.

In this new frame $(\mathbf{e}_i, \mathbf{e}^i)$ the $U_{ij}$ components are directly comparable and each diagonal term $U_{ii}$ is the mean-square displacement (in Å$^2$) in the direction of the direct axis $\mathbf{e}_i$, whilst the mean-square displacement in the direction of the reciprocal axis $\mathbf{e}^i$ is $U_{ii}$ $(\cos\theta_i)^2$. Moreover the $U^{ij}$ components define the $V_{ij}$ matrix, and therefore the probability-density function $t(\mathbf{x})$ in a way that makes it possible to compare the thermal vibrations of an atom in different crystals.

According to the transformation law, in the frame $(\mathbf{e}_i, \mathbf{e}^i)$ the new components of $\mathbf{U}$ are

$$U^{ij} = U^{mn} r^i_m r^j_n \tag{8}$$

and

$$U_{ij} = U_{mn} t^m_i t^n_j \tag{9}$$

where $U^{mn}$ and $U_{mn}$ are the contravariant and covariant component of $\mathbf{U}$ as defined in $(\mathbf{a}_i, \mathbf{a}^i)$ by (5) and (6).

Considering (6) and (8), for the new contravariant components of $\mathbf{U}$, in $(\mathbf{e}_i, \mathbf{e}^i)$ more explicitly we get

$$\begin{aligned} U^{11} &= B^{11}a_1a_1/2\pi^2 & U^{12} &= B^{12}a_1a_1/2\pi^2 \\ U^{22} &= B^{22}a_2a_2/2\pi^2 & U^{13} &= B^{13}a_1a_3/2\pi^2 \\ U^{33} &= B^{33}a_3a_3/2\pi^2 & U^{23} &= B^{23}a_2a_3/2\pi^2 . \end{aligned} \tag{10}$$

Formulae (10) are equivalent to Scheringer's (1966) formula (5) which was derived assuming that Cruickshank's equations (1·6) and (1·7) were valid in orthogonal axes only. In orthogonal axes, formulae (10) are also equivalent to Cruickshank's equation (2·2).

For oblique crystal axes Hirshfeld & Rabinovich (1966) discuss the components of tensor $\mathbf{U}$ in a different affine system whose direct and reciprocal basis vectors are

$$\mathbf{f}_i = \mathbf{e}_i/(\cos\theta_i) , \quad \mathbf{f}^i = \mathbf{e}^i(\cos\theta_i) \quad i = 1,2,3$$

where $\theta_i$ are the angles between the direct and reciprocal axis.*

In this system $|\mathbf{f}^i| = 1$, and therefore the contravariant components $U^{ij}$ are comparable and the diagonal term $U^{ii}$ is the mean-square displacement (in Å$^2$) in the direction of the reciprocal axis $\mathbf{f}^i$, whilst the mean-square displacement in the direction of the direct axis $\mathbf{f}_i$ is $U_{ii}(\cos\theta_i)^2$.

## On the mixed components $U^i_j$

In a general affine system and therefore in the $(\mathbf{e}_i, \mathbf{e}^i)$ frame too, the problem of finding the principal axes of the representation quadric of the symmetric tensor $\mathbf{U}$, requires the solution of either of the following two systems

$$U^{ij} l_j = \lambda l^i . \qquad i = 1, 2, 3 \tag{11}$$

$$U_{ij} l^j = \lambda l_i \qquad i = 1, 2, 3 . \tag{12}$$

In the frame $(\mathbf{e}_i, \mathbf{e}^i)$, the following relationships hold between $l^i$ and $l_i$

$$l^i = g^{ik} l_k , \quad l_i = g_{ik} l^k \quad i = 1, 2, 3 \tag{13}$$

where $g^{ik} = \mathbf{e}^i \,.\, \mathbf{e}^k$ and $g_{ik} = \mathbf{e}_i \,.\, \mathbf{e}_k$ are the metric tensors of the frame.

Taking into account (13) on the right hand side of (11) and (12) we get the following linear homogeneous systems for the covariant and contravariant components of $\mathbf{U}$

$$(U_{ij} - \lambda g_{ij}) l^j = 0 \qquad i = 1, 2, 3$$

$$(U^{ij} - \lambda g^{ij}) l_j = 0 \qquad i = 1, 2, 3$$

whose characteristic equations would be quite cumbersome.

However by substituting (13) in the left-hand side of (11), we get

$$(U^i_k - \lambda\delta^i_k) l^k = 0 \qquad i = 1, 2, 3 \tag{14}$$

where $U^i_k = U^{ij} g_{jk}$ are the mixed components† of tensor $\mathbf{U}$ in the frame $(\mathbf{e}_i, \mathbf{e}^i)$ and $\delta^i_k$ is the Kronecker symbol.

Similarly (12) becomes

$$(U^k_i - \lambda\delta^k_i) l_k = 0 \qquad i = 1, 2, 3 \tag{15}$$

where $U^k_i = U_{ij} g^{jk}$ is the transpose matrix of $U^i_k$.‡

The eigenvalues of the linear homogeneous system (14) and (15) can be easily found by solving the common characteristic equation:

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* We actually obtain Cruickshank's equation (2.2) if we perform a change of bases whose transformation matrices for the direct and reciprocal bases are respectively

$$[s^j_i] = [\delta^j_i(a^j)] \quad \text{and} \quad [v^i_j] = [\delta^i_j/(a^j)]$$

where $\delta^k_i$ is the Kronecker symbol.

† For a symmetric tensor it is $U^i{}_k = U_k{}^i = U^i_k$.

‡ The matrices $U^k_i$ and $U^i_k$ are of course no longer symmetric, even if they represent the symmetric tensor $\mathbf{U}$.

$$\lambda^3-\lambda^2(U_1^1+U_2^2+U_3^3)+\lambda$$

$$\left\{\begin{bmatrix}U_1^1 & U_2^1\\ U_1^2 & U_2^2\end{bmatrix}+\begin{bmatrix}U_1^1 & U_3^1\\ U_1^3 & U_3^3\end{bmatrix}+\begin{bmatrix}U_2^2 & U_3^2\\ U_2^3 & U_3^3\end{bmatrix}\right\}$$

$$-(\det U_k^i)=0\,. \quad (16)$$

Formulae (14) or (15), and especially (16), offer computational advantages in determining the three eigenvalues $\lambda_r$ and the corresponding eigenvectors $v_r$ because they have the same form as the corresponding equations in standard orthogonal systems.

## APPENDIX

In order to calculate the Fourier transform (4), we change the frame from $(\mathbf{a}_i,\mathbf{a}^i)$ to $(\mathbf{b}_i,\mathbf{b}^i)$ as follows

$$\mathbf{b}_i=p_i^j\mathbf{a}_j\,,\quad \mathbf{b}^i=q_j^i\mathbf{a}^j\quad i=1,2,3$$

with $[q_j^i]=[p_i^j]^{-1}$ where $[p_i^j]$ is a suitable transformation matrix, so chosen that the matrices $[V_{ik}]$ and $[U^{ik}]$ are transformed into diagonal matrices

$$S_{ij}=V_{kl}p_i^kp_j^l\,,\quad T^{ij}=U^{kl}q_k^iq_l^j\,. \qquad (A1)$$

The diagonal elements $S_{ii}$ and $T^{ii}$ are the eigenvalues of the matrices $V_{ij}$ and $U^{ji}$, so that considering (3) we get

$$[S_{ij}]=\begin{bmatrix}S_1 & 0 & 0\\ 0 & S_2 & 0\\ 0 & 0 & S_3\end{bmatrix},\qquad [T^{ij}]=\begin{bmatrix}1/S_1 & 0 & 0\\ 0 & 1/S_2 & 0\\ 0 & 0 & 1/S_3\end{bmatrix}.$$

The change of frame involves the following transformations

$$x^i=p_j^iy^j\,,\quad h_i=q_i^jk_j\quad i=1,2,3 \qquad (A2)$$

and

$$d\mathbf{x}=(\det p_j^i)d\mathbf{y}$$

where $(\det p_j^i)$ is the coordinate change Jacobian.

In the new frame $(\mathbf{b}_i,\mathbf{b}^i)$ the triple integral in (4) becomes

$$(\det p_j^i)\iiint\exp\{-i2\pi k_jy^j-\tfrac{1}{2}S_{jl}y^jy^l\}d\mathbf{y}=$$

$$=(\det p_j^i)\Pi_j\int\exp\{-i2\pi k_jy^j-\tfrac{1}{2}S_{jj}y^jy^j\}dy_j.$$

Integrating the last formula we get

$$(\det p_j^i)\,(2\pi)^{3/2}\,(\det S_{jl})^{-1/2}\exp\{-2\pi^2S^{-1}_{jl}k_jk_l\}\,. \qquad (A3)$$

But $[S_{jl}]^{-1}=[T^{jl}]$ and $(\det S_{jl})=(\det V_{ij})\,(\det p_j^i)^2$ so that (A3) becomes

$$(2\pi)^{3/2}\,(\det V_{ij})^{-1/2}\exp\{-2\pi^2T^{ij}k_ik_j\}\,.$$

If the inverse transformation from $(\mathbf{b}_i,\mathbf{b}^i)$ to $(\mathbf{a}_i,\mathbf{a}^i)$ is performed, taking (A1) and the inverse* of (A2) into account, and substituting in (4), we get

$$q(\mathbf{h})=\exp\{-2\pi^2U^{ij}h_ih_j\}$$

which is the generalized formulation of $q(\mathbf{h})$ in any crystal axes.

A program based on this analysis has been written by the author in FORTRAN IV for the IBM 7040 computer, valid in any crystal system for determining the components $U^{ij}$ and $U_j^i$ of tensor $\mathbf{U}$ in the frame $(\mathbf{e}_i,\mathbf{e}^i)$ and the metric quantities of thermal vibration ellipsoids, such as the length of the principal axes, and their orientation with respect to the crystal axes.

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* $y^i=q_j^ix^j$ and $k_i=p_i^jh_j$ with $i=1,2,3$.