

coordinates  $\mathbf{u}_{jk}$ , i.e.  $\mathbf{u}_{jk} = \mathbf{0}$  at  $\mathbf{r}_k$ . The consequences of this situation concerning the meaning of the positional parameters are discussed elsewhere (Scheringer, 1986).

In establishing anharmonic p.d.f.'s, parameters of an 'effective potential' or 'isolated-atom potential' are often used (Willis & Pryor, 1975, ch. 5; Zucker & Schulz, 1982). Our basic result that any atomic p.d.f. has to be conceived as a marginal p.d.f. of the crystal p.d.f. gives rise to the following interpretation: the parameters of the effective potential describe the motions of an atom as if it would vibrate under this potential, *no matter where the remaining atoms of the crystal are actually located* (but within the limits set by the crystal p.d.f.). Note the difference of this interpretation from the common interpretation with the Einstein model (Willis & Pryor, 1975, p. 12) where the atoms are assumed to vibrate independently.

I am indebted to Professor Dr V. Mammitzsch, Mathematisches Institut der Universität Marburg, for a discussion on the treatment of dependent variables in statistics. I thank Dr B. T. M. Willis, Oxford, and Professors A. J. C. Wilson, Cambridge, H. B. Bürgi, Bern, W. Prandl, Tübingen, and V. Schomaker,

Seattle, for their constructive criticism of earlier versions of this paper.

#### References

- COCHRAN, W. & COWLEY, R. A. (1967). *Handbuch der Physik*, Vol. 25, Part 2a, p. 59. Berlin, Heidelberg, New York: Springer.
- JAMES, R. W. (1948). *The Optical Principles of the Diffraction of X-rays*. London: Bell.
- KASHIWASE, Y. (1965). *J. Phys. Soc. Jpn*, **20**, 320-335.
- KRIVOGLAZ, M. A. & TEKHONOVA, E. A. (1961). *Sov. Phys. Crystallogr.* **6**, 399-403.
- LAUE, M. VON (1948). *Röntgenstrahlinterferenzen*. Leipzig: Akademische Verlagsgesellschaft.
- MARADUDIN, A. A. & FLINN, P. A. (1963). *Phys. Rev.* **129**, 2529-2547.
- MARCINKIEWICZ, J. (1938). *Math. Z.* **44**, 612-618.
- MARSHALL, W. & LOVESEY, S. W. (1971). *Theory of Thermal Neutron Scattering*. Oxford: Clarendon Press.
- PRYOR, A. W. & SANGER, P. L. (1970). *Acta Cryst.* **A26**, 543-558.
- SCHERINGER, C. (1978). *Acta Cryst.* **A34**, 905-908.
- SCHERINGER, C. (1980). *Acta Cryst.* **A36**, 497-499.
- SCHERINGER, C. (1985). *Acta Cryst.* **A41**, 79-81.
- SCHERINGER, C. (1986). *Acta Cryst.* **A42**, 356-362.
- SCHERINGER, C. (1987). *Acta Cryst.* **A43**, 706-710.
- STEWART, R. F. & FEIL, D. (1980). *Acta Cryst.* **A36**, 503-509.
- VAN HOVE, L. (1954). *Phys. Rev.* **95**, 249-262.
- WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.
- WOLFE, G. A. & GOODMAN, B. (1969). *Phys. Rev.* **178**, 1171-1189.
- ZUCKER, U. H. & SCHULZ, H. (1982). *Acta Cryst.* **A38**, 563-568, 568-576.

*Acta Cryst.* (1987). **A43**, 706-710

## On the Interpretation of Anisotropic Temperature Factors. IV. The Effect of Interatomic Coupling on the Vibration Tensors

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(Received 11 January 1985; accepted 21 April 1987)

### Abstract

In the harmonic approximation of thermal vibrations, the probability density function (p.d.f.) of a crystal is discussed and the p.d.f. of a single atom is derived. It is shown that Bragg intensities and temperature factors are affected by statistical dependences among the vibrational coordinates but not the covariances (correlations) of the atoms in the crystal. The relation between statistical dependences and interatomic force constants is established, and effective potential parameters are derived as functions of the interatomic force constants. It is shown that a decrease in the

diagonal elements or an increase in the off-diagonal elements of statistical dependence increases the mean-square amplitudes  $\langle u^2 \rangle$  of the atoms. An increase in statistical dependence between different coordinates of space always increases the  $\langle u^2 \rangle$ . Some experimental results ( $\langle u^2 \rangle$ ) in different types of structures are interpreted with simple models of statistical dependence.

### 1. Introduction

The effect of coupling the motions of different atoms in crystals on Bragg intensities and atomic vibration tensors is difficult to analyse. Vibration tensors determined by means of diffraction experiments support

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the opinion that such effects exist. In particular, the thermal ellipsoids of (nearly) rigid molecules form regular patterns that can be interpreted on the assumption of molecular rigid-body motion, *i.e.* highly correlated motion of atoms in the molecule; see *e.g.* Cruickshank (1956), Burns, Ferrier & McMullan (1967), Schomaker & Trueblood (1968), Willis & Pryor (1975, Figs. 6.3 and 6.4). Lattice-dynamical considerations give a general relation between atomic vibration tensors and dynamical matrices (Scheringer, 1972*a*, 1973), but do not give information on the direction in which interatomic coupling affects the vibration tensors. In the preceding paper (Scheringer, 1987) – hereafter I – we have derived the temperature factor with the aid of statistical methods and have included the effects of interatomic coupling. Here we restrict ourselves to the harmonic approximation of atomic motions, and thus gain the advantage that all distributions are Gaussian. We then obtain matrices that are real, symmetric and positive definite and that can be subjected more readily to a mathematical treatment than the complex Hermitian matrices of lattice dynamics. The purpose of this paper is:

(1) to distinguish between two related properties of ‘interatomic coupling’, namely statistical dependences and covariances (correlations) among the vibrational coordinates of different atoms in the crystal;

(2) to establish the relationship between these two properties in the harmonic approximation, and to find their relation to the atomic vibration tensors;

(3) to establish the relationship between statistical dependences, interatomic force constants (potential parameters of the crystal) and ‘effective potential parameters’ of individual atoms; and

(4) to determine cumulative effects of statistical dependences on the atomic vibration tensors.

## 2. Statistical dependences, covariances and their relation to atomic vibration tensors

We begin by setting up the probability density function (p.d.f.)  $f(\mathbf{u})$  of the crystal and determining the marginal p.d.f.’s  $f_k(\mathbf{u}_k)$  of the atoms.  $\mathbf{u}$  denotes the  $3nN - 6$  independent vibrational coordinates of the atoms in the crystal ( $N$  cells in the crystal,  $n$  atoms in each cell), and  $\mathbf{u}_k$  the three vibrational coordinates of the atom  $k$ . In thermal equilibrium, a poly-dimensional harmonic oscillator has a Gaussian distribution for its vibrational coordinates; this is also true in the regime of quantum statistics (Bloch, 1932). The crystal p.d.f. is hence a  $(3nN - 6)$ -dimensional Gaussian function, *i.e.*

$$f(\mathbf{u}) = (2\pi)^{-M} (\det \mathbf{V})^{1/2} \exp\left(-\frac{1}{2}\mathbf{u}^T \mathbf{V} \mathbf{u}\right), \quad (1)$$

where  $M = (3nN - 6)/2$ .  $\mathbf{V}$  is of order  $3nN - 6$  and is symmetric and positive definite, as is  $\mathbf{V}^{-1}$ . By

definition, statistical dependence between the  $3nN - 6$  independent vibrational coordinates is expressed explicitly in the off-diagonal elements of  $\mathbf{V}$ , and the covariance is explicitly expressed in the off-diagonal elements of  $\mathbf{V}^{-1}$ . Thus, in the harmonic approximation, statistical dependences and covariances are related through the matrix inversion  $\mathbf{V} \rightarrow \mathbf{V}^{-1}$ . If the atoms in each cell are counted in the same sequence and in one cell after the other,  $\mathbf{V}$  and  $\mathbf{V}^{-1}$  exhibit the periodicity of the crystal, neglecting the three atoms which carry the six dependent coordinates. Since the crystal is periodic, all pairs of cells (atoms) located relative to each other with regard to the same distance and orientation must have the same  $3n \times 3n$  ( $3 \times 3$ ) off-diagonal blocks. Symmetry elements present in the crystal can impose additional restrictions. Since the crystal should not disintegrate, single atoms or cells cannot vibrate independently. Hence,  $\mathbf{V}$  and  $\mathbf{V}^{-1}$  cannot be  $3 \times 3$  or  $3n \times 3n$  block-diagonal and must have a minimum band structure. However, the atoms may vibrate independently in the three directions of space and thus a block-diagonal form of  $\mathbf{V}$  and  $\mathbf{V}^{-1}$  (three blocks only) is allowed with respect to the vibrations in different directions of space.

The p.d.f. of an atom  $k$  in any cell  $l$ ,  $f_k(\mathbf{u}_k)$ , *i.e.* a three-dimensional marginal p.d.f. of  $f(\mathbf{u})$ , is also Gaussian and its covariance matrix is a  $3 \times 3$  diagonal block of  $\mathbf{V}^{-1}$  (Chatfield & Collins, 1980, p. 98). This block is the vibration tensor  $\mathbf{U}_k$  of the atom  $k$ . Since, with the inversion of  $\mathbf{V}$ , all elements of  $\mathbf{V}$  contribute to  $\mathbf{V}^{-1}$ , the vibration tensors  $\mathbf{U}_k$  receive contributions from all elements of  $\mathbf{V}$ . In this way statistical dependences (off-diagonal blocks of  $\mathbf{V}$ ) are transferred in a unique way to the vibration tensor and thus determine their numerical values. [More generally, the uniqueness is guaranteed by the fact that I(9) – equation (9) of paper I – is mathematically unequivocal in the direction  $f(\mathbf{u}) \rightarrow f_k(\mathbf{u}_k)$  for any cell  $l$ .] From I(12) and I(13), Bragg intensities are unequivocally described by structure factors (temperature factors); hence Bragg intensities also depend unequivocally on the statistical dependences of the vibrational coordinates of different atoms in a given crystal. Also, from I(12) and I(13), only the Fourier transforms of the marginal p.d.f.’s  $f_k(\mathbf{u}_k)$  enter into the expression for the Bragg intensities. Hence only the  $3 \times 3$  diagonal blocks of  $\mathbf{V}^{-1}$ , *i.e.* the vibration tensors  $\mathbf{U}_k$ , can be determined from Bragg intensities. The  $3 \times 3$  off-diagonal blocks of  $\mathbf{V}^{-1}$ , *i.e.* the covariances, and hence  $\mathbf{V}$  and  $f(\mathbf{u})$ , remain unknown. Here we see that I(9) is mathematically unequivocal in the direction  $f_k(\mathbf{u}_k) \rightarrow f(\mathbf{u})$ .

## 3. Statistical dependences and potential parameters

Since Gaussian p.d.f.’s are equal to Boltzmann functions expanded to quadratic terms, simple relations result in the high-temperature approximation

(Boltzmann statistics). From (1) we obtain

$$k_B TV = \mathbf{P}\{\Phi(lk, l'k')\}, \quad (2)$$

where the  $(3nN - 6) \times (3nN - 6)$  symmetric and positive-definite matrix  $\mathbf{P}$  contains the interatomic force constants  $\Phi(lk, l'k')$ , *i.e.* the potential parameters as used in lattice dynamics.  $k_B$  is Boltzmann's constant and  $T$  the absolute temperature. The diagonal elements of  $\mathbf{P}$ ,  $\Phi_{ii}(lk, lk)$ ,  $i = 1, 2, 3$ ,  $l = 1, \dots, N$ ,  $k = 1, \dots, n$ , are not real force constants but are calculated from the condition of translational invariance (Scheringer, 1974). In quantum statistics, the Boltzmann distribution no longer holds but (1) does. Hence, the simple relation (2) is lost: the off-diagonal elements of  $\mathbf{V}$  thus denote the statistical dependences as they arise due to the interatomic forces present in the crystal, and the diagonal elements of  $\mathbf{V}$  essentially denote how strongly an atom 'is bound to its site'.

'Effective' or 'isolated-atom' potentials are of interest because they can be derived from diffraction data. [They are, however, mainly used for a discussion of anharmonic motion (Willis & Pryor, 1975, ch. 5).] The effective potential for a single atom is defined as the crystal potential for all atoms in the crystal. Hence, for a marginal p.d.f. of any dimension  $3m$ , we define a  $3m \times 3m$  matrix  $\mathbf{V}_{\text{eff}}$  corresponding to  $\mathbf{V}$  in the crystal p.d.f. (1). Further, with Chatfield & Collins (1980, p. 98), we find, as in §2,

$$\mathbf{V}_{\text{eff}} = [3m \times 3m \text{ block } \{\mathbf{V}^{-1}\}]^{-1} \quad (3)$$

and, in the high-temperature approximation,

$$k_B T \mathbf{V}_{\text{eff}} = \mathbf{P}_{\text{eff}} = [3m \times 3m \text{ block } \{\mathbf{P}^{-1}\}]^{-1}, \quad (4)$$

where 'block' in (3) and (4) denotes a  $3m \times 3m$  diagonal block cut out from  $\mathbf{V}^{-1}$  or  $\mathbf{P}^{-1}$  respectively. For  $m = 1$  the parameters of the isolated-atom potential ( $\mathbf{V}_{\text{eff}} = \mathbf{U}_k^{-1}$ ) are obtained, and for  $m = n$  the parameters of the unit-cell potential are obtained. For  $m = 2$ ,  $\mathbf{P}_{\text{eff}}$  describes the joint potential parameters for two atoms. An alternative relation to (4) can be obtained by harmonic lattice dynamics, starting from Scheringer's (1972*a*) equation (10*b*), *i.e.*

$$\mathbf{P}_{\text{eff}} = \left[ 3m \times 3m \text{ block } \left\{ (1/N) \sum_{\mathbf{q}} \mathbf{L}^{-1}(\mathbf{q}) \right\} \right]^{-1}, \quad (5)$$

where  $\mathbf{L}(\mathbf{q})$  is the  $3n \times 3n$  dynamical matrix of the wave vector  $\mathbf{q}$ , and  $m \leq n$ . Obviously, there is no direct relation between  $\mathbf{P}_{\text{eff}}$  and any interatomic force constants  $\Phi(lk, l'k')$ ; however, owing to the repeated matrix inversion, the total of the interatomic force constants enters into  $\mathbf{P}_{\text{eff}}$ . Only for  $m = 1$ , *i.e.* an isolated-atom potential, can all parameters of  $\mathbf{P}_{\text{eff}}$  be determined from diffraction data:  $\mathbf{P}_{\text{eff}} = k_B T \mathbf{V}_{\text{eff}} = k T \mathbf{U}_k^{-1}$ . In quantum statistics (4) and (5) are no longer valid but (3) still holds. The off-diagonal terms of  $\mathbf{V}_{\text{eff}}$  thus denote the statistical dependences among the

vibrational coordinates of the marginal p.d.f.; the effect of the remaining atoms is taken into account according to (3) but is not explicitly manifest. The diagonal elements of  $\mathbf{V}_{\text{eff}}$  essentially denote how strongly an atom 'is bound to its site'.

#### 4. The effect of statistical dependences on the mean-square amplitudes

We discuss the effect of the elements of  $\mathbf{V}$  and  $\mathbf{V}_{\text{eff}}$  on the mean-square amplitudes  $U^i$  of the atoms by giving some inequalities and discussing their physical meaning. Firstly, we recall that the diagonal elements of  $\mathbf{V}^{-1}$  and  $\mathbf{V}_{\text{eff}}^{-1}$  are equal to the  $U^i$ . Hence the  $U^i$  are inversely proportional to the absolute magnitudes of  $\mathbf{V}$  and  $\mathbf{V}_{\text{eff}}$ . The magnitude of the diagonal elements relative to the magnitude of the off-diagonal elements is important in assessing the effects of statistical dependences. The following inequalities are derived (see the proofs in the material for deposit\*).

We compare two matrices  $\mathbf{V}$  and  $\mathbf{V}_{\text{eff}}$  which have the same off-diagonal elements but with larger or smaller diagonal elements. Then

$$U^i(\mathbf{V} \text{ diag. larger}) \leq U^i(\mathbf{V} \text{ diag. smaller}), \quad (6)$$

$$\det \mathbf{V}(\mathbf{V} \text{ diag. larger}) \geq \det \mathbf{V}(\mathbf{V} \text{ diag. smaller}) \quad (7)$$

(see proofs 5 and 6\*). Here  $\mathbf{V}$  can be replaced by  $\mathbf{V}_{\text{eff}}$ . Equation (7) also holds for  $\det \mathbf{V}$  with  $\mathbf{V}_{\text{eff}}$  within brackets. If all diagonal elements of one matrix are larger, the unequal sign holds, otherwise either sign may hold. Now we compare two matrices  $\mathbf{V}$  which have the same (block) diagonals. In one of the matrices, denoted by 'general', further off-diagonal elements are added.

$$U^i(\mathbf{V} \text{ diagonal}) < U^i(\mathbf{V} \text{ general}), \quad (8)$$

$$U^i(\mathbf{V} \text{ block-diag.}) \leq U^i(\mathbf{V} \text{ general}), \quad (9)$$

$$\det \mathbf{V}(\mathbf{V} \text{ block-diag.}) \geq \det \mathbf{V}(\mathbf{V} \text{ general}) \quad (10)$$

(see proofs 1 to 4\*).  $\mathbf{V}$  may be replaced by  $\mathbf{V}_{\text{eff}}$  in (8) to (10). We assume that  $\mathbf{V}$  can also be replaced by  $\mathbf{V}_{\text{eff}}$  in the brackets of (10) only but are unable to prove it. The unequal signs in (8) to (10) apply if the addition of elements is 'significant', the equal signs apply if it is 'not significant'. The meaning of 'significant' in this context is explained in the material for deposit.\* Equation (8) is only meaningful for  $\mathbf{V}_{\text{eff}}$  since  $\mathbf{V}$  cannot be diagonal (crystal stability).  $\mathbf{V}$  can, however, be block-diagonal with three blocks referring to the three directions of space.

\* The proofs of inequalities (6) to (10) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43917 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Mean-square amplitudes in benzene and graphite

For benzene, only the internal modes of the molecule are taken into account. The in-plane and isotropic averages were calculated from Johnson (1970).

	C-C distance(Å)	$\langle u^2 \rangle$ (Å <sup>2</sup> )			Reference
		In-plane	Out-of-plane	Isotropic	
Benzene	1.399 (1)	0.0011	0.0017	0.0013	LB, J
Graphite	1.421 (3)	0.0033 (1)	0.0140 (3)		CTS

References: LB Landolt-Börnstein (1976); J Johnson (1970); CTS Chen, Trucano & Stewart (1977).

$\det \mathbf{V}$  determines the height of the crystal p.d.f.  $f(\mathbf{u})$  at  $\mathbf{u} = \mathbf{0}$ . Thus (7) and (10) imply that the maximum of  $f(\mathbf{u})$  is lowered and  $f(\mathbf{u})$  is broadened if the situation is changed from left to right in the sense of these equations. This means that a reduction of the diagonal elements of  $\mathbf{V}$  [inequalities (6) and (7)] or an addition of statistical dependences [inequalities (8) to (10)] broadens the crystal p.d.f. and increases the mean-square amplitudes  $U^{ii}$ . In particular, an increase of statistical dependence of the atomic motions in different directions of space always increases the  $U^{ii}$ , since diagonal elements of  $\mathbf{V}$  or  $\mathbf{V}_{\text{eff}}$  are not involved. The increase noted for the  $U^{ii}$  also holds for the eigenvalues  $\lambda_i$  of the vibration tensors since  $U^{11} + U^{22} + U^{33} = \lambda_1 + \lambda_2 + \lambda_3$ .

As for the physical meaning of the elements of  $\mathbf{V}$  and  $\mathbf{V}_{\text{eff}}$  discussed in § 3, the results (6) to (10) may be interpreted as follows: A reduction of diagonal elements of  $\mathbf{V}$  [inequalities (6) and (7)] implies that the atoms become less strongly 'bound to their sites' and thus the mean-square amplitudes will be increased. An addition of off-diagonal elements of  $\mathbf{V}$  [inequalities (8) to (10)] means that further linkages with other atoms are established. This induces further in-phase and out-of-phase motions among different atoms and the mean-square amplitudes will be increased. Thus the algebraic results (6) to (10) appear to make sense physically.

### 5. The model of independent atomic motions

This model (Busing & Levy, 1964; Scheringer, 1972*b*) is known to give very large values of bond-length correction which are not usually considered realistic. It is interesting to see that the model of independent motion requires a structure of matrix  $\mathbf{V}$  of highly unlikely occurrence. The model of independent (uncorrelated) motions means that  $\mathbf{V}^{-1}$  has a gap structure in each of the  $3n \times 3n$  diagonal cell blocks  $l$ ,  $l = 1, \dots, N$ , with zero  $3 \times 3$  covariance blocks (gaps) for all pairs of atoms that are assumed to vibrate independently. In building up the framework of a crystal, the primary requirements are the interatomic interactions (force constants), here the elements of  $\mathbf{V}$ . It is quite unlikely that  $\mathbf{V}$  is constrained in such a way that  $\mathbf{V}^{-1}$  will assume the gap structure described above, unless this is required by symmetry.

Another type of independent motion results if an atom vibrates independently with respect to the three directions of space. In this case the vibration tensor  $U_k$  is diagonal. Since  $U_k$  is always diagonal in the coordinate system of its principal axes, truly independent motions are obtained only if more than one tensor  $U_k$  is diagonal in any (Cartesian) reference system. (Writing  $\mathbf{V}$  and  $\mathbf{V}^{-1}$  implies that the same coordinate system is used for all atoms.) As in the case above, it is quite unlikely that  $\mathbf{V}^{-1}$  assumes a gap structure (*i.e.* several  $U_k$ 's diagonal), unless this is enforced by site symmetry. This is in agreement with experimental results.

### 6. Mean-square amplitudes in benzene and graphite

We give an interpretation of the large differences in the mean-square amplitudes  $\langle u^2 \rangle$  of the C atoms in graphite and in the isolated benzene molecule (not crystalline benzene). Here we consider the graphite crystal and the benzene molecule as two similar structural systems of different size performing only internal motions. The  $\langle u^2 \rangle$ 's of the benzene molecule were determined from infrared and Raman data at room temperature [no error estimates given (Johnson, 1970)], and the vibration tensors of the graphite crystal from a structure investigation at room temperature (Chen, Trucano & Stewart, 1977). The experimental  $\langle u^2 \rangle$ 's are listed in Table 1. The C-C bond lengths in graphite are larger by 0.022(4) Å (1.6% of the bond length). An assessment of the C-C force constants by means of Badger's rule (see *e.g.* Siebert, 1961) shows that the force constants in graphite and benzene differ by about 1% of their magnitude. Hence, the  $\langle u^2 \rangle$ 's in graphite and benzene should not differ appreciably by more than 1% owing to the difference of the C-C bond lengths (force constants). However, the ratio of  $\langle u^2 \rangle$  actually observed is much larger than 1.01, namely  $0.0033/0.0011 = 3.0$  for vibrations parallel to the graphite layers, and  $0.0140/0.0017 = 8.2$  for vibrations perpendicular to the layers; see Table 1. The large increase of  $\langle u^2 \rangle$  in graphite is caused by the establishment of long-range interactions in the graphite crystal. To understand this, we imagine graphite as composed of many six-C-atom units as they occur in benzene. The  $18 \times 18$  covariance matrix of the six C atoms (obtained from the singular  $36 \times 36$

covariance matrix of all atoms in benzene) is not singular; its inverse is  $V_{\text{eff}}$  (C atoms in benzene). If we put many such  $18 \times 18$   $V_{\text{eff}}$  matrices together in a block-diagonal matrix, we have a model for a large ensemble of uncoupled six-C-atom units (as they vibrate in benzene). If we connect the units and so establish a graphite crystal, we must fill up the off-diagonal blocks. From (9), the  $\langle u^2 \rangle$  of the C atoms will be enlarged by this procedure, the more so as more elements are added (long-range coupling) and the larger the elements. The large value of  $\langle u^2 \rangle$  perpendicular to the layers ( $0.0140 \text{ \AA}^2$ ) is caused by the fact that the interlayer interactions are weak [inequality (6),  $V_{ii}$  small] compared with the interactions within the layers ( $V_{ii}$  large).

The observed  $\langle u^2 \rangle$ 's in benzene and graphite can, of course, be qualitatively explained also by means of dynamics. Since graphite is a much larger system than benzene, normal modes with very large wavelengths can occur in graphite. The acoustic branches of these waves give rise to large  $\langle u^2 \rangle$ 's of the C atoms, which are not possible in the isolated benzene molecule.

### 7. Molecular crystals with rigid-body motions

Thermal ellipsoids of atoms in (nearly) rigid molecules form regular patterns which can be interpreted under the assumption of rigid-body motions. We consider the contributions to the  $V$  matrix corresponding to internal vibrations (IV) and external vibrations (EV) of the molecule separately and show that the vibration tensors  $U_k$  are primarily governed by the EV. To a good approximation, we can assume that the IV and EV are fully separated. The IV of different molecules are uncoupled (by definition) but the EV are coupled so that the crystal does not disintegrate. Since the frequencies of the IV are much larger than those of the EV, the  $V_{ij}$  corresponding to the IV are larger than those of the EV by at least one order of magnitude. In  $V^{-1}$  the order of magnitude

is reversed: the EV elements, at least those on the diagonal of  $V^{-1}$ , are large. Thus the vibration tensors  $U_k$  are primarily governed by the EV whereas the IV contribute only a 'background' to the  $3m \times 3m$  diagonal blocks of  $V^{-1}$  ( $m$  atoms in the molecule) and so prevent these blocks from becoming singular of rank six.

I am indebted to Professor Dr V. Mammitzsch, Mathematisches Institut der Universität Marburg, for having established the mathematical proofs 1-4 given in the material for deposit. I thank Dr B. T. M. Willis, Oxford, Professors V. Schomaker, Seattle, W. Prandl, Tübingen, and Dr Elisabeth Rossmannith, Hamburg, for having expressed constructive criticism on some earlier versions of this paper.

### References

- BLOCH, F. (1932). *Z. Phys.* **74**, 295-335.  
 BURNS, D. M., FERRIER, W. G. & MCMULLAN, J. T. (1967). *Acta Cryst.* **23**, 1098-1099.  
 BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142-146.  
 CHATFIELD, C. & COLLINS, A. J. (1980). *Introduction to Multivariate Analysis*. London, New York: Chapman & Hall.  
 CHEN, R., TRUCANO, P. & STEWART, R. F. (1977). *Acta Cryst.* **A33**, 823-828.  
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 915-923.  
 JOHNSON, C. K. (1970). *Thermal Neutron Diffraction*, pp. 132-160. Oxford Univ. Press.  
 LANDOLT-BÖRNSTEIN (1976). New Series, Vol. 7. *Structural Data of Free Polyatomic Molecules*. Berlin, Heidelberg, New York: Springer.  
 SCHERINGER, C. (1972a). *Acta Cryst.* **A28**, 512-515.  
 SCHERINGER, C. (1972b). *Acta Cryst.* **A28**, 616-619.  
 SCHERINGER, C. (1973). *Acta Cryst.* **A29**, 728-729.  
 SCHERINGER, C. (1974). *Acta Cryst.* **A30**, 295.  
 SCHERINGER, C. (1987). *Acta Cryst.* **A43**, 703-706.  
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63-76.  
 SIEBERT, H. (1961). *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie*. Berlin, Heidelberg, New York: Springer.  
 WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.