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The Significance of Accurate Structure Factors

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The practical significance of accurate structure factors $F(\mathrm{S})$ is discussed and illustrated in terms of different sorts of detailed structural information that become accessible when accurate estimates of $F(\mathrm{S})$ are available and analysed appropriately. The common and contrasting features of X-ray and neutron $F(\mathrm{S})$ (of non-magnetic systems) are considered.

Structure factor formalism is reviewed to show the simplifications that are implicit in the formalism normally adopted for operational data-treatment. Limitations in the normal formalism introduced by the 'spherical atom' approximation and the Gaussian ellipsoid harmonic rectilinear vibration approximation are shown with reference to the generalized formalism which avoids these constraints. The use of the generalized formalism for studying electron distribution aspects of covalent bonding in diamond structures and anharmonic aspects of anionic motions in fluorite structures is considered in detail.

The difficulties of making reliable judgments on the probable real accuracy of $F(\mathrm{S})$-estimates by referring them to 'spherical atom' models are illustrated in terms of different sets of $F(\mathrm{S})$ data reported for MgO. The results of applying a variety of such models to the various data sets are discussed.

The limitations of conventional Gaussian vibration formalism for extended studies (by either X-rays or neutrons, or both) of organic systems possessing appreciable librational behaviour are illustrated in terms of the generalized (neutron) formulation of $F(\mathrm{S})$ that is needed to take proper account of libration in cubic hexamethylenetetramine (HMT). It is shown that limitations of the conventional formalism are such that no simple 'libration correction' is strictly applicable to the atomic positional parameters of HMT as determined *via* the normal structure factor formalism.

1. Introduction

The emphasis of this meeting will be on X-ray structure factors and how we can obtain better estimates of these basic quantities from the intensities measured in Bragg scattering experiments. The problems to be overcome before results of accurate experiment can be converted into structure factor form are evident in the topics to be considered here subsequently. The variety of such problems is quite daunting, and the faint-hearted sceptic may well query two things: (*a*) whether the complicated manoeuvres required to improve accuracy can be justified in terms of their leading to information of a sort not evident in results from coarse experimental practice; and (*b*) perhaps even more importantly, whether current methods for operational handling of these problems will in fact ensure structure factor data of the high accuracy desired.

Both these questions bear on the significance we may attach to accurate structure factors, and this is a matter that can evoke different responses from different people according to their particular interests. I think it is useful here first to discuss this matter in a few general terms and then to consider some detailed examples of the sorts of structural information that appear to be accessible when we have structure factors which are of significantly high accuracy. Although the emphasis of this meeting is on X-ray structure factors, it is profitable to consider these quantities together with the neutron structure factors of non-magnetic systems. The information on aspects of chemical structure that is accessible by these two methods is largely complementary, and we have a quite firm basis for exploiting the differences in the two types of structure factor that arise from the different atomic scattering powers appropriate to the two techniques.

2. Theory

Little basic theory is required for discussion here and we shall use a notation which is sufficiently familiar not to require too much comment: the notation is essentially that of Dawson (1967*a*), where details not included here are available.

The starting point for discussion is the familiar Fourier transform

$$F(\mathrm{S}) = \int \varrho(\mathbf{r}) \exp\{2\pi i \mathrm{S} \, . \, \mathbf{r}\} d\mathbf{r} \qquad (2{\cdot}1)$$

relating the X-ray structure factor with the overall distribution of electron density, ϱ, throughout the unit cell. Subsidiary complications in $F(\mathrm{S})$ associated with anomalous scattering phenomena will be ignored here. The form of ϱ which interests us refers to the space- and time-averaged version of the unit cell contents: this is all we can consider in a bulk experiment on a system possessing zero point and thermal motion behaviour. We must assume in accurate studies that, as far as the space-averaging is concerned, all unit cells in the bulk crystal have equivalent time-averaged contents. Practical usage of (2·1) requires that we reformulate it in discrete-atom terms, which we can do by standard steps and thereby obtain $F(\mathrm{S})$ in the form

$$F(\mathrm{S}) = \sum_j f_j(\mathrm{S}) T_j(\mathrm{S}) \exp\{2\pi i \mathrm{S} \, . \, \mathbf{r}_{e,j}\} \, . \qquad (2{\cdot}2)$$

The essential features here are (i) that we have partitioned the total distribution into a series of 'atomic' distributions centred on the j nuclear positions nominated by the $\mathbf{r}_{e,j}$, and (ii) that we next regard each such distribution as the resultant produced by convoluting the distribution of the stationary 'atom' with the function which smears the distribution out over a greater volume in accord with the effects of thermal vibration in Bragg scattering.

The formalism of (2·2) is quite familiar, and we can take the further step of expanding its f_j- and T_j-factors in accord with the general possibility of non-centrosymmetry in the 'atomic' functions whose Fourier transforms govern the nature of these two factors of (2·2). Writing these functions as

$$\varrho_j(\mathbf{r}')=\varrho_{c,j}(\mathbf{r}')+\varrho_{a,j}(\mathbf{r}')\,,\qquad t_j(\mathbf{r}')=t_{c,j}(\mathbf{r}')+t_{a,j}(\mathbf{r}') \tag{2·3}$$

by separating components possessing centrosymmetry and antisymmetry with respect to the $\mathbf{r}_{e,j}$ (to which the $\mathbf{r}'$ of (2·3) are referred), we then also write

$$f_j(\mathbf{S})=f_{c,j}(\mathbf{S})+if_{a,j}(\mathbf{S})\,,\qquad T_j(\mathbf{S})=T_{c,j}(\mathbf{S})+iT_{a,j}(\mathbf{S})\,. \tag{2·4}$$

These expressions simply state that any unsymmetrical function can be treated as a sum of even and odd components and that the Fourier transform of such a function is complex: however we shall see later that it proves particularly useful to have these facts clear in the forms of (2·3), (2·4). Inserting them in (2·2), and considering just centrosymmetric structures where $F(\mathbf{S})=A(\mathbf{S})+iB(\mathbf{S})$ has $B(\mathbf{S})=0$, we now have

$$\begin{aligned}F(\mathbf{S})=\sum_j[\{&f_{c,j}(\mathbf{S})T_{c,j}(\mathbf{S})\\ &-f_{a,j}(\mathbf{S})T_{a,j}(\mathbf{S})\}\cos 2\pi\mathbf{S}\,.\,\mathbf{r}_{e,j}\\ &-\{f_{c,j}(\mathbf{S})T_{a,j}(\mathbf{S})\\ &+f_{a,j}(\mathbf{S})T_{c,j}(\mathbf{S})\}\sin 2\pi\mathbf{S}\,.\,\mathbf{r}_{e,j}]\,.\end{aligned} \tag{2·5}$$

This formalism retains the familiar threefold subdivision into scattering, vibrational and positional factors but it separates the various terms which arise from dividing the 'atomic 'functions in the even–odd manner of (2·3).

On this basis, another subdivision which proves most useful is to expand the electron density function one stage further to

$$\varrho_j(\mathbf{r}')=\bar{\rho}_{c,j}(r')+\delta\varrho_{c,j}(\mathbf{r}')+\varrho_{a,j}(\mathbf{r}')\,, \tag{2·6}$$

in which case

$$f_j(\mathbf{S})=\bar{f}_{c,j}(S)+\delta f_{c,j}(\mathbf{S})+if_{a,j}(\mathbf{S})\,. \tag{2·7}$$

The centrosymmetric features are now expressed in terms of major spherically symmetric segments and subsidiary non-spherical segments. Among other things, this shows us the simplifications in (2·5) that automatically accrue in neutron (point atom) scattering. All complications associated with $\varrho_j(\mathbf{r}')$- and $f_j(\mathbf{S})$-considerations disappear since only angle-invariant neutron scattering amplitudes $\bar{b}_j$ are then involved. The transition from the X-ray to the neutron situation can be made with the conversion $\bar{f}_{c,j}(S)\rightarrow\bar{b}_j$. With this in mind, rewriting (2·5) as

$$\begin{aligned}F(\mathbf{S})=\sum_j[&\bar{f}_{c,j}(S)T_{c,j}(\mathbf{S})\cos 2\pi\mathbf{S}\,.\,\mathbf{r}_{e,j}\\ &-\bar{f}_{c,j}(S)T_{a,j}(\mathbf{S})\sin 2\pi\mathbf{S}\,.\,\mathbf{r}_{e,j}]\end{aligned} \tag{2·8}$$

provides the neutron version of $F(\mathbf{S})$ which corresponds to (2·5) for X-rays. Apart from this attribute in (2·8), this form of $F(\mathbf{S})$ also leads us to the X-ray (or neutron) structure factor formalism which is normally used in practice. Not only is it customary to treat the atoms as scattering spherically symmetrically but also to regard their vibrational behaviour as describable in the Gaussian terms associated with harmonic rectilinear vibration. In this description, the essential feature is that both the t_j- and T_j-elements are purely centrosymmetric, so that the components of (2·8) involving the $T_{a,j}$-factors are now ignored. The nett result can be accommodated here writing $F(\mathbf{S})$ as

$$F(\mathbf{S})\sim\sum_j\bar{f}_{c,j}(S)T^h_{c.j}(\mathbf{S})\cos 2\pi\mathbf{S}\,.\,\bar{\mathbf{r}}_j\,, \tag{2·9}$$

where the h superscript denotes the harmonic (vibration ellipsoid) approximation and we have replaced the parameter $\mathbf{r}_{e,j}$ by the new parameter $\bar{\mathbf{r}}_j$. In some cases we can confidently write $\mathbf{r}_{e,j}\equiv\bar{\mathbf{r}}_j$, but this is generally not possible, as we shall see later.

It is clear that development of the usual expression (2·9) from the initial forms (2·1) or (2·2) involves a number of quite sweeping simplifications. Further, our problems of justifying any or all of these simplifications are enhanced because, in a complicated structure where atoms are in general positions, we know very little about the various structural details that all contribute to $F(\mathbf{S})$ in (2·2). We have no detailed knowledge of the f_j-terms which refer to scattering from bonded atoms, the T_j-terms which summarize vibrational effects manifested by these bonded atoms, or even the positions $\mathbf{r}_{e,j}$ about which the vibration occurs. In the face of all this doubt, we often have no recourse except to the standard formalism of (2·9), which we use by combining the Gaussian vibration treatment with estimates of the $\bar{f}_{c,j}(S)$ provided by theoretical (*e.g.* Hartree–Fock) calculations of spherical non-bonded atoms.

The adoption of this model for initial approach to all the parameters relevant to (2·2) is not in dispute. However, it is now becoming clear that attempts to define the parameters of (2·2) may be seriously prejudiced by structural artefacts which can arise from over-application of this model to accurate structure factor data. The likelihood of such artefacts will depend roughly on the number of positional and vibrational parameters that need to be defined for (2·2), and dangers arising from abuse of the 'spherical atom' model need further examination. The problem of artefacts reflects our lack of detailed knowledge of the $f_j(\mathbf{S})$ and $T_j(\mathbf{S})$, and systematic study of these factors is required.

3. Applications of theory

(1) *Diamond structures*

(*a*) *Diamond itself*

The structure of diamond (Fig. 1) provides a valuable opportunity for clarifying some aspects of the significance of accurate structure factors. The total structure is cubic and centrosymmetric, each atom is tetrahedrally bonded to four neighbours so that it possesses T_d site symmetry, the equilibrium parameters $\mathbf{r}_{e,j}$ are known since symmetry arguments alone dictate the atomic locations in the unit cell, and vibrational effects at room temperature are very small. This last feature, reflected in the high Debye characteristic temperature ($\Theta_M > 1800\,°\mathrm{K}$), indicates that the t_j- and T_j-functions here can be treated quite safely in isotropic Gaussian terms. With the $\mathbf{r}_{e,j}$ known and the $T_j(\mathbf{S})$ defined in this simple fashion, the principal interest in accurate structure factors for diamond resides in the information they can provide on electron distribution features of covalent bonding between the carbon atoms of this classic structure. The celebrated aspect of this structure is the so-called 'forbidden' reflexion 222, whose significance was recognized initially by Bragg (1921) and whose magnitude was first established reliably by Renninger (1955). Göttlicher & Wölfel (1959) have determined the structure factors of the conventional reflexions by careful X-ray studies of fine diamond powders.

The details of an extended electron distribution study based on these data have been given elsewhere (Dawson, 1967*b*), but the stategy involved and the conclusions that can be drawn may be summarized as follows. We write (2·5) as

$$F(\mathbf{S}) = \sum_j [\{\bar{f}'_{c,j}(S) + \delta f'_{c,j}(\mathbf{S})\} \cos 2\pi\mathbf{S}\,.\,\mathbf{r}_{e,j} - f'_{a,j}(\mathbf{S}) \sin 2\pi\mathbf{S}\,.\,\mathbf{r}_{e,j}] \,, \quad (3{\cdot}1)$$

where the primes denote the temperature-modified components

$$\bar{f}'_{c,j}(S) = \bar{f}_{c,j}(S) T_{c,j}(S) \,,\ \delta f'_{c,j}(\mathbf{S}) = \delta f_{c,j}(\mathbf{S}) T_{c,j}(S) \ etc.$$

with

$$T_{c,j}(S) \equiv T_j(\mathbf{S}) = \exp\{-\bar{B}S^2/4\} \,, \qquad \bar{B} = 8\pi^2\langle u^2\rangle\ (=0{\cdot}20\ \text{Å}^2) \,. \quad (3{\cdot}2)$$

These components correspond to the (temperature-modified) components

$$\varrho'_j(\mathbf{r}) = \bar{\rho}'_{c,j}(r) + \delta\varrho'_{c,j}(\mathbf{r}) + \varrho'_{a,j}(\mathbf{r}) \,, \quad (3{\cdot}3)$$

where for convenience we replace $\mathbf{r}'$ of (2·3) by $\mathbf{r}$. The T_d site symmetry dictates the detailed character of the non-spherical components of (3·3). Expanding these in terms of the Kubic Harmonics of von der Lage & Bethe (1947) and retaining only the leading members of these expansions then leads to (if we drop the atomic subscript j)

$$\begin{aligned} \delta\varrho'_c(\mathbf{r}) &= \delta\varrho'_{c,4}(\mathbf{r}) = G_4(r)\,[\{(x^4+y^4+z^4)/r^4\} - \tfrac{3}{5}] \\ \varrho'_a(\mathbf{r}) &= \varrho'_{a,3}(\mathbf{r}) = F_3(r)\,[xyz/r^3] \,, \end{aligned} \quad (3{\cdot}4)$$

where $F_3(r)$ and $G_4(r)$ are independent radial functions which can be expressed in terms of elementary functions of the form $r^q \exp(-\alpha r^m)$, with $q \neq 0$ to ensure that the components have regular behaviour at $r = 0$. The non-spherical f-components of (3·2) then become (again we drop the j subscript)

$$\begin{aligned} \delta f'_c(\mathbf{S}) &= \delta f'_{c,4}(\mathbf{S}) = [\{(h^4+k^4+l^4)/(h^2+k^2+l^2)^2\} - (\tfrac{3}{5})] f^{p'}_{c,4}(S) \\ f'_a(\mathbf{S}) &= f'_{a,3}(\mathbf{S}) = -[hkl/(h^2+k^2+l^2)^{3/2}] f^{p'}_{a,3}(S) \,, \end{aligned} \quad (3{\cdot}5)$$

where

$$f^{p'}_{c,4}(S) = \int_0^\infty 4\pi r^2 G_4(r) j_4(kr)\,dr$$

$$f^{p'}_{a,3}(S) = \int_0^\infty 4\pi r^2 F_3(r) j_3(kr)\,dr \,,$$

the $j_n(kr)$ being spherical Bessel functions of order n with $k = 2\pi S = 4\pi \sin\theta/\lambda$. Similarly, the spherical $\bar{f}$-component of (3·2) involves

$$\bar{f}'_c(S) = \int_0^\infty 4\pi r^2 \bar{\rho}'_c(r) j_0(kr)\,dr \,, \quad (3{\cdot}6)$$

and we now have $F(\mathbf{S})$ of (3·1) expressed in terms of three principal scattering factors dependent only on S.

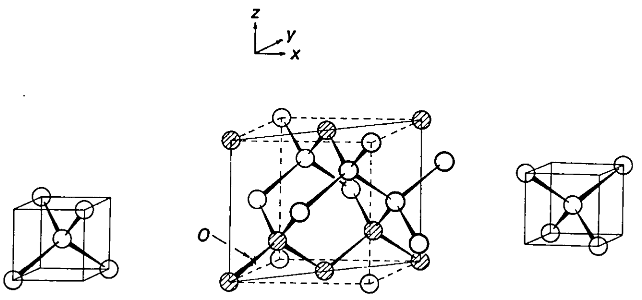


Fig. 1. The diamond structure.

The expansion of (3·3) in the terms of (3·4) means that

$$\int \varrho'(\mathbf{r})d\mathbf{r} = \int_0^\infty 4\pi r \bar{\rho}'_c(r)dr = Z$$

and

$$\int \varrho'_{a,3}(\mathbf{r})d\mathbf{r} = \int \delta\varrho'_{c,4}(\mathbf{r})d\mathbf{r} = 0\,, \qquad (3\cdot7)$$

where Z is the atomic number. The role of the components of (3·4) is to redistribute the Z electrons, the angular nature of the redistribution being set by the relevant Kubic Harmonic and the magnitude being governed by the associated radial functions $F_3(r)$ or $G_4(r)$. Hence, the behaviour of $f'_c(S)$ of (3·6) is quite conventional: its value is Z at $S=0$ and its subsequent diminution as S increases will depend on the detail in $\bar{\rho}'_c(r)$ itself. By contrast, the two principal factors of (3·5) will be zero-valued at $S=0$, thereafter increasing (before finally diminishing again) in accord with the detail in $F_3(r)$ or $G_4(r)$ and also with the order of spherical Bessel function involved.

These considerations provide the basic strategy for detailed examination of the structure factors of diamond, and we apply it in accord with the nature of (3·1) for different types of reflexions. The odd-index ($4n \pm 1$) reflexions involve all features of the bonded atom in (3·3), (3·4), the even-index ($4n$) reflexions involve only the centrosymmetric components, and the 222 reflexion involves only the antisymmetric component of the atom. The sparsity of the diamond data imposes two restrictions in using this strategy, and we assume first a Hartree–Fock basis for the spherical component of (3·3). This enables us to rewrite (3·6) as

$$f'_c(S) = f(\text{H.F., } 3P) \exp\{-\bar{B}S^2/4\}\,, \qquad (3\cdot8)$$

where $\bar{B}$ is the parameter required to modify the static Hartree–Fock f-values (of the spherically averaged charge distribution of the atom in its lowest ground state configuration, $3P$) for the effects of thermal vibration: we take $\bar{B}=0{\cdot}20$ Å^2 at room temperature. Next, we assume a simple, common, representation for the radial functions $F_3(r)$ and $G_4(r)$. With these two assumptions, it transpires (Dawson, 1967*b*) that non-spherical features of the diamond structure factors can be interpreted extensively with

$$F_3(r) = K_{22}r^2 \exp\{-\alpha r^2\}\,,$$
$$G_4(r) = L_{22}r^2 \exp\{-\alpha r^2\}\,, \qquad (3\cdot9)$$

where the K-, L- and α-parameters have the values 7·5, −2·0 and 2·2 Å^2.

The meaning that attaches to these versions (3·9) of the components of (3·4) is shown in Figs. 2 and 3. These illustrate essential aspects of covalent bonding in diamond, Fig. 2 showing, for a single C–C bond, the way in which the non-spherical atomic charge density components behave in the directions $\langle 111\rangle$ and $\langle 100\rangle$ of the diamond structure. Fig. 3 shows the overall effects of non-spherical charge distribution as we see them manifested in the $(1\bar{1}0)$ plane of diamond (where the shaded atoms of Fig. 1 are located). Full discussion of these figures has been given elsewhere (Dawson, 1967*b*) and we note only salient features here. The upper part (*a*) of Fig. 2 shows how the $\delta\varrho'_{c,4}$- and $\varrho_{a,3}$-components of each atom in the bond have redistributed charge to produce the pile-up in the middle of the bond, and (*a*) of Fig. 3 shows the complete structural analogue in the plane $(1\bar{1}0)$. Part (*a*) of Fig. 3 can be construed as a theoretical 'difference Fourier' map, and all its features are the outcome of superposition of the non-spherical atomic features *which emanate from, and are therefore referred to, the atomic sites themselves.* By contrast, (*b*) of Fig. 3 shows the conventional 'difference Fourier' map associated with use of the 'spherical atom' model. The differences between (*a*) and (*b*) are minimal and we shall not discuss them here (see however Dawson, 1967*b*). The essential point of the relation of (*b*) to (*a*) is that interpretation of (*b*) alone is normally attempted by arguments of 'charges in the bonds', made with the implication that features of bonding redistribution are features which require special treatment and which are not amenable to treatment in terms of the natural reference origins, the atomic sites themselves. The generation of (*a*) by the treatment outlined above shows very clearly that such an interpretation of (*b*) for diamond is not only unnecessary but also confusing. *All* features of accurate structure factors for diamond can be interpreted in straightforward terms when we recognize the implications of T_d symmetry for the bonded carbon atom and treat the $F(\mathbf{S})$ accordingly.

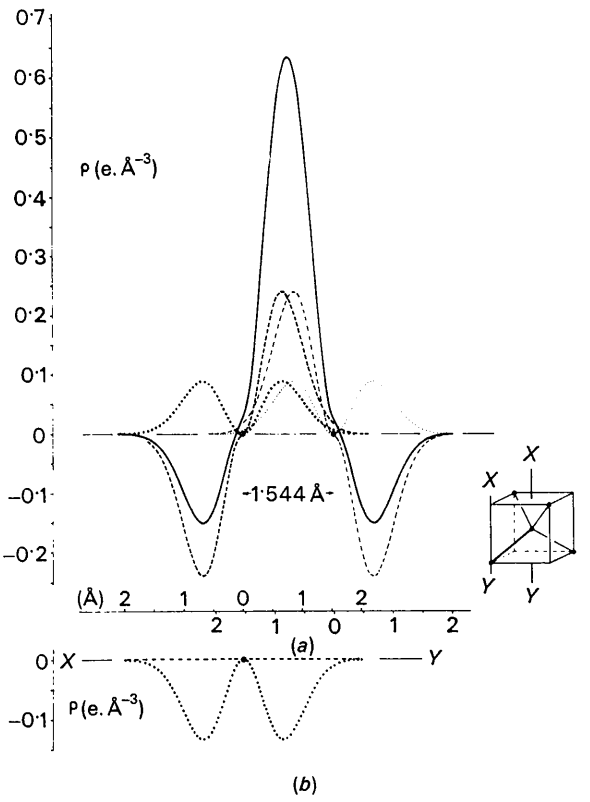
This approach to the charge distribution in diamond now puts us in a useful position for assessing the significance of attempts to calculate this distribution from fundamental theoretical principles. Such calculations are of the greatest importance for extending our basic knowledge of solid-state phenomena, and a number of such calculations have been undertaken since the pioneering attempt of Ewald & Hönl (1935) to reproduce the 222 reflexion. It is fair to say that this reflexion has held a quite hypnotic fascination for theorists, virtually to the exclusion of all other diffraction features of diamond, and this fascination has been evident in the results of many calculations: improvements in theoretical estimates of 222 have not been accompanied by improved estimates of all the other reflexions. It is clear from (3·1) however that 222 is only one, albeit unusual, manifestation of bonding effects in diamond and that all reflexions over a very considerable angular range must be considered jointly if these effects are to receive a properly comprehensive description. The recent basic calculation of Goroff & Kleinman (1967) appears to have taken significant steps forward towards reproducing a wide range of diamond structure factors, and the comparison of their and others' predictions with existing experiment is shown in Table 1.

The significance of accurate structure factors for diamond takes on special importance now that basic theory and accurate experiment appear to be reaching the point of profitable interaction. On the experimental side, the analysis of future $F(\mathrm{S})$ data in the terms outlined above should permit close and ready appraisal of the authenticity or otherwise of the $F(\mathrm{S})$-values derived from subsequent experiment. On the theoretical side, we may hope that confrontation with highly reliable $F(\mathrm{S})$ data may spur the theoretician to yet more comprehensive basic calculations such that he can take the initiative in asserting what the absolute structure factors of diamond really are.

(*b*) *Silicon and germanium*

Although these are just the heavier structural analogues of diamond, possessing all the same diffraction features including 222 (Renninger, 1960), the difficulties of experimentation and interpretation increase rapidly with the rise of atomic number. We can still approach the $F(\mathrm{S})$ data in the fashion of (3·1), but problems of comprehensive electron redistribution interpretation are greater because the scattering effects of the non-spherical components of (3·3) are now very much smaller fractions of the total scattering power of the bonded atom. Except for 222, the problems are virtually impossible for germanium (Dawson, 1967*d*), and only silicon offers any real prospect for useful examination in the manner used for diamond (Dawson, 1967*c*).

X-ray studies of silicon are unusual in the sense that this structure is one of the few whose structure factors have been determined other than by the method of first measuring Bragg intensities. Kato and his colleagues (Hattori, Kuriyama, Katagawa & Kato, 1965) have exploited Pendellösung fringe phenomena in wedge-shaped perfect crystal specimens and shown how dynamical X-ray theory allows the fringe spacings observed to be converted into estimates of the structure factors. This is a very specialized technique, possible and useful only when strain-free crystal specimens of very high perfection are available, and its subtleties will be the subject of discussion by Professor Kato, Dr M. Hart and others later in this meeting. Only the potentially great attractions of this technique for estimating structure factors need be noted here, namely that problems of extinction which colour intensity measurement are entirely absent and that the structure factor estimates are on the absolute basis. This novel method has yielded estimates which are quite similar to those obtained in two careful intensity experiments on silicon, one using powder techniques (Göttlicher &



(*a*)

(*b*)

Fig. 2. Features of the covalent bond between any pair of atoms in diamond. (*a*) The assemblage of the non-spherical atomic components along the bond direction. Broken lines are $\varrho'_{a,3}$-components and dotted lines the $\delta\varrho'_{c,4}$-components for the K, L and α parameters discussed in the text. The heavy full line shows the total resultant along the bond. (*b*) The $\delta\varrho'_{c,4}$-component (for either atom in the bonded combination) along directions corresponding to ⟨100⟩ in diamond. The $\varrho'_{a,3}$-component is zero in these directions.

Table 1. *Comparison of experimental and theoretical* $|F(\mathrm{S})|$ *of diamond*

hkl	$\lvert F(\text{experiment})\rvert$	$\lvert F(7{\cdot}5\text{–}2{\cdot}0)\rvert$	$\lvert F(\mathrm{C})\rvert$	$\lvert F(\mathrm{B})\rvert$	$\lvert F_1(\mathrm{GK})\rvert$	$\lvert F_2(\mathrm{GK})\rvert$
111	$18{\cdot}69_6 \pm 0{\cdot}04_0$	18·73	18·53	17·95	18·72	18·71
220	$15{\cdot}39_2 \pm 0{\cdot}07_2$	15·46	15·01	14·81	15·57	15·62
311	$9{\cdot}06_0 \pm 0{\cdot}04_0$	9·03	9·18	8·58	9·07	9·06
222	$1{\cdot}16_0 \pm 0{\cdot}08_0$	1·16	0.49	0·99	0·80	0·80
400	$11{\cdot}19_2 \pm 0{\cdot}07_2$	11·35	11·82	11·34	11·37	11·36
331	$8{\cdot}34_4 \pm 0{\cdot}02_8$	8·27	8·10	—	8·42	8·40
422	$10{\cdot}57_6 \pm 0{\cdot}01_6$	10·54	—	—	11·31	11·29
333	$7{\cdot}26_3 \pm 0{\cdot}02_8$	7·06	—	—	7·82	7·82
511		7·00	—	—	7·60	7·59

$F(\mathrm{C})$, $F(\mathrm{B})$, $F_1(\mathrm{GK})$ and $F_2(\mathrm{GK})$ are the theoretical values of Clark (1964), Bennemann (1964) and Goroff & Kleinman (1967), respectively, obtained after applying the factor $\exp\{-0{\cdot}20 \sin^2 \theta/\lambda^2\}$ to bring them into accord with the (scaled) F(experiment) of Göttlicher & Wölfel (1959). The scaling and the $F(7{\cdot}5\text{–}2{\cdot}0)$ are discussed in Dawson (1967*b*). The $F_1(\mathrm{GK})$ and $F_2(\mathrm{GK})$ involve respectively, the Herman–Skillman and Jucys estimates of 1*s* scattering noted in the text of Goroff & Kleinman.

Wölfel, 1959) and the other single-crystal technqiues (DeMarco & Weiss, 1965).

The existence of these three sets of $F(\mathrm{S})$ data thus offers an unusual opportunity for comparison of three different techniques, each of which has its own peculiar problems and difficulties. It transpires, however, that comparison with reference to the predictions of the 'spherical atom' model is quite inconclusive: all three sets appear roughly equally good, or bad, in terms of this model. A much sharper criterion is required before we can make any useful judgment on the relative merits of the three sets, and the results found from studying diamond in terms of (3·1) have a special relevance here. The arguments from (3·1) onwards are basically group theoretical consequences of T_d site symmetry so that, with appropriate modification of the $\bar{B}$ parameter of (3·8) and the K, L and α parameters of (3·9), we must expect that they will be equally applicable to accurate structure factors of silicon. When the above three sets of data are approached on this basis (Dawson, 1967*c*), it emerges that only Kato's results are amenable to systematic detailed interpretation.

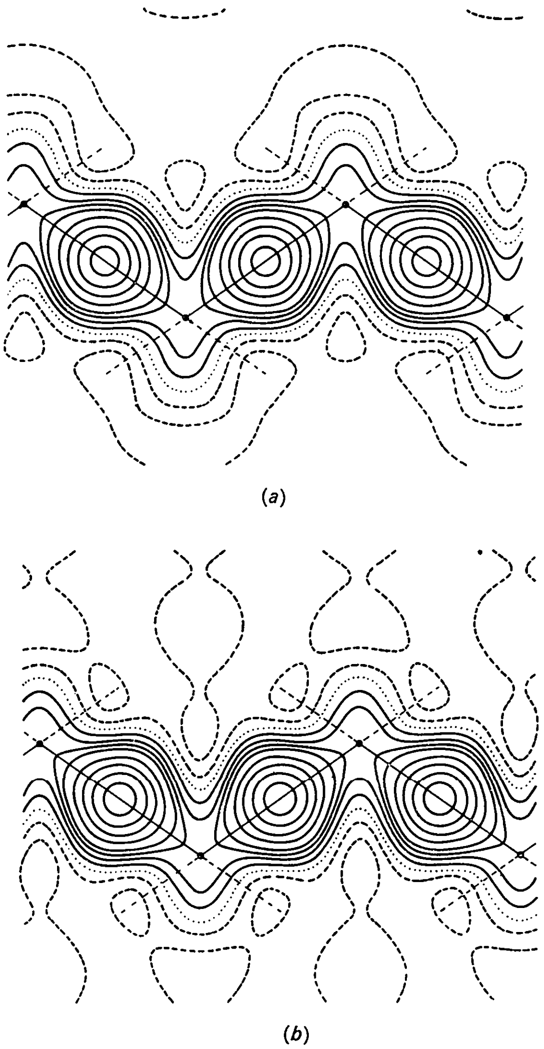


Fig. 3. Fourier representation of covalent bonding manifested in (1$\bar{1}$0) of diamond. (*a*) The representation given theoretically by using the K, L and α parameters used previously for Fig. 2. (*b*) The corresponding representation given by conventional 'difference' Fourier methods. Positive contours (full lines) are at intervals 0·05, 0·10, 0·20, 0·30, *etc.* e.Å^{-3}, negative contours (broken lines) are at the intervals $-0·05$, $-0·10$ e.Å^{-3}, and the zero contour is dotted. These results apply to reflexions of diamond with $\sin\theta/\lambda < 0·7$ Å^{-1}.

This conclusion focuses attention on the immediate need for further experimental X-ray studies of silicon by both intensity and Pendellösung methods. The former are required if systematic resolution of deficiencies in the earlier such experiments is to be achieved, and the latter are required to resolve some residual uncertainties which seem to exist in Kato's 1965 estimates. The present evidence of covalent bonding effects in silicon (Dawson, 1967*c*) shows that much more stringent levels of accuracy in structure factor measurement must be achieved here if a comprehensive electron distribution study is contemplated.

(2) *Fluorite structures*

Another important example of structural information that becomes accessible with accurate structure factors is provided by detailed neutron studies of compounds possessing the fluorite structure. This structure (Fig. 4) is possessed by compounds such as $\mathrm{CaF_2}$, $\mathrm{BaF_2}$, $\mathrm{UO_2}$ and many others. Like diamond, this structure is also cubic and centrosymmetric, and all atoms (ions) occupy special positions so that their $\mathbf{r}_{e,j}$ are known. However, greater complexity exists here since this structure is essentially ionic and the site symmetries of the two ions are different. The cations (X) have O_h symmetry and the anions (Y) have T_d symmetry. The X-ray structure factor (2·2) therefore now implies many more details of both electronic charge distribution and thermal motion than are possible in the diamond structure. With this complexity, accurate neutron experiments become attractive since they allow us to study structural features free of uncertainty regarding electronic distributions. In effect, the neutron point atom characteristic allows us to perform different charge density studies on fluorite compounds. These are *nuclear* charge density studies, in other words studies of the smearing functions $t_j(\mathbf{r})$ which summarize the effects in Bragg scattering caused by vibrational excursions about the $\mathbf{r}_{e,j}$ which we know from symmetry.

The general features we expect to find in accurate neutron structure factors emerge when (2·8) is written in the form appropriate to fluorite structures. This is:

$$\left.\begin{array}{ll}
\text{(i)} & F(\mathrm{S}) = 4\bar{b}_{\mathrm{X}}T_{c,\mathrm{X}}(\mathrm{S}) + 8\bar{b}_{\mathrm{Y}}T_{c,\mathrm{Y}}(\mathrm{S})\,, \\
 & \qquad\qquad (h+k+l)=4n \\
\text{(ii)} & F(\mathrm{S}) = 4\bar{b}_{\mathrm{X}}T_{c,\mathrm{X}}(\mathrm{S}) - 8\bar{b}_{\mathrm{Y}}T_{c,\mathrm{Y}}(\mathrm{S})\,, \\
 & \qquad\qquad (h+k+l)=4n+2 \\
\text{(iii)} & \left\{\begin{array}{l}
F(\mathrm{S}) = 4\bar{b}_{\mathrm{X}}T_{c,\mathrm{X}}(\mathrm{S}) - 8\bar{b}_{\mathrm{Y}}T_{a,\mathrm{Y}}(\mathrm{S})\,, \\
\qquad\qquad (h+k+l)=4n+1 \\
F(\mathrm{S}) = 4\bar{b}_{\mathrm{X}}T_{c,\mathrm{X}}(\mathrm{S}) + 8\bar{b}_{\mathrm{Y}}T_{a,\mathrm{Y}}(\mathrm{S})\,, \\
\qquad\qquad (h+k+l)=4n-1
\end{array}\right.
\end{array}\right\} (3·10)$$

The O_h site symmetry dictates that $T_{a,\mathrm{X}}(\mathbf{S})=0$ but a non-zero $T_{a,\mathrm{Y}}$-factor is permitted by the T_d symmetry of the anions Y. We see that the effects of this factor should appear in accurate structure factors for the odd-index reflexions, and this feature of these reflexions provides an immediate contrast with the normal structure factor formalism involving harmonic vibration theory. The harmonic treatment requires that both $T_{c,\mathrm{X}}(\mathbf{S})$ and $T_{c,\mathrm{Y}}(\mathbf{S})$ have isotropic Gaussian forms and that $T_{a,\mathrm{Y}}(\mathbf{S})=0$, in which case the odd-index structure factors should have isotropic behaviour governed only by cation scattering. This behaviour implies that different odd-index reflexions with a common scattering angle should have identical intensities. Thus, detailed study of such reflexions should give the best indications of failure of the harmonic formalism to account for experimental observations.

This failure has been evident for quite some time as a result of careful experiments conducted at Harwell by Dr B.T.M. Willis and colleagues on UO_2 (Willis, 1963*a*,*b*; Pryor, Rouse & Willis, 1968), CaF_2 (Willis, 1965) and, most recently, BaF_2 (Cooper, Rouse & Willis, 1968). The measurements on BaF_2 are particularly comprehensive, extending over the range 20–600°C, and their interpretation within the framework of (3·10) has produced important information on anharmonic vibrational behaviour.

The development of (3·10) in detail follows lines very similar to those associated with (3·1) for diamond, except that our concern now is with the smearing functions $t_j(\mathbf{r})$. The isotropic Gaussian smearing function of harmonic theory is the starting point, and a convenient general form for $t_j(\mathbf{r})$ is obtained by multiplying this form by an expansion in powers of the displacement of the ion from its equilibrium position (Dawson, Hurley & Maslen, 1967). To the fourth order of displacements, this gives

$$t_j(\mathbf{r})=\bar{t}_{c,j}(r)+\delta t_{c,j}(\mathbf{r})+t_{a,j}(\mathbf{r})\ (j=\mathrm{X},\mathrm{Y}) \tag{3·11}$$

where

$$\bar{t}_{c,j}(r)=N_j\exp\{-(x^2+y^2+z^2)/2\sigma_j^2\}$$
$$\delta t_{c,j}(\mathbf{r})=\bar{t}_{c,j}(r)\ \{C_j(x^4+y^4+z^4)+D_j(x^2y^2+y^2z^2+z^2x^2)\}$$
$$t_{a,j}(\mathbf{r})=\bar{t}_{c,j}(r)A_jxyz\ .$$

The parameters σ_j, A_j, C_j, D_j determine the detailed shape of $t_j(\mathbf{r})$, N_j ensures that $t_j(\mathbf{r})$ is normalized, $t_{a,\mathrm{X}}(\mathbf{r})=0$ by the O_h symmetry. Just as with (2·7), the transform $T_j(\mathbf{S})$ can be written as

$$T_j(\mathbf{S})=\bar{T}_{c,j}(S)+\delta T_{c,j}(\mathbf{S})+iT_{a,j}(\mathbf{S})\ , \tag{3·12}$$

but now there is some complication in the $\bar{T}_{c,j}$ component ensuing from the $\delta t_{c,j}$ component of $t_j(\mathbf{r})$ (see Dawson, Hurley & Maslen, 1967). A much simpler result occurs if we ignore the quartic terms of (3·11), and this case leads to

$$\left.\begin{aligned}&\bar{T}_{c,j}(S)\equiv\bar{T}^h_{c,j}(S)=\exp\{-\bar{B}_jS^2/4\}\ ,\ \ \bar{B}_j=8\pi^2\sigma_j^2\\&T_{a,j}(\mathbf{S})=-(\bar{B}_j/4\pi a)^3\bar{T}^h_{c,j}(S)A_jhkl\ ,\end{aligned}\right\}\tag{3·13}$$

where a is the linear unit-cell dimension, h, k and l are the Miller indices of any S, and we can identify the σ_j^2 parameter with $\langle u_j^2\rangle$, the harmonic mean square displacement parameter. The T_a factor exists only when j refers to the anion Y.

The explicit nature of $T_{a,j}(\mathbf{S})$ makes it clear how accurate odd-index neutron structure factors should deviate from the harmonic predictions. The $4n+1$ values should be greater and the $4n-1$ values smaller than harmonic prediction, with the departures varying for each reflexion according to the size of the index product hkl involved. A key group of reflexions is the common-angle trio 755, 771 and 933 with index products $+175$, -49 and -81, whose intensities should be such that $755>771>933$. This trend is shown quite strikingly by the BaF_2 experiments where the ratio $I(755)/I(933)$ varies from about 1·15 at 20°C to about 2·4 at 600°C.

Data analysis in terms of (3·13) thus involves two conventional parameters $\bar{B}_\mathrm{X}$ and $\bar{B}_\mathrm{Y}$ and the anharmonic parameter A_Y. The predictions of (3·10) for structure factors at various temperatures can then be assessed very simply by considering the even-index data separately from the odd-index data. The former data can reflect only centrosymmetric vibrational effects and thus, in the harmonic treatment, just the conventional parameters $\bar{B}_j$ of (3·13). As found earlier for CaF_2 and UO_2 (see Dawson, Hurley & Maslen, 1967), so it is found for BaF_2 (see Cooper, Rouse & Willis, 1968) that these two parameters are quite adequate to interpret the even-index data. Consistently, the crystallographic R value for these BaF_2 reflexions is ~1% at all temperatures. The odd-index situation is quite different when harmonic interpretation is attempted in terms of just $\bar{B}_\mathrm{X}$. The resultant R values for these BaF_2 reflexions now rise rapidly for data at higher tempera-

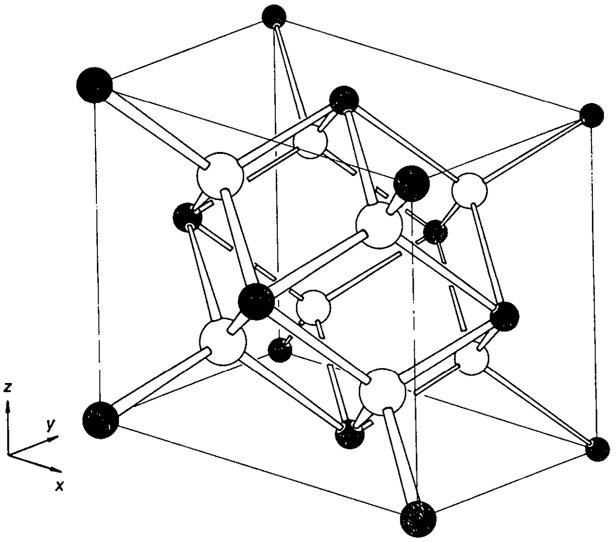


Fig. 4. The fluorite structure for XY_2 compounds. The cations X are the full circles.

tures, varying quite smoothly from about 2·5% at 20 °C to about 11·5% at 600 °C. This is consistent with the expectations of (iii) of (3·10), and the introduction of the extra A_Y parameter immediately allows one to achieve R values which, like those for the even-index data, are consistently $\sim 1\%$ at all temperatures. It is thus evident that all BaF_2 data, when properly analysed, give equal indications of reliability in measurement. The results for BaF_2 yielded by such analysis are typified* by the contents of Figs. 5 and 6. Fig. 5 shows $\bar{B}_j$-values increasing with temperature in accord with normal expectations, and Fig. 6 shows the variation of the A_F parameter with temperature. The lines in the Figures will be discussed below.

It is of interest to consider how we can convert these experimental parameters into some form of 'more basic' information. An attractively simple method for reinterpreting these parameters is to consider them as the outcome of effective one-particle potential fields $V_j(\mathbf{r})$ experienced by the ions in the (small) vibrational excursions about their $\mathbf{r}_{e,j}$. In this approach, which is essentially all that can be done consistent with the version of thermal vibration that we see in Bragg scattering, we write $V_j(\mathbf{r})$ in the form analogous to $t_j(\mathbf{r})$ of (3·11) as (Dawson, Hurley & Maslen, 1967)

$$V_j(\mathbf{r}) = \bar{V}_{c,j}(r) + \delta V_{c,j}(\mathbf{r}) + V_{a,j}(\mathbf{r}) \quad (j = \mathrm{X}, \mathrm{Y})$$

where (3·14)

$$\bar{V}_{c,j}(r) = V_{0,j} + \tfrac{1}{2}\alpha_j(x^2+y^2+z^2)$$

$$\delta V_{c,j}(\mathbf{r}) = \gamma_j(x^4+y^4+z^4) + \varepsilon_j(x^2y^2+y^2z^2+z^2x^2)$$

$$V_{a,j}(\mathbf{r}) = \beta_j xyz\,,$$

where the $\alpha, \beta, \gamma, \varepsilon$ parameters define the $V_j(\mathbf{r})$ and again $V_{a,\mathrm{X}} = 0$ by the O_h site symmetry. Classical statistical mechanics relates $V_j(\mathbf{r})$ with $t_j(\mathbf{r})$ as

$$t_j(\mathbf{r}) = N_j \exp\{-V_j(\mathbf{r})/k_BT\}\,, \qquad (3·15)$$

where k_B is Boltzmann's constant, and, if the cubic and quartic terms of (3·14) are small, we then have

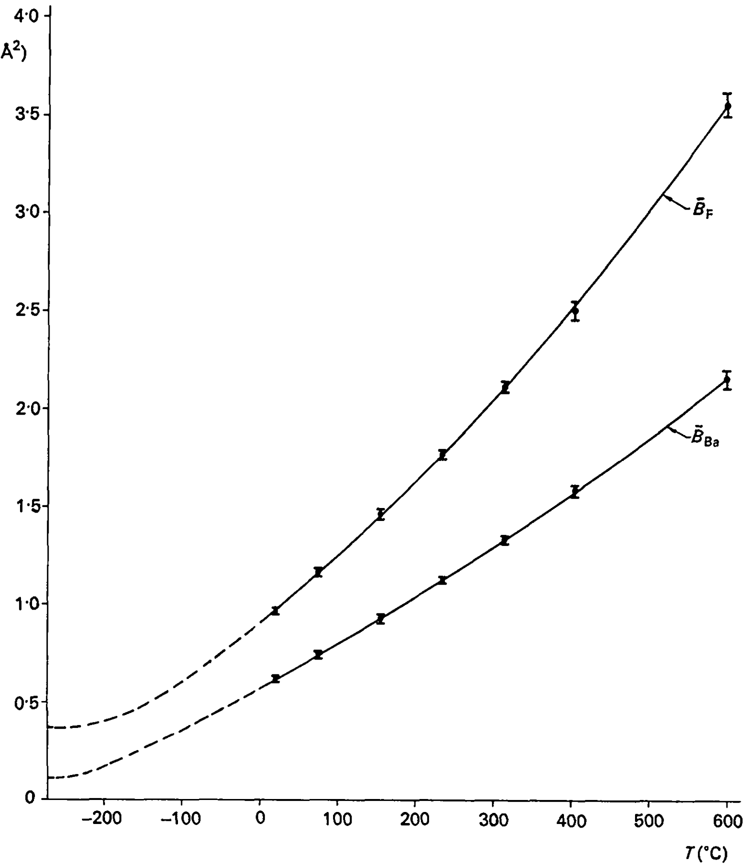


Fig. 5. Estimates of $\bar{B}_{Ba}$ and $\bar{B}_F$ in BaF_2 at various temperatures given by preliminary analysis (Dawson, 1967*e*) of the extensive neutron experiments reported and more completely analysed elsewhere by Cooper, Rouse & Willis (1968). See the footnote in the text. The lines relate to equation (3.17).

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* The $\bar{B}_j$- and A_Y-values shown in Figs. 5, 6 are *not* those obtained by Cooper, Rouse & Willis (1968) after applying detailed corrections for perturbations associated with thermal diffuse scattering (Cooper & Rouse, 1968) and extinction. The values shown are from earlier analysis (Dawson, 1967*e*) before corrections for these perturbations had been applied: they should not be construed as the final quantitative results for BaF_2.

$$\sigma_j^2 \equiv \langle u_j^2 \rangle = k_B T/\alpha_j\,,\ A_j = -\beta_j/k_B T\,,$$
$$C_j = -\gamma_j/k_B T\,,\ D_j = -\varepsilon_j/k_B T\,. \quad (3\cdot16)$$

Since quartic terms were neglected by operational use of (3·13), the principal interest of (3·14) and (3·16) lies in the α_j and β_{Y}.

The classical basis of the relations (3·16) is evident in their unrealistic predictions at $T=0\,°\mathrm{K}$: they predict zero values for the $\bar{B}_j$ so that no account is being taken of zero point motion, and they predict infinite values for A_j *etc.* Both these deficiencies are rectified by using a quantum rather than a classical treatment, and the quantum relation between $\bar{B}_j$ and α_j follows from the results of Bloch (1932). Instead of the relation in (3·16), we then have

$$\langle u_j^2 \rangle_T = [(8\pi^2 m_j \nu_j^T/h) \tanh (h\nu_j^T/2k_B T)]^{-1} \quad (3\cdot17)$$

with

$$\nu_j^T = (2\pi)^{-1}(\alpha_j^T/m_j)^{1/2}\,,$$

where h is Planck's constant, m_j is the mass of the ion, α_j^T is the 'force constant' of $\bar{V}_j(r)$ in (3·14) at any T, and ν_j^T is the resultant characteristic frequency at any T. At high temperatures where $k_B T \gg h\nu_j^T$, we see that (3·17) converges to the classical result (3·16), while at $T=0\,°\mathrm{K}$ we have

$$\left.\begin{aligned}\langle u_j^2 \rangle_0 &= (h/4\pi)\,(\alpha_j^0 m_j)^{-1/2}\\ \bar{B}_{j,0} &= 2\pi h(\alpha_j^0 m_j)^{-1/2}\,.\end{aligned}\right\} \quad (3\cdot18)$$

The effects of zero point motion in the $\bar{B}_j$ of experiment are now included, and the lines of Fig. 5 show the $\bar{B}_j$-behaviour predicted by (3·17) for the two ions in $\mathrm{BaF_2}$.

The corresponding relation between A_{F} and β_{F} is more difficult. Strictly, we need the quantum version of the smearing function of a three-dimensional isotropic harmonic oscillator as perturbed by a cubic anharmonic component of T_d symmetry: the precise form of this tetrahedral perturbation is what we need for proper association with Bloch's result in (3·17). In the absence of this information, we can approach the relation we require *via* the results provided by Reitan (1958) for the smearing function of the one-dimensional harmonic oscillator as perturbed by a cubic anharmonic component. This provides the essential features (Dawson, 1969*a*) of the relation we desire between A_{F} and β_{F}, except for a minor ambiguity introduced by the attempt to adapt the one-dimensional results to the three-dimensional T_d situation. Abbreviating ν_j^T

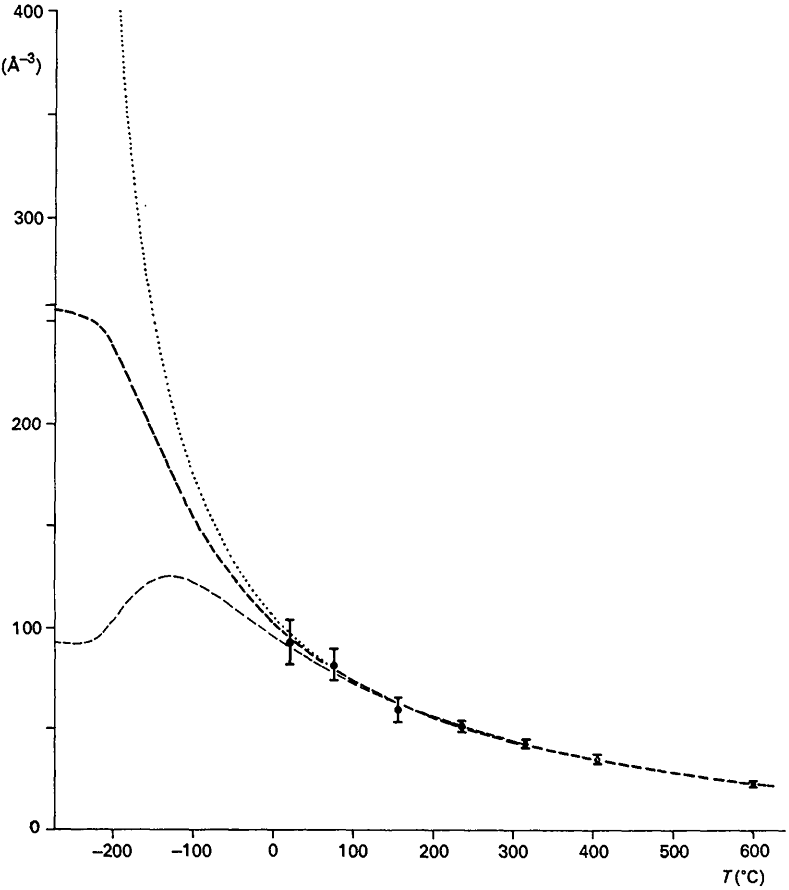

Fig. 6. Estimates of A_{F} in $\mathrm{BaF_2}$-based on the same analysis as that relevant to Fig. 5. The lines relate to equations (3·16), (3·19) and (3·20).

of (3·17) to simply ν_j, the required result is then best written as

$$A_j^T = -\beta_j^T\{\tanh(h\nu_j/2k_BT)\,.\,2/h\nu_j\}\times[\nu_j,T]\,, \quad (3{\cdot}19)$$

where

$$[\nu_j,T]=\frac{1+10\exp\{-h\nu_j/k_BT\}+\exp\{-2h\nu_j/k_BT\}}{3(1+\exp\{-h\nu_j/k_BT\})^2}\,, \quad (3{\cdot}19a)$$

(3·19*a*) being the part whose relevance to T_d symmetry is not certain. No problem exists at high temperature where $h\nu_j \gg k_BT$, for then all parts of (3·19) converge to the classical result $A_j=-\beta_j/k_BT$ given earlier. The term $[\nu_j,T]$ enters only as the temperature falls: this is shown most clearly by the results at $T=0$°K that follow according to whether we (*a*) ignore (3·19*a*) by setting it to unity or (*b*) include it. The results are then

$$(a)\ A^0=-2\beta_j/h\nu_j^0\,,\quad (b)\ A^0=-2\beta_j/3h\nu_j^0\,. \quad (3{\cdot}20)$$

The two possibilities for the behaviour of A_j with temperature lead to the broken lines in Fig. 6.

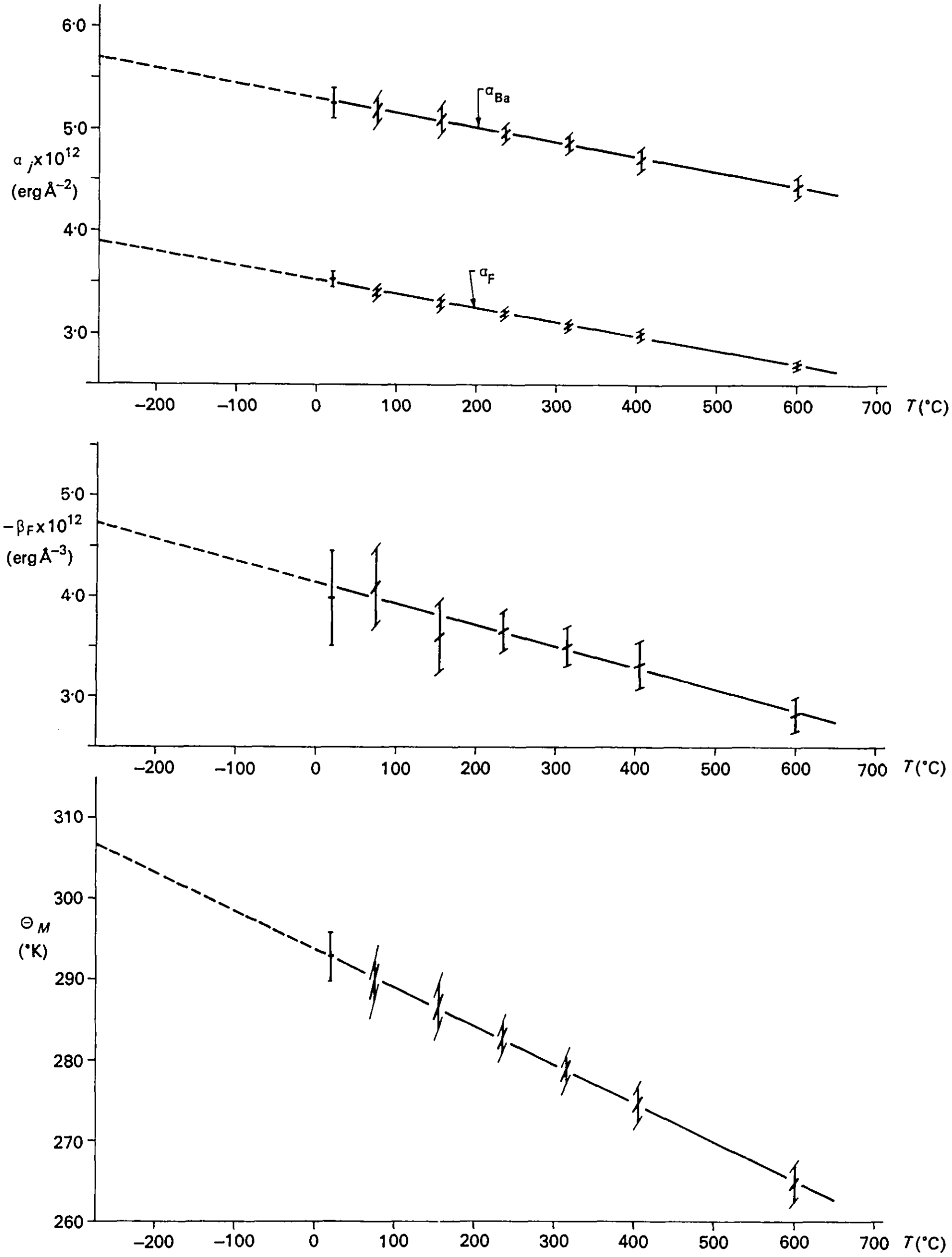

Fig. 7. Conversion of the experimental values of Figs. 5 and 6 into estimates of the α_j and β_F parameters of the text. The lower part of the Figure gives the values of Θ_M which correspond to the $\bar{B}_j$ parameters of Fig. 5.

These α- and β-considerations enable us to reinterpret the $\bar{B}$ and A parameters obtained directly from the experimental data. Fig. 7 shows the result of converting the parameters of Figs. 5 and 6 into α_j^T and β_j^T form by use of (3·17) and (3·19) (but ignoring (3·19*a*) in the latter), together with the result of re-expressing the $\bar{B}_j$ parameters as values of the Debye Θ_M at various temperatures. Note however that the results of Fig. 7 also involve the considerations in the footnote (p. 19). The results of Fig. 7 show a minor dependence on temperature which, as Willis (1968) has discussed, accords with 'quasi-harmonic' expectations. In their final analysis of BaF_2, Cooper, Rouse & Willis (1968) show that their estimates of the α and β parameters are consistent with a Grüneisen γ of value 2·1.

It is clear that accurate neutron structure factors of fluorite compounds enable a significant amount of quite detailed structural information to be derived. The BaF_2 experiments are of particular interest since they incorporate extensive considerations of extinction and thermal diffuse scattering. The results from this one system show in a quite striking way the profit to be gained from accurate structure factors.

(3) *Magnesium oxide*

MgO has the classic alkali halide (NaCl) structure which is cubic and centrosymmetric: the atomic positions are again dictated by symmetry so that the $\mathbf{r}_{e,j}$ are known, and this time both ions have common centrosymmetric (O_h) site symmetry. This structure has none of the non-centrosymmetric atomic features which we have discussed for the diamond and fluorite structures. At most, accurate structure factors of MgO can reflect only spherical and (possibly) other centrosymmetric features in the electronic charge densities and thermal smearing functions of the two ions. On the evidence of the neutron studies on fluorite compounds, we may safely assume Gaussian harmonic character for the smearing functions here, so that only the electronic charge densities assume significance when we have accurate structure factors for MgO.

The ionic character of MgO then focuses attention on the detailed nature of the anion of this compound. Within the Hartree–Fock (H.F.) approximation, calculations for O^{2-} suggest that this anion is unstable in the free state, and Clementi & McLean (1964) have shown that a stable 'solution' can only be forced when unsatisfactory constraints are imposed to assist convergence in this H.F. calculation. Their solution involves an extremely diffuse $2p$ radial function, and their version of O^{2-} can be usefully summarized for our discussion by the value $\langle r^2\rangle_{\text{ion}} = 61{\cdot}9_7$ (a.u.)^2 where $\langle r^2\rangle_{\text{ion}}$ is the mean square radius of the ionic charge distribution. The existence of O^{2-} in MgO thus implies that this ion is stabilized by lattice forces which are, of course, absent for the free state version. Watson (1958) has investigated H.F. versions of O^{2-} associated with stabilizing potential wells of +1 and +2 charge. The two resultant versions are naturally different in detail, but both show the essential feature that the stabilized ion is materially less diffuse than the free state 'version': the values of $\langle r^2\rangle_{\text{ion}}$ are now $27{\cdot}5_3$ and $24{\cdot}7_3$ (a.u.)^2 for the +1 and +2 calculations respectively. More recently, Yamashita (Togawa, 1965; Tokonami, 1965) has adopted Watson's +1 results for the $1s$ and $2s$ functions to calculate the $2p$ function of O^{2-} in MgO from considerations of Madelung potential and exchange interactions with the Mg^{2+} ions. Yamashita's version of O^{2-} is still more contracted than either of Watson's, and his version corresponds to $\langle r^2\rangle_{\text{ion}} \sim 20{\cdot}9$ (a.u.)^2. In more detail, the versions of O^{2-} calculated by Clementi & McLean (C–M), Watson [W(1) and W(2)] and Yamashita (Y) have the characteristics given below in (3·20) for one-electron mean square radii:

$$\left.\begin{array}{lllll} & \langle r^2\rangle_{1s} & \langle r^2\rangle_{2s} & \langle r^2\rangle_{2p} & \langle r^2\rangle_{\text{ion}} \\ \text{C–M} & 0{\cdot}0531 & 1{\cdot}7513 & 9{\cdot}7266 & 61{\cdot}97 \\ \text{W(1)} & 0{\cdot}0530 & 1{\cdot}8353 & 3{\cdot}9590 & 27{\cdot}53 \\ \text{W(2)} & 0{\cdot}0530 & 1{\cdot}8645 & 3{\cdot}4828 & 24{\cdot}73 \\ \text{Y} & (0{\cdot}0530) & (1{\cdot}8353) & \sim 2{\cdot}85 & \sim 20{\cdot}9 \end{array}\right\} \quad (3{\cdot}20)$$

This problem of O^{2-} in MgO has prompted several careful X-ray studies of this compound in recent years, and structure factor estimates have been reported by Burley (1965), Togawa (1965), and Raccah & Arnott (1967) in the literature. These three studies have been discussed extensively by their authors, who have considered both the reliability of their respective structure factor estimates and also the conclusions that can be drawn regarding the relative merits of the Watson and Yamashita models. Rather different claims are made by these authors, and it is difficult for an outsider to obtain a clear picture of how these three investigations fit together since the three sets of data have not only been analysed but also scaled in different ways. A systematic survey, consistently applied to all three experiments, is required and we summarize here the results of such a survey made recently (Dawson, 1969*b*) by considering the structure factors in the following terms.

Including anomalous dispersion effects not previously introduced explicitly here, the structure factors of MgO can be written as

$$F(\mathbf{S}) = 4\{[\vec{f}_{d,\mathrm{A}}(S) + \delta f_{c,\mathrm{A}}(\mathbf{S})]T^{\text{har}}_{c,A}(S) \pm [\vec{f}_{d,\mathrm{B}}(S) + \delta f_{c,\mathrm{B}}(\mathbf{S})]T^{\text{har}}_{c,B}(S)\}\,, \quad (3{\cdot}21)$$

where + refers to even index data, − to odd index data, A and B differentiate the two ions, and the thermal factors have the familiar isotropic Gaussian forms of (3·13). The dispersion-affected components $\vec{f}_{d,j}(S)$ have the forms

$$\vec{f}_{d,j}(S) = \vec{f}_{c,j}(S) + \Delta f_j'' \text{ with } \vec{f}_{c,j}(S) = f^0_{c,j}(S) + \Delta f_j' \quad (3{\cdot}22)$$

if we regard the dispersion corrections $\Delta f_j'$, $\Delta f_j''$ as invariant with angle. The component $f^0_{c,j}(S)$ is then the part related to the spherical charge distribution through the familiar Fourier transform relation (3·6). If we now (*a*) ignore the non-spherical components $\delta f_{c,j}(\mathbf{S})$ of (3·21) possible for the two ions, and (*b*) assume equal amplitudes of vibration for the ions, then (3·21) can be rewritten as

$$|F(\mathbf{S})| = 4\bar{T}_c^{\text{har}}(S)\,\{[\bar{f}_{c,\mathrm{A}}(S) \pm \bar{f}_{c,\mathrm{B}}(S)]^2 + (\Delta f''_A \pm \Delta f''_B)^2\}^{1/2}\,, \quad (3\cdot23)$$

where

$$\bar{T}_c^{\text{har}}(S) = \exp\{-\bar{B}S^2/4\}\,,\ \textit{i.e.}\ \bar{B}_\mathrm{A} = \bar{B}_\mathrm{B} \equiv \bar{B}\,.$$

We shall return to assumption (*b*) later. The form of (3·23) is such that, given $\bar{f}^0_{c,j}(S)$ values and $\Delta f'_j$- and $\Delta f''_j$-estimates, we can apply 'Wilson plot' considerations to examine the various sets of data (by least squares) for the optimum values of scale factor (k) and $\bar{B}$ that apply when we use the $\bar{f}^0_{c,j}(S)$ that refer to different models for the charge distribution of O^{2-}. Barnea (1966) has given the values $\Delta f'_{\mathrm{Mg}} = 0\cdot16$, $\Delta f''_{\mathrm{Mg}} = 0\cdot17$, $\Delta f'_{\mathrm{O}} = 0\cdot04_9$, $\Delta f''_{\mathrm{O}} = 0\cdot03_2$, and Wagenfeld & Guttman (1967) have reported (for the dipole component) $\Delta f'_{\mathrm{Mg}} = 0\cdot19_1$, $\Delta f''_{\mathrm{Mg}} = 0\cdot17_3$; all are for Cu radiation.

Results of the survey (Dawson, 1969*b*) are summarized in Figs. 8 and 9, where we compare values of $\bar{B}$, k, $r\ (= \Sigma\, w\Delta^2)$, the crystallographic R value, and the Debye Θ_M corresponding to the $\bar{B}$ value, which follow when we use (3·23) to treat the $|F(\mathbf{S})|$-estimates of Burley, Togawa and Raccah & Arnott in terms of different sets of $\bar{f}^0_{c,j}$-values corresponding to different interpretations of the total charge distribution in MgO. The heavy circles refer to Barnea's estimates of the anomalous terms and the light circles to Wagenfeld's. The codes *N*, *S*, *D*, W(1) *etc.* in the Figures indicate the different models adopted in the survey here. *N* denotes the neutral atoms Mg and O as described in the H.F. tabulation of Clementi (1965). *S* denotes the single ions Mg^+ and O^-, again from Clementi's tabulation. *D* refers to double ions, Mg^{2+} from the same tabulation and O^{2-} from Clementi & McLean. All other models also refer to double ions, with Mg^{2+} always as in *D* but combined with various models of the O^{2-} charge distribution. W(1), W(2) and Y represent the use of the Watson and Yamashita versions discussed above, and the remaining three versions used for O^{2-} are hypothetical and based on the following considerations. Y(C) is the modification of Yamashita's model that follows if we replace his choice of Watson's +1 result for the 2*s* function by the 2*s* function of O^{2-} as calculated by Clementi & McLean. As seen from

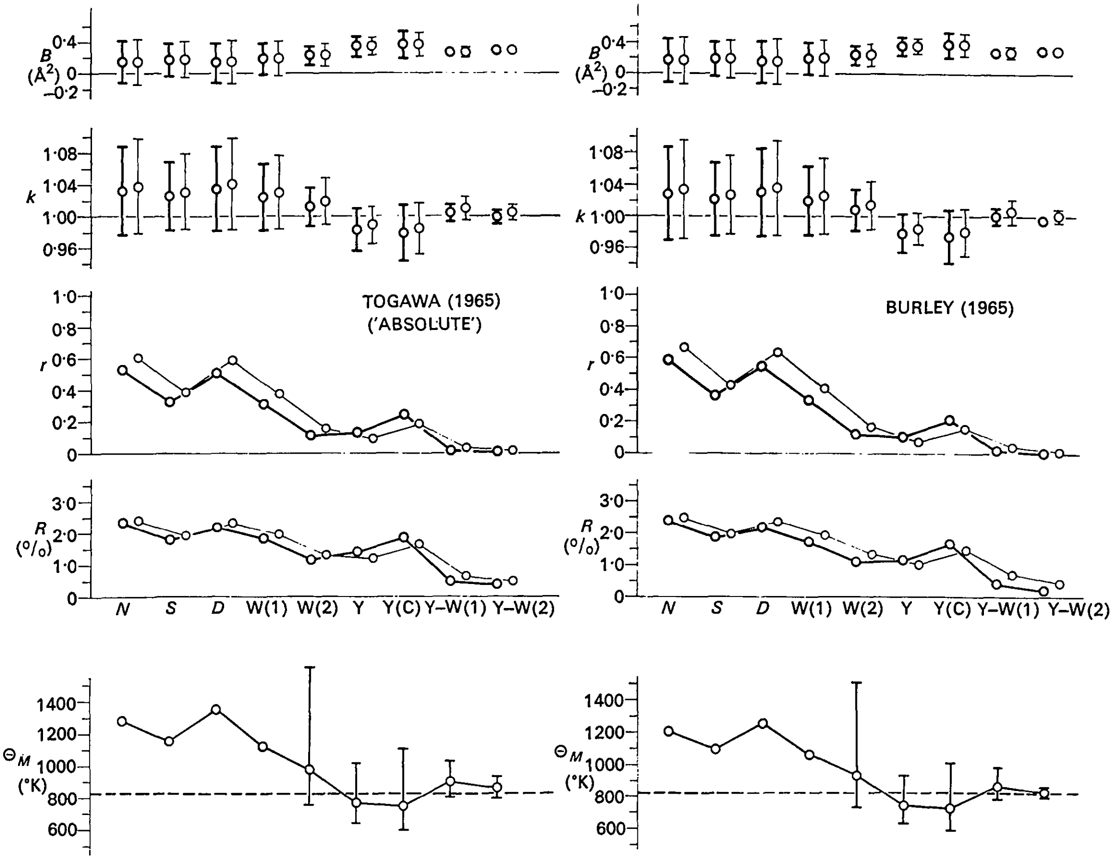

Fig. 8. The results of the survey (Dawson, 1969*b*) of MgO data discussed in the text. Togawa 'absolute' involves the *F* data as listed by Togawa from his absolute scaling experiment. The Burley *F* data used here were based on direct reduction of his reported intensities.

(3·20), this modification produces a slightly more contracted ion than Yamashita's and it has $\langle r^2\rangle_{\text{ion}} \sim 20{\cdot}7$ (a.u.)^2. Y–W(1) results if we retain Yamashita's 1*s* and 2*s* functions [which are those of W(1)] but describe the six 2*p* electrons half in terms of Yamashita's and half in terms of Watson's +1 results. Thus, Y–W(1) is the mean of the charge distributions as calculated by W(1) and Y, and its $\langle r^2\rangle_{\text{ion}}$-value, by (3·20), is $\sim 24{\cdot}2$ (a.u.)^2. Y–W(2) represents a more extensive modification. This combines Watson's +2 results for the 1*s* and 2*s* functions with the mean 2*p* distribution given by taking equal parts of the W(2) and Y versions of the 2*p* function. In this case, $\langle r^2\rangle_{\text{ion}} \sim 22{\cdot}8$ (a.u.)^2 and, in more detail, we see from (3·20) that the '2*s*' part of Y–W(2) is more expanded than that of Y–W(1) although the opposite applies to the '2*p*' parts of Y–W(2) and Y–W(1). It is better, however, to regard Y(C), Y–W(1) and Y–W(2) simply as three more possibilities for the charge distribution of O^{2-} as it exists in MgO. The lack of any conventional theoretical basis for these possibilities is no impediment to our using them, for it is clear that Watson's and Yamashita's calculations can only be regarded as crude estimates of the actual situation prevailing for O^{2-} in MgO.

Of more possible concern is the common $\bar{B}$ assumption associated with using (3·23) for this survey. However, this is not seriously violated when we consider the individual $\bar{B}_j$-values which correspond to the 'shell model' parameters used by Peckham (1967) in his inelastic neutron scattering study of the phonon dispersion relations of MgO. Peckham's parameters yield theoretical estimates in quite good agreement with his experimental results, and the conversion of these parameters to $\bar{B}_j$ form gives (Sanger, 1968) the estimates $\bar{B}_{\text{Mg}} = 0{\cdot}28$ and $\bar{B}_{\text{O}} = 0{\cdot}34$ Å^2 at 300°K. The corresponding Debye Θ_M is then 821°K, a value which is in good agreement with the estimates of Θ_M given by Yates (1966) from thermodynamic data and by Baldwin & Tompson (1964) from their X-ray studies of MgO at various temperatures. Pending better $\bar{B}_j$-estimates from parameters which better reproduce Peckham's measurements, we may regard the common $\bar{B}$ assumption as the sensible starting point for our present purposes.

Figs. 8 and 9 show that quite striking changes occur when we examine the different experimental data by (3·23) for the various models. (We shall disregard the minor features which differentiate the F(S)-estimates labelled as Togawa 'absolute' and Togawa 'combined'

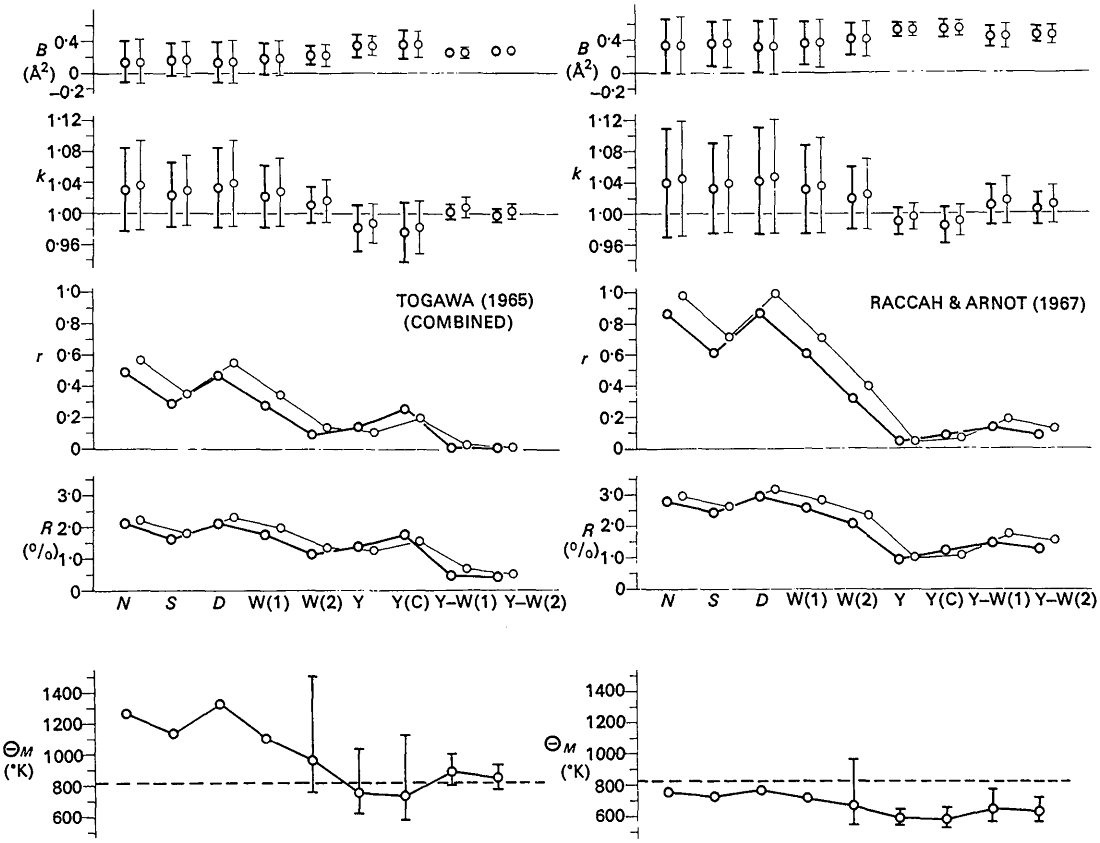

Fig. 9. Continuation of the survey on MgO. Togawa 'combined' here represents the use of his 'absolute' results for 111 and 200 in combination with the *mean* of the separate values he lists for the other reflexions from his absolute and relative experiments. The Raccah & Arnott F data used here were based on direct reduction of their reported intensities.

in these two Figures, and hereafter consider only the 'absolute' plot in Fig. 8; these refer to Togawa's measurements made in terms of an absolute scaling technique.) It is clear that the data of Togawa, Burley and Raccah & Arnott concur on the trends in r and R which arise when we use the models N, S, D, W(1) and W(2) to determine the optimum values of k and $\bar{B}$. All show the same downward trend for these models but, thereafter, rather striking differences become evident among the three sets of data. We can summarize these differences in r, R and $\bar{B}$ form as follows for the models W(2), Y and Y–W(2).

	r	R (%)	$\bar{B}$ (Å^2)
Model W(2)			
Togawa	0·1115 (0·1546)	1·13 (1·28)	0·23 ± 0·12 (0·23 ± 0·14)
Burley	0·1224 (0·1694)	1·09 (1·33)	0·24 ± 0·13 (0·24 ± 0·15)
R. & A.	0·3211 (0·4004)	2·08 (2·34)	0·43 ± 0·20 (0·43 ± 0·22)
Model Y			
Togawa	0·1306 (0·0931)	1·40 (1·19)	0·34 ± 0·13 (0·34 ± 0·11)
Burley	0·1044 (0·0706)	1·15 (1·02)	0·36 ± 0·12 (0·36 ± 0·10)
R. & A.	0·0502 (0·0490)	0·95 (1·01)	0·54 ± 0·09 (0·54 ± 0·08)
Model Y–W(2)			
Togawa	0·0102 (0·0163)	0·37 (0·48)	0·28 ± 0·04 (0·28 ± 0·05)
Burley	0·0033 (0·0132)	0·20 (0·44)	0·30 ± 0·02 (0·30 ± 0·04)
R. & A.	0·0854 (0·1276)	1·28 (1·56)	0·48 ± 0·10 (0·48 ± 0·12)

The leading figures are the result of using Barnea's dispersion estimates for both atoms and those following (in brackets) are for Wagenfeld's estimates for Mg. All values above, together with the remainder underlying Figs. 8 and 9, arise from using (3·23) in least squares assigning equal weight to the nine lowest-angle F(S) of MgO. Completely analogous results, trends, *etc.* follow if the two lowest-angle reflexions 111 and 200 are given half weight in forming the least-squares normal equations.

It is evident that the results of Raccah & Arnott are in a different category from the others. Whereas these estimates can be best accounted for in terms of the Yamashita version of O^{2-}, all the others are in best accord with model Y–W(2). The support for Yamashita's model provided by Raccah & Arnott becomes extremely dubious, however, when we consider the Θ_M evidence of Figs. 8 and 9, where the horizontal broken line indicates $\Theta_M = 821\,°$K discussed above. Raccah & Arnott's estimate of Θ_M from model Y is *ca.* 200 °K too low, and this is quite at variance with what we should expect from subsidiary perturbations in their F(S) introduced by neglect of thermal diffuse scattering (TDS) effects: neglect of these effects would tend to reduce their $\bar{B}$-estimate and thus raise their Θ_M-estimate above that appropriate when TDS has been corrected for. The $\bar{B}$- and Θ_M-estimates from both Togawa and Burley for model Y–W(2) are, on the other hand, quite consistent with these TDS considerations so that both these sets of data are behaving in accord with expectation. Further, we note that the application of Y–W(2) to Togawa's 'absolute' measurements yields a scale factor which differs only fractionally from the unit value implicit if Togawa's absolute technique had been exact.

The assembled evidence argues strongly that Raccah & Arnott's experiment cannot be regarded as having given reliable estimates of the true structure factors of MgO: there is some serious angle-dependent error obviously afflicting their measurements. By contrast, no such error is apparent in either Togawa's or Burley's experiments. Indeed, these two experiments appear to have produced F(S)-estimates which are in remarkably close agreement, a feature which is not apparent from the way these workers have tabulated their results in their respective papers. This agreement is most interesting considering the quite different methods of specimen preparation employed in the two experiments.

Regarding the intrinsic merit of model Y–W(2) for O^{2-} in MgO, we must be more cautious since this survey has been based on (3·23) rather than (3·21). With reservations, however, we see that this model does not contravene physical expectations based on the mean square ionic radii of (3·20) for the models W(2) and Y. The results of this survey suggest that only very extensive theoretical calculations of charge distribution in MgO will suffice to interpret accurate structure factors for this most interesting compound.

(4) *Hexamethylenetetramine*

The crystal structure of hexamethylenetetramine (HMT) is another instance of cubic symmetry, but this system is very different from the simple inorganic systems discussed so far. The HMT structure is body-centred and polar, and it contains the molecules $N_4(CH_2)_6$ of T_d symmetry located about the origin and body-centre of the unit cell. This structure is much more complicated than the previous examples since here the $\mathbf{r}_{e,j}$ are not specified explicitly by symmetry considerations, although symmetry does impose certain constraints on the x, y and z components of the $\mathbf{r}_{e,j}$. Hence, the problem of interpreting the F(S) of this structure now encounters the difficulties of having to define where the atoms are located as well as how they are vibrating: HMT therefore embodies many of the familiar problems so common in analysing organic crystal structures with atoms in general positions. A major feature of this structure is that the HMT molecules move essentially as rigid bodies (again a common feature of organic systems), so that their total motional behaviour is the resultant of features which arise from rectilinear translational motion and features which arise from rocking or librational motion about the centre of inertia (here coincident with the centre of mass) of the molecule.

The occurrence of librational motion introduces material complications into accurate structure analysis, as we know from the important early work of Cruickshank (1956*a*) which has since been elaborated by Pawley (1964, 1968) and Schomaker & Trueblood (1968). The essential difficulty here is that the Gaussian vibration ellipsoid formalism for thermal motional effects breaks down when libration is an important feature of the atomic motions, and we see this breakdown evidenced in the need to apply 'libration corrections' (Cruickshank, 1956*b*, 1961) to the atomic positional coordinates generated by use of the Gaussian formalism. As we noted in § 2, we can summarize this difficulty in general terms by writing

$$F(\mathbf{S})\sim \sum_{j}\bar{f}_{c,j}(S)T^{h}_{c,j}(\mathbf{S})\exp\{2\pi i\mathbf{S}\,.\,\bar{\mathbf{r}}_j\}\,, \quad (3{\cdot}24)$$

indicating by the $\bar{\mathbf{r}}_j$ that the use of this formalism with its $T^{h}_{c,j}$-factors will not generate the equilibrium $\mathbf{r}_{e,j}$ of (2·2).

The evidence of libration is well established and characterized for HMT by the extensive studies of various sets of experimental data, collected at various temperatures, that have been made by Becka & Cruickshank (1963*a*,*b*) in terms of (3·24). HMT is a key structure for studying libration effects since the molecular symmetry obviates problems of correlation between translation and libration, and the **t**,**ω** tensor treatment of Cruickshank (1956*a*) holds without complication. Further, the cubic symmetry of the HMT crystal structure reduces the tensor treatment to two simple isotropic quantities t and ω, which refer respectively to the mean square amplitudes of isotropic translation and libration which characterize the total molecular rigid body motion. Becka & Cruickshank have established these amplitudes quite closely by their analysis of the various HMT data, and shown how the application of Cruickshank's 'libration correction' removes the apparent temperature dependence of the C–N bond length which appears to exist when direct use is made of the $\bar{\mathbf{r}}_j$ determined from (3·24). In addition, Cochran & Pawley (1964) have made an extensive lattice dynamical study of HMT and obtained **t** and **ω** estimates in close accord with those of Becka & Cruickshank for room temperature structure factors of HMT.

Much is thus already known about the structure of this compound, but the need remains to establish whether the formalism of (3·24) is really adequate for very detailed studies of this compound. Essentially, we require to examine the chain of simplification involved in proceeding from the generalized formalism of (2·2) to the operational version (3·24) before we can be confident that the latter is adequate for any detailed studies that may be contemplated when more accurate $F(\mathbf{S})$ data for HMT become available.

We can best consider this matter in the neutron scattering situation where no subsidiary f_j complications intervene. In this case, it transpires (Dawson, 1969*c*) that the structure factor for HMT can be written in the general form

$$F(\mathbf{S})=2\{\sum_{r}\bar{b}_r\sum_{s}T^{h}_{c,rs}(\mathbf{S})\delta T^{\mathrm{lib}}_{rs}(\mathbf{S}) \times \exp i[2\pi\mathbf{S}\,.\,\mathbf{r}_{rs}+\Phi_{rs}(\mathbf{S})]\} \quad (3{\cdot}25)$$

where r is the summation over different atom types (C, N, H) and s is the summation of the various subset members of an individual HMT molecule. We choose the one located about the unit-cell origin so that $|\mathbf{r}_{rs}|=r_r$ is simply the equilibrium distance of each atom-type from the origin. The elements of (3·25) have the form

$$T^{h}_{c,rs}(\mathbf{S}) = \exp\{-2\pi^2S^2[\langle U_r^2\rangle^{\parallel}\cos^2\Theta_{rs} + \langle U_r^2\rangle^{\perp}\sin^2\Theta_{rs}]\}\,, \quad (3{\cdot}26)$$

where

$$\langle U_r^2\rangle^{\parallel} = \langle U_r^2\rangle^{\parallel}_{\mathrm{r.b.}}+\langle u_r^2\rangle^{\parallel}_{\mathrm{int}}\ \textit{etc.} \quad (3{\cdot}26a)$$

$$\langle U_r^2\rangle^{\parallel}_{\mathrm{r.b.}} = \langle u^2\rangle_{\mathrm{trans}}+\langle u_r^2\rangle^{\parallel}_{\mathrm{lib}}\ \textit{etc.} \quad (3{\cdot}26b)$$

$$\langle u_r^2\rangle^{\parallel}_{\mathrm{lib}} = r_r^2(\langle\omega^2\rangle)^2\,,\ \langle u_r^2\rangle^{\perp}_{\mathrm{lib}}=r_r^2\langle\omega^2\rangle \quad (3{\cdot}26c)$$

and

$$\delta T^{\mathrm{lib}}_{rs}(\mathbf{S})= \exp\{2\pi^4S^4r_r^4(\langle\omega^2\rangle)^3\sin^2 2\Theta_{rs}\}\,. \quad (3{\cdot}27)$$

The angle Θ_{rs} is the angle between $\mathbf{r}_{rs}$ and **S**, so that (3·26) is simply the conventional Gaussian formalism for oblately spheroidal vibration referred, for each subset member, to the polar axis defined by $\mathbf{r}_{rs}$. We have assumed here that the internal vibration amplitudes $\langle u_r^2\rangle^{\parallel}_{\mathrm{int}}$ *etc.* have spheroidal character referred to these polar axes. This is convenient [although not essential (Dawson, 1969*c*)] as it allows the internal and rigid body amplitudes to be combined as in (3·26*a*). The rigid body amplitudes for each atom are seen from (3·26*b*), (3·26*c*) to depend on the two basic mean square displacement parameters $\langle u^2\rangle_{\mathrm{trans}}$ and $\langle\omega^2\rangle$ which are simply another notation for t and ω.

Within the exponential of (3·25), $\Phi_{rs}(\mathbf{S})$ can be written as

$$\Phi_{rs}(\mathbf{S})=\delta_{rs}(\mathbf{S})\Omega_{rs}(\mathbf{S})-\arctan\delta_{rs}(\mathbf{S}) \quad (3{\cdot}28)$$

where

$$\delta_{rs}(\mathbf{S})=2\pi Sr_r\langle\omega^2\rangle\cos\Theta_{rs}=2\pi\mathbf{S}\,.\,\mathbf{r}_{rs}\langle\omega^2\rangle \quad (3{\cdot}28a)$$

$$\Omega_{rs}(\mathbf{S})=2\pi^2S^2r_r^2\langle\omega^2\rangle\sin^2\Theta_{rs}\,. \quad (3{\cdot}28b)$$

Neglecting the $\delta T_{rs}^{\mathrm{lib}}$-factor which is of order $(\langle\omega^2\rangle)^3$, (3·25) can then be simplified to

$$F(\mathbf{S})=2\{\sum_r \bar{b}_r \sum_s T^h_{c,rs}(\mathbf{S}) \exp\,[2\pi i\mathbf{S}\,.\,\bar{\mathbf{r}}_{rs}(\mathbf{S})]\}\;, \quad (3{\cdot}29)$$

where

$$\bar{\mathbf{r}}_{rs}(\mathbf{S})=\mathbf{r}_{rs}[1-\langle\omega^2\rangle+\langle\omega^2\rangle\Omega_{rs}(\mathbf{S})]\;, \quad (3{\cdot}29a)$$

which is correct to order $(\langle\omega^2\rangle)^2$.

The key feature of (3·29) is the unusual parameter $\bar{\mathbf{r}}_{rs}(\mathbf{S})$, and its presence has three consequences. First, it means that each of the s members of a crystallographic subset will have, for every scattering vector $\mathbf{S}$, a magnitude $|\bar{\mathbf{r}}_{rs}(\mathbf{S})|$ which depends on the value of $\sin^2\Theta_{rs}$ that applies to each member of the subset. Second, it means that each such individual quantity varies from reflexion to reflexion according to the nature of S^2 associated with each $\mathbf{S}$. Third, it means that the variation will be the greater for outer atoms of HMT through the dependence on r_r^2. These are quite unusual features, and we see from (3·29*a*) that they arise from second-order effects in $\langle\omega^2\rangle$. If we could neglect these, then we could write (3·29*a*) as

$$\bar{\mathbf{r}}_{rs}(\mathbf{S})\sim\bar{\mathbf{r}}_{rs}=\mathbf{r}_{rs}(1-\langle\omega^2\rangle)\;, \quad (3{\cdot}29b)$$

in which case we could identify this relation with the $\bar{\mathbf{r}}$-parameter of (3·24). This would give a simple basis to the idea of 'libration correction', for we see that (3·29*b*) simply implies that the molecule appears shrunken inwards towards its centre, the shrinkage for each atom being $r_r\langle\omega^2\rangle$. Further, this first order argument would convert the $T^h_{c,rs}$-factors into the exact form associated with the original $\mathbf{t},\boldsymbol{\omega}$ treatment of Cruickshank (1965*a*).

Unfortunately, we cannot replace (3·29*a*) by (3·29*b*) unless very small libration amplitudes are involved (say $\langle\omega^2\rangle\sim7$ deg²), and this is not satisfied in HMT except at very low temperatures: at room temperature, $\langle\omega^2\rangle\sim44$ deg². Neglect of the unusual feature of (3·29) then means that the position parameters extracted by use of (3·24) must be viewed only as the resultants yielded by the operation of two sorts of averaging procedures, one over the different subset members and the other over the various $F(\mathbf{S})$ data being treated in terms of (3·24). The precise numerical character of these resultants will depend on the weighting, angular range and specific nature of the $F(\mathbf{S})$ being analysed in the conventional fashion, and now the idea of 'libration correction' takes on a quite new meaning. Among other things, it is not possible to compare parameters derived from different sets of experimental data unless it can be guaranteed that the same processes of averaging are relevant to the analyses of the different data sets.

The contrast between (3·29) and (3·24) has considerable implications for attempts to correlate parameters from neutron and X-ray studies as a preliminary to seeking the electron distribution information contained in the f-terms of the X-ray $F(\mathbf{S})$. Such a philosophy has great appeal, the philosophy being that neutron determination of vibrational and positional parameters opens the way to reliable X-ray electron distribution studies, and this philosophy is now being applied quite intensively to small organic molecular structures where libration effects are often quite prominent. Without challenging the philosophy itself, it would appear from the HMT formalism of (3·29) that the *practice* of this philosophy by data-analysis based on (3·24) may well introduce artefacts of a size not unlike the authentic features of electron distribution that this philosophy aims to seek out.

4. Conclusion

This discussion of the significance of accurate structure factors is limited in its coverage of the detailed structural information that appears to be now emerging from extended diffraction studies. Nevertheless, the examples quoted do serve to illustrate the two points of quite basic importance that must colour our approach to the general matter of accurate structure factors.

(*a*) If we do indeed happen to achieve accurate structure factor estimates, then we must ensure that their significance is not dissipated by subjecting them to analysis procedures which are too coarse to allow adequate resolution of the detailed structural information being sought. The obvious dangers here involve abuse of the 'spherical atom' model and the Gaussian ellipsoid harmonic rectilinear vibration model. The structures of diamond and fluorite provide interesting commentaries on the limitations of these models. Regarding the strategy of joint X-ray–neutron studies as a means of circumventing the 'spherical atom' limitations for detailed X-ray studies of molecular structures where libration effects are present, the structure factor of HMT sounds a useful warning that the combination of the Gaussian ellipsoid model with conventional structure factor formalism may seriously prejudice the outcome of ventures based on this joint strategy.

(*b*) The other point, perhaps of more immediate practical concern, is that of deciding between nominal precision and genuine accuracy achieved in structure factors in the light of all the difficulties and correction procedures that arise when we proceed from raw experimental data to final estimates of structure factors. The long chain of complication that is involved here is to be the main preoccupation of this meeting, and the subsequent discussions of TDS effects, extinction effects and multiple elastic scattering effects will clear our thoughts on how to treat adequately the perturbations which are introduced by such effects. It is clear, however, from the MgO survey and also the results for silicon, that we must exercise considerable care when trying to judge the ultimate structure factor accuracy achieved experimentally by reference to theoretical 'spherical atom' models that are too crude to provide definitive guidance on what has been the real outcome of careful experiment.

The whole aim of accurate experiment is, of course, to provide a useful commentary on detailed aspects of current theory of the solid state. At present, it appears that this aim can be implemented profitably only if we allow theory and experiment to interact in the manner illustrated by the discussion given in §§ 2 and 3.

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DISCUSSION

SCHOMAKER: Have you tested the introduction of the first anharmonic terms in the libration treatment of HMT and would this be more important for this type of molecule than in CaF_2, just as this effect in CaF_2 is greater than for diamond?

DAWSON: No. The present description involves treating rectilinear and libration motion by the harmonic approximation. Concerning anharmonic libration, I have gone no further than pondering on the possibilities. For anharmonic rectilinear motion, the development is elementary since the fluorite philosophy carries over straightforwardly because of site symmetry but, of course, here it is the whole molecule and not the single atom as in CaF_2. For the molecule, the problem in detail becomes more complicated since separability does not hold. One advantage of working in the harmonic approximation is that it is possible to eliminate your extra tensor due to site symmetry. Beyond the harmonic approximation, it is uncertain how much correlation comes in but my opinion is that, due to the restraint of tetrahedral site symmetry, it will probably not be large.

JEFFERY: Is it likely that atoms are sufficiently dipolar for neutron diffraction results to give something other than the centre of charge distribution which is obtained from X-ray studies particularly in the case of hydrogen?

DAWSON: Using spherical atom treatment on non-spherical atoms there is no guarantee, unless the non-sphericity is centric, that the centroid (XRD) will coincide with the nuclear position (N.D.) but the situations are sufficiently well characterized now to make it possible to anticipate what magnitude of differences would be involved in such investigations.

BRAGG: This, it seems to me, is the fine flowering of the first phase of the calculations concerning an atom which we thought we knew something about, making the result of calculation agree with the observations. Does the other way of presenting the comparison of theory and experiment, the difference Fourier, give us another angle on the same problem?

DAWSON: The difference Fourier is certainly a splendid method of visually presenting the results. There are, however, problems of interpretation of difference map features which are complicated by matters such as the normal notions of charges in the bonds. The other way, working directly with atomic scattering powers in the structure factors themselves, allows estimation of the influence of each of the non-spherical components to each structure factor. A Fourier or difference Fourier involves compounding all these aspects together in one distribution so that individual items are difficult to detect. Also, in cubic cases, multiplicity terms introduce further complications. However the Fourier illustration does give an estimate of overall magnitude valuable for comparisons in lower-symmetry structures.

HAMILTON: Concerning anharmonic terms referred to here in respect of fluorite systems, has any lattice dynamic work by inelastic neutron scattering been interpreted in terms of an anharmonic model and come up with numbers of the same order of magnitude of terms derived from the X-ray work?

DAWSON: I cannot answer but will pass the question to Professor Cochran.

COCHRAN: Sorry, I do not think I can give an answer. Some systems have been studied. UO_2 has been looked at fairly thoroughly. Some indications of anharmonicity are given by the widths of peaks but nothing has been done yet to give numbers of the type mentioned by Dawson.

ABRAHAMS: Can you offer comments on what would be the maximum amount of systematic error in the original diffraction data, F_{meas}, which could be tolerated before correlation produces unacceptable error in the anharmonic vibration terms, *e.g.* 10% error?

DAWSON: The essence of analysing the experimental measurements for this effect is governed by the nature of the temperature factor component with *hkl* dependence. Thus one can map the results in terms of reflexion type (*e.g.* $h^2+k^2+l^2=4n\pm1$) and their distribution in reciprocal space. If there are uncertainties in the observational data, this will show up when anharmonic predictions are atypically at variance with the experimental results.

This may be profitably illustrated by reference to the early stages of the BaF_2 neutron diffraction study. The trends pointed suspicion at the counting chain and much time was devoted to checking. It was shown that the counting chains were indeed 'on the blink' although only to the extent of a few per cent. The moral of this was that knowing what to look for gave a sharper criterion for judging the performance of the experimental equipment. Of course these are used as indications and actual defective operation must be decided by independent test. However, the example given indicates the importance of a profitable theory–experiment interaction.

COPPENS: You have successfully described the electron density of a diamond with your non-centric density thesis and can do this because diamond is highly symmetrical. Do you see any obvious way of extending your model to sites of lower symmetry?

DAWSON: This is very much a function of one's mathematical ability. I have never rated mine particularly highly but I can see what would have to be done and I think it could be extended. Are you thinking of $\sigma\pi$ bonding and this sort of separation, or of the degeneration to pseudo-trigonal symmetry? These things can be done, but it means a much more expansive version of components which must be included. The purely trigonometrical situation is reasonably comprehensible, as also are any deviations from this. Perturbations will arise but these can probably be handled.

You are asking whether you can continue to analyse the structure factors directly rather than through the intermediary of the difference Fourier?

COPPENS: No. For the simpler molecules I would take an atomic model, including (subsidiary) density peaks between atoms, which I consider essentially a different model from yours.

DAWSON: I agree (as to the distinction). However, I have doubts as to the usefulness of this alternative. The diamond situation shows that the process of building up the peak (in the middle of the bond) is at the expense of scooping charge from other regions. It is, in fact, the whole distribution around the peak which must be taken into account rather than just the excess peak in the middle of the bond. You have to have the facility to extract from one side to build up between the atoms. This is one feature where angular harmonics work well because correct normalization is built into the expressions.

SRINIVASAN: The application of the anomalous dispersion method for the determination of the absolute configuration of molecules is not applicable if the structure consists of only one species of atom. The treatment, presented in this paper, seems to indicate that the aspherical electron density distribution involves a complex scattering factor very similar to the one met in anomalous scattering although much smaller in magnitude. Could this possibly lead to determination of absolute configuration in the case of a structure involving atoms of one type?

DAWSON: No. Although highly reminiscent of anomalous scattering in appearance, the functions are different in behaviour. The formalism here is in accord with Friedel's law and it is only when genuine anomalous dispersion occurs that the conditions allow determination of absolute configuration.

MASLEN: As a question of terminology, are we justified in regarding libration motion as harmonic?

DAWSON: This is an interesting point since there may perhaps be possible confusion. In my talk, I was at pains to refer where necessary to the rectilinear harmonic approximation. Correspondingly, it is perfectly correct to talk about libration as torsional harmonic motion. I have retained the term *anharmonic* for motions other than those which can be described in quadratic components, whether linear or angular.

HIRSHFELD: Can you estimate the validity of the Hartree–Fock approximation from an examination in the close neighbourhood of the atomic nuclei? Most models tend to give featureless curves at these positions, but the Hartree–Fock calculations show a steep slope here.

DAWSON: I think it is beyond the bounds of normal possibility to observe these effects. We have to remember that, as Higgs showed, the peak electron density for a static atom can be ~ 700 e.Å^{-3}. In diamond, even with a very small range of vibration and an admittedly limited angular range, it was 21 e.Å^{-3}. Relative to the theoretical situation, everything is pulled down. It seems unlikely ever to expect to be able to interpret features, at or near the atomic centre, significantly in respect of quantum mechanical molecular orbital calculations. There is however a genuine need for the theoreticians to convert their calculations to distributions somewhat nearer in scale to what we, in fact, deal with.