

17.1-1 SEARCH FOR A FRAGMENT OF KNOWN GEOMETRY BY INTEGRATED PATTERSON AND DIRECT METHODS. By Ernst Egert and George Sheldrick, Anorganisch-Chemisches Institut der Universität Tammannstraße 4, D-3400 Göttingen, F.R.G.

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17.2-1 ESTIMATING THE THREE-PHASE STRUCTURE INVARIANT VIA ITS QUINTET EXTENSION. By Herbert Hauptman, Medical Foundation of Buffalo, 73 High St., Buffalo, NY 14203, United States.

Let h, k, ℓ be fixed reciprocal lattice vectors satisfying $h + k + \ell = 0$. Then the linear combination of three phases,

$$T = \phi_{\underline{h}} + \phi_{\underline{k}} + \phi_{\underline{\ell}}, \quad (1)$$

is a structure invariant. One embeds T in a five-phase structure invariant Q (quintet) by means of

$$Q = \phi_{\underline{h}} + \phi_{\underline{k}} + \phi_{\underline{\ell}} + \phi_{\underline{H}} + \phi_{\underline{H}} \equiv T, \quad (2)$$

where \underline{H} is an arbitrary reciprocal lattice vector, in order to obtain the extension Q of the structure invariant T . Then the second neighborhood of T is defined to consist of the ten distinct magnitudes $|E|$ which constitute the second neighborhood of Q . Since \underline{H} is arbitrary there are many extensions and many second neighborhoods.

Suppose that a crystal structure is fixed and that the six non-negative numbers $R_1, R_2, R_3, R_1, R_2, R_3$ are also specified. The reciprocal lattice vector \underline{H} is taken to be the primitive random variable which is assumed to be uniformly distributed over the subset of reciprocal space defined by

$$\left. \begin{aligned} |E_{\underline{h}+\underline{H}}| &= R_1, & |E_{\underline{k}+\underline{H}}| &= R_2, & |E_{\underline{\ell}+\underline{H}}| &= R_3; \\ |E_{\underline{h}-\underline{H}}| &= R_1, & |E_{\underline{k}-\underline{H}}| &= R_2, & |E_{\underline{\ell}-\underline{H}}| &= R_3; \end{aligned} \right\} \quad (3)$$

where the six magnitudes $|E|$ in (3) are seen to be a subset of the ten-magnitude second neighborhood of T . Then $|E_{\underline{H}}|$, as a function of the primitive random

variable \underline{H} , is itself a random variable, and its conditional probability distribution P , assuming as known the six magnitudes $|E_{\underline{h}+\underline{H}}|, |E_{\underline{k}+\underline{H}}|, |E_{\underline{\ell}+\underline{H}}|$ [Eq. 3] be-

longing to the second neighborhood of T , has been found. By suitable choice of the six numbers $R_1, R_2, R_3, R_1, R_2, R_3$, the distribution P leads to linear relationships among the cosines of the three-phase structure invariants and the observed magnitudes $|E|$. In this way one obtains estimates for the cosines of the three-phase structure invariants in terms of observed magnitudes $|E|$.

It is particularly noteworthy that the method described here is readily generalized to the case that anomalous scatterers are present and anomalous data available. In this case however, estimates of the invariants themselves, i.e. both their sines and cosines, are available. In recent work (Hauptman, Acta Cryst., 1982, A38, 632-641) estimates of the three-phase structure invariant in terms of the six magnitudes

$$|E_{\pm\underline{h}}|, |E_{\pm\underline{k}}|, |E_{\pm\underline{\ell}}| \quad (4)$$

in the first neighborhood were obtained; in the present work the estimates are expressed in terms of the six magnitudes (4) plus the 12 additional magnitudes

$$|E_{\pm\underline{h}+\underline{H}}|, |E_{\pm\underline{k}+\underline{H}}|, |E_{\pm\underline{\ell}+\underline{H}}| \quad (5)$$

in the second neighborhood. The reciprocal lattice vector \underline{H} is again arbitrary.

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17.2-2 COMBINATIONS OF ISOMORPHOUS REPLACEMENT AND ANOMALOUS DISPERSION DATA FOR THE EVALUATION OF TRIPLET PHASE INVARIANTS. By J. Karle, Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C., U.S.A. 20375.

On the basis of a common characteristic observed in previously derived formulas for the evaluation of triplet phase invariants from either isomorphous replacement data or anomalous dispersion data, it has been found possible to combine mathematical expressions, certain differences of magnitudes, arising in the analysis of the two techniques to form a myriad of new mixed formulas. The common characteristic is that the various types of differences of magnitudes that are involved in the formulas all are definable in terms of the heavy-atom structure. The formulas involve the mixing of terms arising from several isomorphous derivatives or from a combination of such terms with various types of terms arising in anomalous dispersion or the mixing of various terms arising in anomalous dispersion alone. The evaluation of the triplet phase invariants is facilitated by the use of a simple rule, called the General Rule, that is generally applicable to the case of one predominant type of anomalous scatterer. In the case of more than one predominant type of anomalous scatterer, a slightly more complicated calculation is required and will be described. Test calculations show that a very large number of invariants may be evaluated by these means with reliabilities that are potentially high, but depend, of course, on the reliability of the experimental data. A benefit from having the large variety of formulas is that triplet phase invariants can be evaluated at many points throughout the range $-\pi$ to π and their reliability is enhanced because much information is obtained from only the largest differences of magnitudes.

17.2-3 EFFECT OF HEAVY ATOMS ON THE TWO PHASE STRUCTURE SEMINVARIANT $\phi_{\underline{h}} + \phi_{\underline{k}}$ IN $P\bar{1}$. By Sikha Ghosh and G.D. Nigam, Department of Physics, Indian Institute of Technology, Kharagpur, India.

A crystal structure in $P\bar{1}$ consisting of P heavy atoms (known) and Q light atoms (unknown) in the unit cell is considered, and the random variable vectors \underline{h} and \underline{k} , subject to well defined restrictions, are assumed to be uniformly and independently distributed in the reciprocal space. The linear combination of two phases $\psi = \phi_{\underline{h}} + \phi_{\underline{k}}$ is a structure seminvariant if and only if $\underline{h} + \underline{k} = 0 \pmod{\underline{\omega}}$ where $\underline{\omega} = (2, 2, 2)$. $E_{\underline{h}}, E_{\underline{k}}$ are the two normalised structure factors associated with the phases $\phi_{\underline{h}}$ and $\phi_{\underline{k}}$ and $E_{\underline{h}}, E_{\underline{k}}$ are two contributions of the heavy atoms respectively. The first neighbourhood of ψ consists of the four magnitudes $E_{\underline{h}} = R_1, E_{\underline{k}} = R_2, E_{(\underline{h}+\underline{k})/2} = R_{1/2}$ and $E_{(\underline{h}-\underline{k})/2} = R_{1/2}$. In the present investigation, the conditional probability distribution of ψ , given the four magnitudes and the known contributions of the heavy atoms is derived to the approximation of $1/N$, N being the number of atoms in the unit cell. The expression is more general than the one derived by Green & Hauptman (Acta Cryst. (1976) A32, 940) as it includes the known information from the heavy atoms. In favourable cases, i.e., when the phases indications from the four magnitudes neighbourhood of the seminvariant and the heavy atoms coincide, one obtains a reliable estimate of ψ . The result obtained has been applied to the structure of a derivative of β -lactam and the anticipated improvement in the estimate of the seminvariant is in fact realised.