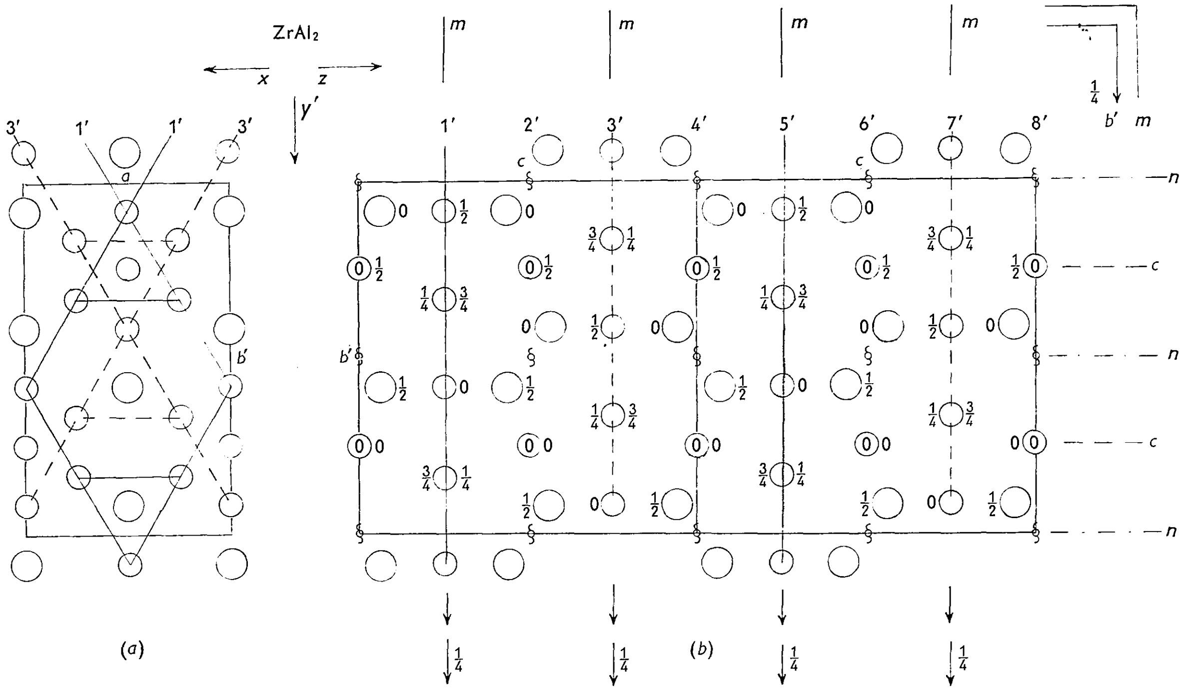

Fig. 2. (*a*) A projection of $ZrAl_2$ from the layer 1′ to the layer 3′ down the *z* axis. (*b*) A projection of $ZrAl_2$ down the *x* axis indicating the cell chosen for the comparison and giving the *x* co-ordinates of the atoms as fractions.

parallel to the layers at 3′, whereas in Zr_2Al_3 the sequences 1–3 and 3–5 are related by a *d* glide plane at 3. The relationship between 5′–7′ and 7′–1′ differs in this same way from that between 5–7 and 7–1. The repeat units 1′–5′ and 5′–1′ of $ZrAl_2$ are related by a mirror plane parallel to the layers at 5′ whereas in Zr_2Al_3 the units 1–5 and 5–1 are related by a *d* glide plane at 5.

It should be noted that in $ZrAl_2$ the hexagons of a kagomé net are centred by zirconium atoms from both sides. In Zr_2Al_3 the sequences are staggered so that one of these zirconium atoms is placed at the vacant site of the kagomé-type aluminium layer, thus producing a puckered triangular net. This might be taken to account for a relative contraction in the direction of stacking. From the figures other differences will be observed to be slight. The formulae are reconciled by noting the difference in the composition of the kagomé-type aluminium layers.

The two structures might therefore be considered as made up from sequences which are fundamentally similar, the main difference between them being the way in which the sequences are staggered.

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Some aspects of minimum-function diagrams.

By S. Raman, *Department of Chemistry, Harvard University, Cambridge* 38, *Massachusetts, U.S.A.*

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Presently the deconvolution of the Patterson function is attempted by the minimum function which is calculated by shifting the origin of the Patterson diagram by any interatomic vector $\mathbf{u}_{ab}$ and plotting the minima of the two values that superimpose. Though it is well known that the diagram gives the structure duplicated by its inverse about the midpoint of the shift-vector the symmetry of the diagram, $S(M)$, has not been completely investigated. We try to carry out this study here and indicate that $S(M)$ depends on the shift-vector and therefore can possibly lead to a method of distinguishing some of the Harker peaks from ghosts and some methods for solving centrosymmetric structures.

The theory is developed through an application of the matrix theory to the Patterson diagram (Buerger, 1950). In our discussion the set of N^2 interatomic vectors are represented as a square array $\mathbf{u}_{ij}$ where $\mathbf{u}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, $\mathbf{r}_j$ being the atomic position-vector. The matrix $u_{ij}+u_{ab}$ implies shifting the Patterson by the vector $\mathbf{u}_{ab}$. We first consider the case where $\mathbf{u}_{ab}$ is a general vector, i.e. atoms

a and b are not symmetry-related. The elements of one particular column and row of the first matrix will be identical with some one column and row of the second matrix and are defined by u_{aj} and u_{ib}. Thus the M-function drawn for the vector $\mathbf{u}_{ab}$ gives a centric configuration of $(2N-2)$ peaks at $\pm(\mathbf{r}_j-\frac{1}{2}(\mathbf{r}_a+\mathbf{r}_b))$ with strengths of f_j Min (f_a, f_b) where Min (f_a, f_b) is the lesser of f_a and f_b. The $S(M)$ is just $P\bar{1}$, $A\bar{1}$, $F\bar{1}$ or $I\bar{1}$ according as the lattice is P, A, F, or I. The lattice-type of the fundamental space is retained in $S(M)$ but the rest of the symmetry degenerates into just an inversion-center. The M-function consists of two 'molecules' related by inversion. By a 'molecule' is meant the composite configuration of the N atoms of one unit cell of the crystal. Thus the minimum function gives this composite configuration and its enantiomorph. $S(M)$ can be higher only if the shift-vector $\mathbf{u}_{ab}$ is a special type of Harker vector. It is not enough if the atoms a and b are symmetry-related. It is necessary that the vector $\mathbf{u}_{ab}$ passes through the symmetry-element in question, for example, $(2x, \frac{1}{2}, 2z)$ in $P2_1$ or $P4_1$. The M-function, then, contains the composite structure and its 'enantiomorph', the symmetry-element involved and its 'enantiomorph' coming into juxta-position. The resultant symmetry is then what is common to both sets. In $P1$, all vectors are general and $S(M)$ is only $P\bar{1}$. In $P2$, special Harker vectors are possible and $S(M)$ can be $P2/m$. In $P3$, they are impossible and $S(M)$ can never be greater than $P\bar{1}$. In $P4$, they are possible and $S(M)$ can even be $P4/m$. When screw axes, in general n_p, are present then, (1) when n is odd $S(M)$ can equal only $P\bar{1}$ because special Harker vectors are impossible and (2) when n is even but p/n is not half, $S(M)$ is only $P2_1/m$ but (3) when n is even and p/n is half $S(M)$ can equal the space group plus inversion. An example of (1) is $P3_1$, while examples of (2) are $P4_1$, $P6_1$ and $P6_2$ and of (3) are $P2_1$, $P4_2$ and $P6_3$. When the mirror and glide planes are present, they lead only to special Harker vectors and higher symmetry is possible, for example, $S(M)=P2/a$ in Pa. In a case like $P2_1/a$ where both screw axes and glide planes are present two types of special vectors are possible. The first passes through the screw 2_1 and the corresponding $S(M)$ eliminates the glide and gives $P2_1/m$ while the second passes through the glide plane and the corresponding $S(M)$ is $P2/a$, the screw having been eliminated. Thus all vectors except special Harker vectors give only $S(M)=P\bar{1}$. Hence, if for a specific vector, $S(M)>P(\bar{1})$ it is a special Harker vector. Therefore, if one studies the symmetry of the M-function of all the peaks on a Harker section systematically, then, those which give $S(M)=P(\bar{1})$ are just ghosts and not genuine Harker peaks.

We next consider a centrosymmetric crystal of N point atoms of unit strength at $\mathbf{r}_{Nj}$ $(j=1$ to $N/2$; $\mathbf{r}_{Nj}=-r_{(N-Nj)})$. The matrix u_{ij} has besides the usual anti-symmetry, an interesting property that anyone column of the matrix has a corresponding row identical with it. This is equivalent to the statement that the Patterson consists of N single points corresponding to the through-center vectors $\pm 2\mathbf{r}_{Nj}$ and $(N^2-2N)/2$ double points at $\pm(\mathbf{r}_{Ni}\pm\mathbf{r}_{Nj})$ $(i\neq j)$, besides the usual origin-point N. The single-point vector is a special vector and refers to the symmetry element, inversion-center. The double-point vector refer to general vectors and also special Harker vectors produced by symmetry elements other than the inversion-center. A double-point general vector gives $S(M)=P(\bar{1})$. We have two 'molecules' as before. Each 'molecule' possesses the symmetry of the fundamental structure and in particular, an inversion-center. This inversion-center acts only within the group. Thus we have two groups of points each possessing an auxiliary inversion-center and both related by the main inversion-center. If the double-point vector corresponds to a special Harker vector then $S(M)$ can be greater than $P\bar{1}$ because in this case the main inversion-center lies on the symmetry element in question. Thus a diad, tetrad or hexad will be followed by a perpendicular mirror plane while a mirror plane will be followed by a diad and so on. The M-function corresponding to a single-point-vector will give the structure; only in this case will $S(M)$ equal the space group.

The above discussion suggests two methods for solving centrosymmetric structures. If the N-single points are resolved from the $(N^2-2N)/2$ double points then the structure is there right in the Patterson function though on twice the scale. This straightforward procedure may not work if the Patterson function has strong overlap in three dimensions. However, even in such a case, at least some of the atomic positions may be obtained by finding the total weight around each Patterson peak. If this were normalized in terms of the weight of the single-point then a peak of odd number corresponds to a possible atomic coordinate on twice the scale. At first sight it appears that single points can overlap with only double points. If this were true then all the N atomic positions can be obtained by the above odd-weight method. But unfortunately single points can overlap among themselves, if, by accident, two atoms have coordinates (x_a, y_a, z_a) and (x_a+e, y_a+e, z_a+e) where $e=0$ or $\frac{1}{2}$. Hence the number of odd-weight peaks will be less than N so that only a partial solution of the structure is possible. The second method is based on the minimum function. A direct method demands the identification of at least one single point in the Patterson function. The corresponding M-function gives the structure. But the number of single peaks is, in general, much smaller than the number of double peaks. Therefore, it may be possible to identify only the double points. The corresponding M-function will give two images of the structure, that is, $(2N-2)$ distinctly different peaks unless the double point is the result of superposition of two single points, in which case, the minimum function will give only N peaks. The problem of extracting one image is solved by locating the auxiliary inversion-centers by a trial and error method. Any two out of the $(2N-2)$ points are randomly joined and with the mid-point of this straight line as origin it is tested whether there exist two others centrically related about this origin. If so, it is a possible auxiliary center and the other $(N-4)$ points that are centrically related about this origin can be discovered pair by pair.

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Reference

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