diffraction neutronique (Centre d'Études Nucléaires de Saclay, P. Mériel) a été spécialement réalisé avec une fente antidivergente $\alpha = 2/400$. Mais il ne nous a pas été possible d'évaluer la contribution d'harmonique $\lambda/2$ avec une bonne précision car la région correspondant aux réflexions 24.4, 22.12 comporte un grand nombre de raies dont les pics se superposent. Nous avons pu toutefois limiter la valeur de cette intensité de la manière suivante:

$$0{,}20 \leq (F_o^2)_{12,2} + (F_o^2)_{11,6} \leq 0{,}40 \, .$$

Il résulte de cette étude que les données expérimentales dont nous disposons actuellement ne sont pas suffisantes pour déterminer sans ambiguité toutes les coordonnées. Néanmoins, notre étude permet d'exclure d'une façon certaine un grand nombre de modèles structuraux. Nous constatons aussi, que si l'on admet le groupe $R\bar{3}c$, les valeurs que nous avons données en 1964 vérifient les relations décrites dans la présente note.

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Weighting factors in image-seeking methods*.

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One of the more popular methods of extracting information from a Patterson function involves using an image-seeking or Patterson superposition technique in conjunction with the minimum function. The purpose of this technique is to reduce the number of peaks in the Patterson function leaving, in the limit, a single image of the structure. More specifically, the minimum function, $M(\mathbf{u})$, is given by

$$M_1(\mathbf{u}) = \text{Min}[P(\mathbf{u}), w_1 P(\mathbf{u}-\mathbf{s}_1)] \qquad (1)$$

where $P(\mathbf{u})$ is the three-dimensional Patterson function and $P(\mathbf{u}-\mathbf{s}_1)$ is the Patterson function shifted by the vector $\mathbf{s}_1$, which for a rational superposition is an interatomic vector; w_1 is a weighting factor. Weighting factors have been included by other investigators (Buerger, 1959; Simpson, Dobrott & Lipscomb, 1965) in their image-seeking functions, but it is our feeling that the full usefulness of these weighting factors has not been realized, and some further comments in this regard are in order.

Consider an acentric structure of n atoms with atom i at $\mathbf{r}_i$ having scattering power f_i. The corresponding Patterson function will consist of n^2-n peaks at $\mathbf{r}_i-\mathbf{r}_j$ with strengths $f_i f_j$. If some single vector $\mathbf{s}_1$ is chosen as the shift vector and the minimum taken of the Patterson values at $P(\mathbf{u})$ and $P(\mathbf{u}-\mathbf{s}_1)$, it is well known that the resulting minimum function ideally has $2n-2$ peaks describing the structure and its inverse related by the center of symmetry at the midpoint of $\mathbf{s}_1$. If the weighting factor is not included in equation (1) and one minimization is done with $\mathbf{s}_1 = \mathbf{r}_b - \mathbf{r}_a$, and if $M(f_a, f_b)$ means take the minimum of f_a and f_b, then each point in the structure image is weighted as $f_i M(f_a, f_b)$ where $i=0, \ldots, n$ except when $i=a$ or b in which case the weight is $f_a f_b$. In the inverse image for $i \neq a$ or b, each point is weighted as $f_i M(f_b, f_a)$. Clearly the structure and its inverse are now weighted equally, and in a structure of any complexity there would be no way of distinguishing between the two images.

Suppose the scattering power of atom a is somewhat greater than atoms $b, c, \ldots, n$; now the structure contains one heavy atom (H) and many light atoms (L) such that $f_a = f_H$ and $f_b, f_c, \ldots, f_n = f_L$ (Fig. 1). In this case the structure image and its inverse would be weighted according to the smallest scattering power giving, in the general case, $f_i f_L$ as illustrated in Fig. 2(*a*); also, a poor peak to background ratio would result as pointed out by Buerger (1959). If the weighting factor is included in equation (1) the structure image would be weighted as $f_i M(f_H, w_1 f_L)$ for all i. The inverse is now weighted as $f_i M(f_L, w_1 f_H)$ for $i=0, \ldots, n$ except for $i=a$ or b; the points for $i=a$ or b belong to the structure image and are weighted accordingly. Since the scattering power of atom a is greater than that of atom b, the weighting factor can be set equal to f_a/f_b (f_H/f_L) so that the structure image is weighted by the largest weight giving $f_i f_H$, and its inverse by the smallest weight giving $f_i f_L$. The result of including such a weighting factor in the superposition function is shown in Fig. 2(*b*). It is evident that the center of symmetry along the shift vector has now been destroyed since the peak heights of the structure image are higher than those of the related inverse image. Also in general the peak to background contrast has been improved.

Because of overlap and multiple vectors in complex problems, it is usually necessary to do several superpositions. In particular, if there is one heavy atom in a structure in a symmetry group of order p, initially $p-1$ superpositions would be done with the shift vectors being the $p-1$ *HH* vectors. Any further superpositions, p at a time, would most logically involve shift vectors of the *HL* type where the weighting factors should be included. Generally, this procedure can be expressed as

$$M_n(\mathbf{u}) = \text{Min}[P(\mathbf{u}), w_1 P(\mathbf{u}-\mathbf{s}_1), \ldots, w_n P(\mathbf{u}-\mathbf{s}_n)] \, . \qquad (2)$$

For a given structure the best choice of $\mathbf{s}$ may depend on many factors, but let it suffice to say that the shift vectors would be chosen here as in the ordinary superposition

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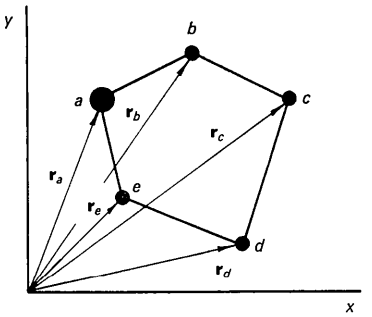

Fig. 1. A structure with the atoms at the ends of the position vectors.

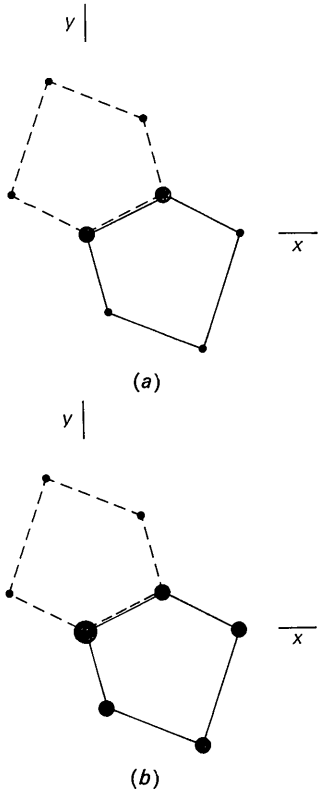

Fig. 2. The $M_1(\mathbf{u})$ function with $\mathbf{s}_1=\mathbf{r}_b-\mathbf{r}_a$. The structure image and its inverse are indicated by the solid and dotted imgaes. The circles represent the *LL*, *HL*, and *HH* interactions by their increasing size. (*a*) The weighting factor is not included. (*b*) The weighting factor is included.

method, *i.e.* using space group symmetry and expected distances and angles.

In the first approximation weights may be taken as the ratios of the atomic numbers (Z_H/Z_L); for larger Z_H to Z_L ratios the ratios of the appropriate observed single peak heights will work better, especially when 'sharpened' data are used. The contrast between the structure image and its inverse obtained by using a suitable weighting factor will be more distinct as the number of overlapping peaks is decreased and as the Z_H to Z_L ratio is increased provided the ratio of Z_L to background is sufficiently large. Although only the single heavy atom case has been discussed, the weighting factors can be used to advantage in structures having more than one heavy atom, or in centrosymmetric structures as well, when superpositions are done using unsymmetrical shift vectors. Of course with symmetrical shift vectors the weighting factors are set equal to unity as they are in the equal atom case.

The effect, then, of including weighting factors in superposition methods using the minimum function is (i) to eliminate partially the center of symmetry resulting from the first superposition and (ii) to keep the peak height of the structure image at the *HH* and *HL* level. This affords a convenient aid in sorting out a single image of the structure and is simple to apply in practice since computer programs can be easily adapted to allow for the scaling of successive shifted Pattersons. If the product function is used instead of the minimum function, weighting factors would have no effect other than on the scaling of the resultant map. If the sum function is used and one superposition done with $\mathbf{s}_1=\mathbf{r}_b-\mathbf{r}_a$ (Fig. 1) the two most prominent images would be weighted as $f_af_i+w_1f_bf_i$ and $f_bf_i+w_1f_af_i$. In this case some effect would be expected from weighting, but the results would not be as clear cut as with the minimum function, especially in view of the high backgrounds produced in the sum function.

The effectiveness of including such weighting factors in the minimum function was demonstrated by us recently in the structure determination of $C_{16}H_{11}O_3Cl$ (Guggenberger & Jacobson, 1966), a photochemical oxidation product of 2-(*p*-chlorophenoxy)-4,5-benzotropone. This compound crystallizes in the orthorhombic space group $P2_12_12_1$. The structure was solved using image-seeking methods where $f_{Cl}=H$ and $f_O=L$. Using the unweighted minimum function involving seven shifted Patterson functions with three shift vectors of the *HH* type and four of the *HL* type, the image of the structure was not discernible, as a large number of peaks remained, many of which were not much above the general background level. After weighting the four Patterson functions shifted by *HL* vectors, the molecular structure was clearly evident with the peak heights well above the background level.

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