Acta Cryst. (1963). **16**, 1071

Nuclear magnetic resonance in crystals.

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(*Received* 1 *May* 1963)

Dr. J. M. Dereppe, Dr. Pedro W. Lobo and Ing. R. Touillaux, of the Laboratoire de Chimie Physique, Louvain, Belgium, have drawn our attention to a number of errors in our paper under the above title (McCall & Hamming, 1959).

The coefficient of the term ab^3c^2d, in equation (3), should be 108.

The × on the third line of equation (5) should be +.

The expressions for $h(\theta_p,5)$ and $h(\theta_p,6)$ are interchanged in equations (7). These quantities should be given as:

$$h(\theta_p,5)=a_{65}\sin 2\theta_p+a_{85}\sin 4\theta_p$$

$$h(\theta_p,6)=a_{06}(1-\cos 4\theta_p)+a_{26}(\cos 2\theta_p-\cos 4\theta_p)$$

The statement 'A sufficient set of measurements consists of θ-dependences at $\varphi_p=0, \pi/4, \pi/2$ and a φ-dependence at $\theta_p=\pi/2$.' (near the bottom of the first column, page 83) is incorrect. These allow for the determination af $A, B, C, L, M, R, S, U, V$ but not D, E, F, G, N, Q.

The first sentence at the top of the second column of page 83 should read: $g(\varphi_p,n)=0$ for $n=1, 3, 5, 7$ for any θ-dependence at constant φ and $h\ (0,m)=0$ for $m=1, 3, 5, 7$.

Certain errors appear in Appendix V. The correct relations for these cases are:

$$L=6a_{26}-8a_{06}$$

$$S=8a_{06}-10a_{26}-8a_{28}$$

$$U=8a_{06}-10a_{26}+8a_{28}$$

$$M=7a_{02}+3a_{42}-(5/2)a_{00}+(19/6)a_{20}-(7/6)a_{40}\ .$$

Appendix VI is sufficiently in error that it should be disregarded entirely. A corrected table for $A, B, C, L, M, R, S, U, V$ follows.

REVISED APPENDIX VI

$$\begin{aligned}A &=(15/4)g(0,\ 0)+(21/4)g(0,\ 2)+(7/4)g(0,\ 4)\\ &\quad -(3/2)g(\pi/2,\ 0)-(7/2)g(\pi/2,\ 4)+2h(\pi/2,\ 4)\\ B &=-(19/6)g(0,\ 0)-(23/6)g(0,\ 2)-(1/2)\mathrm{g}(0,4)\\ &\quad +(2/3)g(\pi/2,\ 0)+(10/3)g(\pi/2,4)-(4/3)h(\pi/2,\ 4)\\ C &=(5/12)g(0,\ 0)-(5/12)g(0,\ 2)-(1/4)g(0,\ 4)\\ &\quad +(1/6)g(\pi/2,\ 4)+(5/6)g(\pi/2,\ 0)-(2/3)h(\pi/2,\ 4)\\ L &=-8g(\pi/4,\ 0)+4g(0,\ 0)+4g(\pi/2,\ 0)-6h(\pi/2.\ 4)\\ &\quad -3h(\pi/2,\ 6)\\ M &=(5/2)g(0,\ 4)-(11/3)g(\pi/2,\ 4)+(23/6)g(0,\ 0)\\ &\quad -(19/3)g(\pi/2,\ 0)+(19/6)g(0,\ 2)+(8/3)h(\pi/2,\ 4)\\ R &=(17/4)g(0,\ 0)-(1/2)h(\pi/2,\ 2)-2g(\pi/2,\ 0)-2h(\pi/2,\ 4)\\ &\quad +(9/4)g(0,\ 4)-(15/4)g(0,\ 2)\\ S &=8g(\pi/4,0)-4g(0,0)-4g(\pi/2,0)+6h(\pi/2,4)+5h(\pi/2,6)\\ &\quad +4h(\pi/2,\ 8)\\ U &=8g(\pi/4,\ 0)-4g(0,\ 0)-4g(\pi/2,\ 0)+6h(\pi/2,\ 4)\\ &\quad +5h(\pi/2,\ 6)-4h(\pi/2,\ 8)\\ V &=(1/4)g(0,\ 0)-(15/4)g(0,\ 2)+(9/4)g(0,\ 4)+2g(\pi/2,\ 0)\\ &\quad -(11/2)h(\pi/2,\ 2)-2h(\pi/2,\ 4)\end{aligned}$$

The quantities D, E, F, G, N, Q can be found by an additional φ-dependence at $\theta_p=\pi/4$.

We are indebted to Dr. Dereppe, Dr. Lobo and Ing. Touillaux for considerable efforts in the preparation of this communication.

Reference

McCall, D. W. & Hamming, R. W. (1959). *Acta Cryst.* **12**, 81.

Acta Cryst. (1958). **16**, 1071

A computational technique for the coincidence method of sign determination.

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(*Received* 25 *March* 1963 *and in revised form* 23 *May* 1963)

Introduction

It is well known that the signs of the unitary structure factors $U(\mathbf{h})$, $U(\mathbf{h}')$, $U(\mathbf{h}+\mathbf{h}')$ are related by

$$S(\mathbf{h}) \approx S(\mathbf{h}')S(\mathbf{h}+\mathbf{h}')\ , \tag{1}$$

where $S(\mathbf{h})$ denotes the sign of $U(\mathbf{h})$ *etc*, with a probability increasing with increasing $|U(\mathbf{h})U(\mathbf{h}')U(\mathbf{h}+\mathbf{h}')|$. One way in which this relation has been applied to certain plane groups (Grant, Howells & Rogers, 1957) uses special relations between $S(0kl)$ and $S(0\bar{k}\bar{l})$ *etc* for these groups: *e.g.* in plane group *pgg* $S(0\bar{k}l)=S(0kl)$ for $(k+l)$ even, and $S(0\bar{k}l)=-S(0kl)$ for $(k+l)$ odd. Such terms may be said to be symmetry-related. Only reflexions of high unitary structure factor are used, and a necessary step is a procedure for finding all the relations of type (1) which exist between the reflexions considered. An important part of the method is the recognition of 'coincidences'. These are two or more terms $\mathbf{h}$ occurring with the same pair of terms $\mathbf{h}'$, $\mathbf{h}+\mathbf{h}'$, or their symmetry-related terms, in a relation of type (1): *e.g.* in plane group *pgg* the (023) and (063) terms can form a coincidence since (023) can occur with (045) and (022), and (063) with (045) and $(0\bar{2}2)$. The discovery of the sign relations and coincidences is followed by an iterative process to adjust and extend a tentative initial set of signs obtained from the coincidences so as to obtain best agreement with the original data. The method described by Grant, Howells & Rogers is two-dimensional. It can, with very considerable advantage, be extended to three-dimensional data (Grant, Hine & Richards, 1960) provided the full set of sign relations and coincidences can be found.

The coincidence method is simple and compact, and enables large amounts of reflexion data to be handled provided suitable computational techniques are used to find the sign relations and coincidences in a reasonable time. This is particularly important in a crystallographic laboratory equipped with a small computer when unsuitable computational methods will severely restrict the number of data able to be handled in a given time. For this reason a general description, without details peculiar to the particular computer used, is given below of a sign-relation and coincidence-search technique which has been developed for the Stantec Zebra computer. This is a small computer having 8192 33 binary-digit words of magnetic drum storage, arranged in 256 tracks of 32 words each, together with 12 immediate access registers. The word time is 312 μsec giving an average drum access time of 5 msec. It is a very basic computer and the techniques developed for it should be applicable with advantage to any small drum-based machine.

Discovery of the sign relations and coincidences

The relation (1) can more usefully be written in the form

$$S(\mathbf{h}) \approx S(\mathbf{h}_1)S(\mathbf{h}_2)\,, \tag{2}$$

where $\mathbf{h}=\mathbf{h}_2-\mathbf{h}_1$. In this, sign relations are required for all terms $\mathbf{h}$, from among all terms $\mathbf{h}_1$ and $\mathbf{h}_2$ including symmetry-related terms. In the description of the coincidence method given by Grant, Howells & Rogers the procedure adopted was to find all the sign relations for a given term $\mathbf{h}$ and then to proceed to the next $\mathbf{h}$. Coincidences were obtained by a subsequent analysis of all the sign relations obtained. This procedure, though suitable for graphical working, is quite unsuitable in analytical form on a small computer. This is because the $\mathbf{h}_1$ and $\mathbf{h}_2$ terms include those generated from a unique set by the operation of the space-group symmetry. For a search among the $\mathbf{h}_1$, $\mathbf{h}_2$ to be fast it will be necessary to store in the computer both the unique terms plus the symmetry-related ones. The alternative of storing only the unique terms and generating symmetry related ones will be extremely time-consuming since the symmetry application will need to be repeated for each term $\mathbf{h}$, and, for given $\mathbf{h}$, will require very frequent exits from the main search loop. There is also the complication that further processing of the sign relations will be necessary to obtain the coincidences.

Instead of this procedure, therefore, the following one is recommended: find all terms $\mathbf{h}$ having a sign relation involving a given pair $\mathbf{h}_1$, $\mathbf{h}_2$ including symmetry-related terms, and then proceed to the next pair of $\mathbf{h}_1$, $\mathbf{h}_2$. This results in the innermost loop of the program being concerned with a search through the (unique) $\mathbf{h}$ terms and means that no inefficient exits for symmetry application are required. The symmetry operation needs to be applied to the $\mathbf{h}_1$, $\mathbf{h}_2$ much less frequently, and it is now practicable to store only the unique $\mathbf{h}_1$, $\mathbf{h}_2$ terms and to generate symmetry-related ones. Furthermore, the terms $\mathbf{h}$ having a sign relation with a particular pair of $\mathbf{h}_1$ and $\mathbf{h}_2$, including symmetry-related terms, are the coincidences and are automatically found and recognized during the sign-relation search. A separate search among the sign relations to find coincidences, as required in the previously described procedure, is not needed.

For example, in space group $P2_1/c$, $U(hkl)=sU(h\bar{k}l)=sU(\bar{h}kl)=U(\bar{h}\bar{k}\bar{l})$ where s represents the sign of the term and is plus for $(k+l)$ even and minus for $(k+l)$ odd. In this case the terms exist, in general, as quartets where, denoting (hkl) by $\mathbf{h}$, the quartet may be generated by ${}^i\mathbf{h}={}^iC\mathbf{h}$, where ${}^iC$ applies the sign change to the indices, *i.e.* ${}^1C$ gives (hkl), ${}^2C$ gives $(h\bar{k}l)$ *etc*, and also applies the sign change s to $U(hkl)$ *etc*. Now a sign relation exists between two terms ${}^iC\mathbf{h}_1$ and ${}^jC\mathbf{h}_2$ for a term $\mathbf{h}$ if $\mathbf{h}={}^jC\mathbf{h}_2-{}^iC\mathbf{h}_1$, and if, for given $\mathbf{h}_1$ and $\mathbf{h}_2$ (but different ${}^iC$ and, or, ${}^jC$), two or more $\mathbf{h}$ satisfy this, then these $\mathbf{h}$ form a coincidence.

The current Stantec Zebra program in which this has been applied stores the $\mathbf{h}$, $\mathbf{h}_1$ and $\mathbf{h}_2$ as data. Pairs of $\mathbf{h}_1$ and $\mathbf{h}_2$ are selected and all the combinations ${}^jC\mathbf{h}_2-{}^iC\mathbf{h}_1$ possible for the particular space group are set up and a search made through the $\mathbf{h}$'s with each combination in turn. All sign relations and coincidences found are stored for later output. When all combinations have been checked, a new $\mathbf{h}_1$ and $\mathbf{h}_2$ are selected and the process repeated. As usual, considerable time is saved by dividing the initial data into parity groups *eee*, *eeo*, *etc*, according to whether the indices h, k and l are even or odd, and using only those $\mathbf{h}_1$ and $\mathbf{h}_2$ parity groups for which sign relations can occur for the particular $\mathbf{h}$ parity group involved. Output of sign relations and coincidences normally occurs when the complete set for a parity group of $\mathbf{h}$ has been found. At any time, therefore, the store will be required to hold only one eighth of the total number of sign relations and coincidences possible for the complete set of $\mathbf{h}$. If, however, this still exceeds capacity, the list to that point can be output and the search continued with no serious consequences.

Some computational details

Best use will be made of the computer in the above procedure if the indices h, k, l of each term of the data are packed into one computer word. If this is done, once the combinations ${}^jC\mathbf{h}_2-{}^iC\mathbf{h}_1$ have been set up, the search among the $\mathbf{h}$ will be fast. This will be so even on a computer with purely drum storage since the problem is simply one of comparing one computer word, representing a given ${}^jC\mathbf{h}_2-{}^iC\mathbf{h}_1$, with a serial list of words, representing the $\mathbf{h}$, until equality is found or until all the $\mathbf{h}$ have been examined. The application of the appropriate symmetry to the indices of the $\mathbf{h}_1$, $\mathbf{h}_2$ terms when their indices are packed into one word is a simple matter and can be carried out in a few word times even in a computer such as Zebra where the only logical arithmetic operation is an *and* order. This symmetry variation can be controlled by code words representing the ${}^iC$ for each parity group, one word for each ${}^iC$. In the present Zebra program provision is made for up to 128 terms per parity group, *i.e.* a total of 1024 terms for eight parity groups, with indices of magnitudes not greater than 63.

I wish to express my thanks to Dr D. F. Grant, Mr R. G. Howells and Dr J. P. G. Richards for extremely helpful discussions during the course of this work.

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