THE FOURIER AND THE NEW POINT DIAGRAM SYNTHESES IN X-RAY CRYSTALLOGRAPHY

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ABSTRACT

A newly developed synthesis of X-ray data for crystal analysis, called the point diagram synthesis, is compared with the classical Fouriers. The fundamental assumption in the method is first explained. A correlation matrix of index 10 is then quoted. Some mathematical properties of the correlation matrices, that is, the absolute convergence, and the h- and μ-summation rules are described and illustrated. The method is next applied in parallel with the Fouriers to an arbitrary structure along with its two component structures. The crystal NaCl is next studied, using the actual experimental data. It is shown that on the basis of exactly the same experimental data the information given by the two types of syntheses are entirely different. Conclusions about the method drawn in the previous articles are then discussed in the light of the new studies and approved once more.

INTRODUCTION

In the past nine years the writer has attempted to find some new way of interpretation of X-ray data for crystal analysis. As a result, four independent methods are found which appear possible not only to locate the position of a peak but also its nature in the mapping of a structure. Two of the methods are limited to simple structures; for, in the case of complicated structures, the solutions, though still theoretically applicable, are too complicated to be manageable practically. The first one called "the Improved Algebraic Method" was published in brief account[1], and its application to specific example illustrated[2]. The second method called "the Identification Method" has not been published yet. The remaining two methods are closely related to each other and somewhat similar to the classical Fouriers in their manipulation. One of them, which may be called "the Point Diagram Method", was outlined in *Nature*[3] and also applied to study actual examples[4]. The method has been much discussed and given rise to many

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1. S. H. Yü, *Science Records, Aca. Sin.*, **1** (1943), 109.
2. S. H. Yü, *Science Records, Aca. Sin.*, **1** (1945), 361.
3. S. H. Yü, *Nature* **149** (1942), 638.
4. S. H. Yü, and C. P. Ho, *Nature* **149** (1942); S. H. Yü and C. P. Ho, *Science Records, Aca. Sin.*, **1** (1943), 111.

comments[5,6,7,8], some of which reveal that the method has not been understood correctly. It is therefore thought necessary to compare the method with the classical Fouriers in applying both of them to a real crystal based on the exactly identical real experimental data to see if the informations derived from the two different methods are really different and if the informations derived from the new synthesis are really much more quantitative than the informations derived from the classical Fouriers. Since the actual X-ray data of rocksalt taken by James and Firth[9] are very accurate and the Debye temperature factor for the crystal can be most accurately corrected for, the comparison of the two syntheses is made on this crystal. Besides this comparison, some of the mathematical properties of the new synthesis together with other discussions are also presented in this article. For the sake of simplicity the fundamental mathematical theory will not be related here.

THE FUNDAMENTAL ASSUMPTION AND EQUATIONS

The fundamental equations of the one-dimensional Fouriers.

What we call here the classical Fourier syntheses in crystal analysis are those which are based on the direct application of the results of the theory of Fourier series. In the one-dimensional case these syntheses may be represented by a general formula of the form,

$$\varrho(x) = \sum_{h=-\infty}^{\infty} C(h) \exp(2\pi i h x),$$

where $\varrho(x)$ represents some kind of density at a point whose coordinate expressed as a fraction of the unit axial length is x; $C(h)$ are quantities independent of x and derived from X-ray intensities indirectly or directly, depending on what type of Fourier we are dealing with; the other notations have the usual significances. In this article only structures possessing centers of symmetry will be considered. The equation is then reduced to the form

$$\varrho(x) = \sum_{h=-\infty}^{\infty} C(h) \cos 2\pi h x. \tag{1}$$

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[5] *Nature* **149** (1942), 729.

[6] H. Lipson, *Nature* **150** (1942), 25.

[7] A. J. C. Wilson, *Nature* **150** (1942), 152.

[8] C. S. Lu, *Nature* **150** (1942), 407.

[9] James and Firth, *Proc. Roy. Soc.* A, **117** (1927), 62.

We shall consider the following four types of Fouriers:

(1) The ordinary Fourier,

$$\varrho_F(x) = \sum_{h=-\infty}^{\infty} F(h) \cos 2\pi hx. \tag{1a}$$

(2) The simplified Fourier,

$$\varrho_{FS}(x) = \sum_{h=-\infty}^{\infty} E(h) \cos 2\pi hx, \tag{1b}$$

where

$$E(h) = F(h)/\bar{f}(h), \tag{1b'}$$

$$\bar{f}(h) = e^{-M} \cdot \sum_{i=1}^{n} f_i(h) / \sum_{i=1}^{n} Z_i. \tag{1b''}$$

$f_i(h)$ is the atomic structure factor of the *i-th* atom, Z_i, the number of the shell electrons in the *i-th* atom, e^{-M}, the Debye-Waller temperature factor. The quantity $E(h)$ is formulated somewhat in the way after Patterson[10] who, however, defined $\bar{f}(h)$ without including the temperature factor. The simplified Fourier is introduced here in analogy with the simplified Patterson-Fourier shown below which was first formulated by Patterson.

(3) The Patterson-Fourier,

$$\varrho_P(x) = \sum_{h=-\infty}^{\infty} F^2(h) \cos 2\pi hx. \tag{1c}$$

(4) The simplified Patterson-Fourier,

$$\varrho_{PS}(x) = \sum_{h=-\infty}^{\infty} E^2(h) \cos 2\pi hx. \tag{1d}$$

The fundamental assumption and formula in the new point diagram synthesis

The fundamental assumption upon which the new synthesis is developed is that in the case of a linear crystal all the atoms lie exclusively on some or all of those N points (to be called the N reference points) in the unit axial length, whose coordinates x are zero or multiples of $1/N$ where N is an even

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[10] Patterson, *Z. Kristallogr.* (A), **90** (1935). 517.

integer, that is $x=\mu/N$ where μ is an integer equal to or smaller than N. The assumption is based on the observation that we can determine the coordinates of the atoms in a structure always with only a finite accuracy. Thus usually the coordinates are determined only accurate to the second decimal figure, that is, $x=\mu/100$. On the basis of this assumption we shall, after some mathematical and physical considerations with the aid of the fundamental identity in Yü L (denotes Yü's letter to Nature[3]), obtain an equation given below for structures possessing centers of symmetry,

$$P_\mu=\sum_{h=-\infty}^{\infty} C(h)\, a_{\mu h}, \tag{2}$$

where P_μ denotes the number of certain kind of particles at the μ-*th* of the N reference points, the coordinate of the μ-*th* reference point being μ/N. $a_{\mu h}$ is a function of the parameters N, μ and h with possible values of μ ranging from 0,1,2,.... to (N-1), and values of h ranging from $-\infty$,....-3,-2,-1,0,1,2,....to ∞ , the totality of $a_{\mu h}$ forming a matrix which may be called the "correlation matrix of index N". In the detailed mathematical theory we shall show how the matrix is obtained and with what functional relations it depends on N, μ and h. Here we just need to know it to be a set of known numbers which may be used to correlate, in the way given by equation (2), the quantities $C(h)$ defined by Eqs. (1), (1a), (1b), (1c), or (1d) of the structure in question to obtain a set of numbers P_μ which will give us in turn informations useful in the determination of the structure concerned. It must be born in mind that the numbers P_μ are referred to the N reference points alone, all the other points being assumed free from atoms according to our fundamental assumption. Two types of structures will be considered, the fundamental equations for them are:

(1) The new synthesis of Fourier structures,

$$F^{P_\mu}=\sum_{h=-\infty}^{\infty} E(h)\, a_{\mu h}. \tag{2a}$$

(2) The new synthesis of Patterson structures,

$$P^{P_\mu}=\sum_{h=-\infty}^{\infty} E^2(h)\, a_{\mu h}. \tag{2b}$$

Knowing these fundamental equations in the new syntheses we may now proceed to see what the correlation matrix $a_{\mu h}$ is.

THE CORRELATION MATRICES

The Correlation matrix of index 10.

So far correlation matrices of $N=4$, 10, 16 and 52 have been evaluated. As an illustration the correlation matrix of index 10 is given in Table 1:

Table 1—Values of $a_{\mu h}$ of Index 10

h	$\mu=0,10$	1,9	2,8	3,7	4,6	5
0	0.1040	0.1920	0.2096	0.1880	0.2200	0.0979
± 1	0.0960	0.1650	0.0695	-0.0725	-0.1660	-0.0979
± 2	0.1050	0.0694	-0.1589	-0.1670	0.0415	0.0976
± 3	0.0940	-0.0726	-0.1671	0.1649	0.0791	-0.0969
± 4	0.1100	-0.1660	0.0415	0.0793	-0.1360	0.0946
± 5	0.0490	-0.0979	0.0977	-0.0970	0.0946	-0.0496
± 6	-0.0079	0.0036	0.0166	-0.0129	-0.0229	0.0461
± 7	0.0040	0.0069	0.0041	0.0008	-0.0080	-0.0232
± 8	-0.0025	-0.0044	-0.0013	0.0039	0.0115	0.0172
± 9	0.0019	-0.0012	-0.0033	0.0050	-0.0001	-0.0108
±10	-0.0014	0.0029	-0.0037	0.0045	-0.0065	0.0102
±11	0.0011	-0.0022	-0.0021	0.0025	0.0029	-0.0073
±12	-0.0009	-0.0015	-0.0022	0.0006	0.0028	0.0057

where the notation $\mu=0,10$ means $\mu=0$ or $=10$ and $h=\pm h$ means $h=1$ or $=-1$, and so on.

Absolute convergence.

It is seen from Table 1 that $a_{\mu h}$ are small when $h>\frac{1}{2}N=5$. The truth of this character is not confined merely to the correlation matrix of index 10, but holds for N equal to any even integer. Now in the series on the right hand side of equation (2), $C(h)$ can never be larger than $C(0)$ and so $a_{\mu h}$. $C(h)$ becomes very small as h increases beyond the value $\frac{1}{2}N$. Consequently the series mentioned is convergent so long as N is not indefinitely large. In fact the series is absolutely convergent; the omission of all the terms with absolute values of h larger than $\frac{1}{2}N$ causes so small an error in the series in the calculation of P_μ according to equation (2) that this error is really negligible in comparison with the errors in $C(h)$ due to the limited accuracy in the experimental measurement of X-ray intensities. Actual evidence in supporting this statement will be seen below in the application of the method to the study of the crystal NaCl. It may be interesting to recall that the use of the absolutely convergent series in the new method is directly in contrast with the use of some divergent series in some of the classical Fourier methods such as the simplified Patterson-Fourier for $x=\frac{1}{2}$ represented by equation (1d).

The h-summation rule.

Suppose we have a linear crystal consisting of two electrons, one at the ω-*th* and the other at the $(N\text{-}\omega)$-*th* reference point. Then $E(h)=F(h)=2\cos(2\pi h\omega/N)$. Substituting this into equation (2a) and remembering that $P_\mu=1$ when $\mu=\omega$, or $=N-\omega$, and $P_\mu=0$ otherwise, we have,

$$\sum_{h=-\infty}^{\infty}(\cos 2\pi h\omega/N)\,a_{\mu h}=\delta_{\mu\omega}, \tag{3}$$

where $\delta_{\mu\omega}=1$ when $\mu=\omega$ or $=N-\omega$, and $\delta_{\mu\omega}=0$ otherwise. To see whether this summation rule is true or not in the matrix given above, let us put $\omega=0$. Then we should have

$$\sum_{h=-\infty}^{\infty}a_{0h}=1 \tag{3a}$$

and

$$\sum_{h=-\infty}^{\infty}a_{\mu h}=0, \qquad \mu\neq 0 \text{ and}=1,2,\ldots\text{or } \tfrac{1}{2}N. \tag{3b}$$

Actual substitution of the values of $a_{\mu h}$ listed in table 1 gives,

$$\sum_{h=-12}^{12}a_{0h}=1.0008; \qquad \sum_{h=-12}^{12}a_{1h}=-0.0021;$$

$$\sum_{h=-12}^{12}a_{2h}=-0.0044; \qquad \sum_{h=-12}^{12}a_{3h}=\ 0.0061;$$

$$\sum_{h=-12}^{12} a_{4h} = 0.0028; \qquad \sum_{h=-12}^{12} a_{5h} = 0.0347.$$

We see that the first sum is very near to the value unity while all the others are nearly equal to zero in comparison with unity except the last one which differs from zero by little more than three per cent referring to unity. Thus the rule is confirmed within the calculation error.

The μ-summation rule.

There is another rule which is proved to be equally interesting, It may be deduced in the following way. Suppose we assume another structure whose atoms are distributed in such a way that we have $E(0)=\frac{1}{2}$, $E(1)=E(2)=E(3)=\cdots=E(\frac{1}{2}N)=0$. Then from the definition of $E(h)$ given by equation (2) in Yü L., it can be shown that,

$$\sum_{\mu=0}^{\frac{1}{2}N}{}' \left\{ a_{\mu k} + \sum_{m=1}^{\infty} [a_{\mu,\,(mN+k)} + a_{\mu,\,(mN-k)}] \right\} = \delta_{0k},$$

where $\delta_{00}=1$, and $\delta_{0k}=0$ for $k\neq 0$. The equations may be called the μ-summation rule, the validity of which can be tested in the same way as shown above for the h-summation rule.

Whether the two rules given above have or have not any more general mathematical interest we cannot tell without further investigation. (It is interesting to observe that the h-summation rule is somewhat like a generalized normality and orthogonality property such as that possessed by the ordinary orthogonal functions.) Nevertheless. one thing is certain that they are useful at least as a different independent method to check up against any mistakes which might creep into the values of $a_{\mu h}$ during their evaluation. Another application of the rules is their simultaneous use to localize which $a_{\mu h}$ got wrong numerical value in a matrix of $a_{\mu h}$.

AN ARBITRARY LINEAR CRYSTAL

Now let us make an actual comparison between the classical and the new syntheses by studying an arbitrary structure, the study of the actual NaCl will be followed next. The arbitrary structure to be studied consists of five dimensionless atoms, the number of electrons belonging to any atom being denoted by Z. The distribution of atoms at various reference points whose positions are indicated by $\mu=10x$ is listed below:

Table 2—The Fourier Structure

$\mu = 10x =$	0	1	2	3	4	5	6	7	8	9	10
$Z =$	6	0	0	7	3	0	3	7	0	0	6

The derived Patterson structure has a distribution $\Sigma Z_\alpha Z_\beta$ listed below:

Table 3—The Patterson Structure

$\mu = 10x =$	0	1	2	3	4	5	6	7	8	9	10
$\Sigma Z_\alpha Z_\beta =$	152	84	18	252	170	0	170	252	18	84	152
$P_\mu =$	152	70	19	247	195	0	196	247	19	70	152

From the structure so assumed we obtain the values of $E^2(h)$ given as:

Table 4

$h =$	0	± 1	± 2	± 3	± 4	± 5
$E^2(h) =$	676	10.4	11.9	367.9	30.2	6

We can now make a new synthesis of the derived Patterson structure according to equation (2b), using the values of $E^2(h)$ given in table 4 and the values of the correlation matrix given in table 1. The resulted values of P_μ are listed in table 3, the third row. It is seen that the agreement between $(\Sigma Z_\alpha Z_\beta)$, the real distribution, and P_μ, the distribution obtained by the new synthesis is within the error introduced in the experimental measurement of $F^2(h)$, though in making the synthesis, the series on the right hand side of equation (2b) is stopped at the term of maximum $h = 5 = \frac{1}{2}N$, a fact which supports the conclusion drawn in the section of absolute convergence. The classical simplified Patterson-Fourier according to equation (1d) based on exactly the same $E^2(h)$ is plotted in figure 1.

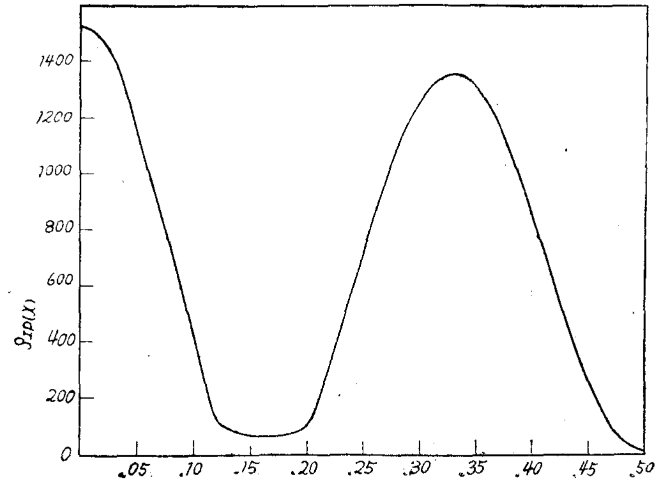

Fig. 1. The simplified Patterson-Fourier of an arbitrary linear crystal

Here the peak at $\mu=1$ or $x=0.1$ is absorbed into the peak at $x=0$ while the peaks at $x=0.2$, 0.3, and 0.4 are grouped together into a big peak; the same is true for the peaks whose $x>0.5$. Thus, the fine details, that is, the distribution of the atoms in numerical quantities shown up in the new synthesis, are not revealed here, the classical simplified Patterson-Fourier synthesis. The contrast between the classical and the new syntheses can be brought out even clearer, if we study the other two component structures; one has peaks at $x=0$ and $=1.0$ of strength 152 while the other has peaks at $x=0.1$ and $=0.9$ of strength 84. The peaks at $x=0$, 0.1, 0.9 and 1.0 in the original Patterson structure, that is, in the structure shown in table 3 are then the result of superposition of these two component structures. The synthesis of the first component structure gives the result in the third row of table 5. The assumed actual structure is indicated in the second row:

Table 5

$\mu=$	0	1	2	3	4	5	6	7	8	9	10
$Z=$	152	0	0	0	0	0	0	0	0	0	152
$P_\mu=$	154	-1.8	-3.8	5.2	7.0	-0.9	7.0	5.2	-3.8	-1.8	154

The corresponding simplified Fourier is plotted as curve A in figure 2:

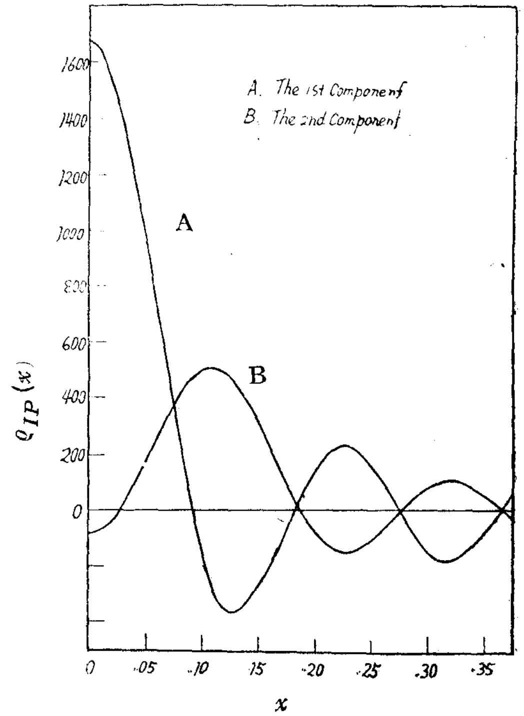

Fig. 2. The simplified Fouriers of the two component structures

Similarly we have table 6 and curve B in figure 2 for the second component structure.

Table 6

$\mu=$	0	1	2	3	4	5	6	7	8	9	10
$Z=$	0	84	0	0	0	0	0	0	0	84	0
$P_\mu=$	-0.8	84.9	5.3	-5.9	-4.4	0.4	-4.4	-5.9	5.3	84.9	-0.8

A perusal of tables 3,. 5, and 6 will reveal not only to what extent but also for what reason the new method yields the quantitative detailed informations about the structures in question as in contrast to the rather vague informations conveyed by the classical method. It is seen that, both in the classical and the new, the same $E^2(h)$ are used; and so if there is any difference between the results of the two methods, this difference cannot be attributed to anything else except the difference in the nature of the two methods.

Another point worth demonstrating, is the variation in the classical and in the new of the numerical value of a peak strength with the variation of the number of terms employed in the summation of the respective series on the right hand side of equations (1d) and (2b). Let us denote by H the maximum h we choose in the series and do the syntheses for various values of H, from $\frac{1}{2}N$ upward. The resulted peak strength $\varrho(0)$ for the classical and P_0 for the new are listed in the second and the third rows of table 7.

Table 7

$H=$	5	6	7	8	9	10	11	12	∞
$\varrho(0)=$	1529	1480	1252	1260	1276	2628	2645	2653	∞
$P_0=$	152	151	154	154	154	152	152	152	152

We may observe that while P_0 has no material change for all these H, $\varrho(0)$ is quite indefinite depending upon what H we choose. This reveals what an indifferent significance is attached to the numerical value of ϱ at a peak in the classical synthesis and the great significance attached to the numerical values of P_μ in the new synthesis.

THE NaCl STRUCTURE

We may now come to the study of an actual crystal and see to what extent the approximations involved in the deduction of $E(h)$ from $F(h)$ or the deduction of $E^2(h)$ from $F^2(h)$ will affect the quantitative nature of informations yielded by the new method. In other words, let us see to what extent the usefulness of the new method will be maintained in the study of an actual crystal. In making this study, the first step is to transform, in the case of Fourier structure, the experimental $F(h)$ into the corresponding $E(h)$. In order to make this transformation, we have to know the average $\overline{f}(h)$, which, in turn, involves the determination of the Debye-Waller temperature factor for each atom or, if not possible, its average values for the whole unit cell. This can be obtained experimentally. In the present case we may determine this factor from the Debye-Waller equation using the characteristic temperature 281° of NaCl. The step for the evaluation of $\overline{f}(h)$ is illustrated in table 8:

Table 8

h	0	2	4	6	8	10	12
$\sin\theta/\lambda$	0	0.177	0.355	0.533	0.710	0.877	1.065
f_{Na^+}	10.0	8.56	5.88	3.77	2.59	1.99	1.64
f_{Cl^-}	18.0	12·24	8.57	6.94	5.65	4.50	3.53
M_{Na^+}	0	0.059	0.236	0.533	0.945	1.474	2.120
$(fe^{-M})_{Na^+}$	10.00	8.07	4.65	2.21	1.00	0.456	0.197
$(fe^{-M})_{Cl^-}$	18.00	11.80	7.35	4.93	3.06	1.73	0.897
$\overline{f}(h)$	1.000	0.710	0.393	0.253	0.145	0.078	0.039
$F(h00)$	112.00	82.60	46.60	27.56	16.16	8.88	4.48
$E(h00)$	112.00	116.0	118.0	108.0	111.0	113·0	115.0

$F(h00)$ given in table 8 is four times James and Firth's values[9] because we have four molecules in one unit cell according to the theory of space group, whereas $F(h00)$ given by James and Firth is only for one molecule. The symbols M_{Na^+} and M_{Cl^-} stand for 1.87 $(\sin\theta/\lambda)^2$ and 1.21 $(\sin\theta/\lambda)^2$ respectively, the two constants before the brackets being calculated in the way just mentioned. From $\overline{f}(h00)$ and $F(h00)$ we obtain $E(h00)$ or briefly $E(h)$ listed in the last row. It is interesting to see that the approximation involved in the derivation of $E(h)$ is really not bad judging from the fact that all the values of $E(h)$ differ not very far from the same theoretical value 112.

We may now sum up $E(h)$ according to equation (2a) using the correlation matrix given in table 1, the summation being taken from $h=-4$ to $h=4$. The P_μ so obtained are given below:

Table 9

$\mu=$	0	1	2	3	4	5	6	7	8	9	10
$\Sigma Z_\alpha=$	56	0	0	0	0	56	0	0	0	0	56
$P_\mu=$	62.0	-1.6	-3.6	1.0	2.2	55.9	2.2	1.0	-3.6	-1.6	62.0

The agreement between $P_0=62$ and $P_5=55.9$ with the theoretical value $\Sigma Z_\alpha=2(Z_{Cl^-}+Z_{Na^+})=2(18+10)=56$ is obvious. The smallness of the background is also noticeable. These results are rather remarkable in considering that the synthesis is made only on the basis of two experimental values, that is, $F(200)$ and $F(400)$. In fact, if we use a correlation matrix of index 4 or 6 one experimental value would be enough, that is, $F(200)$, so far as the making of the synthesis alone is concerned. Again it is anticipated that a new synthesis of $F(hhh)$ would be even more interesting; for, then, the two kinds of atoms are separated from each other; P_0 and P_5 would be $4Z_{Cl^-}$ and $4Z_{Na^+}$ respectively. However, we need not make the illustration any more, the result can be expected. The classical Fourier and the classical idealized Fourier based on the same experimental data are plotted in figure 3:

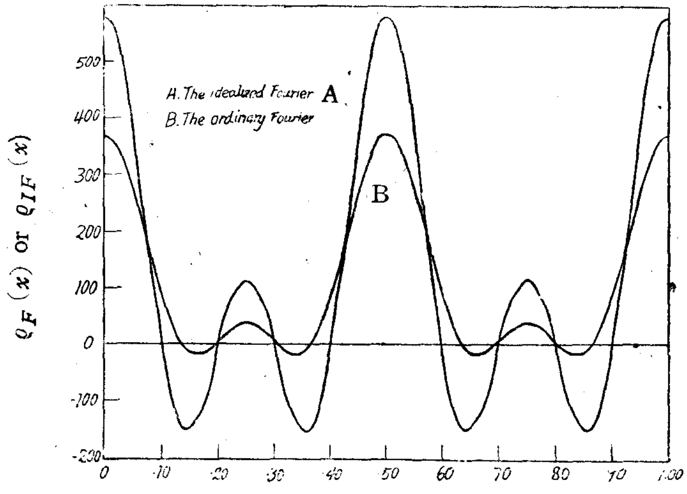

Fig. 3. The Fourier and the idealized Fourier of NaCl

It is not difficult to see what kind of different informations are revealed in the classical and in the new when a careful examination is made of table 9 and figure 3.

CONCLUSIONS AND DISCUSSIONS

We may now come to discuss the conclusions drawn in Yü L[3]. and elsewhere[4]:

Conclusion 1. The new method tells us not only the position but also the nature of a peak, whereas the classical Fouriers merely give the position together with some vague notion of heaviness or lightness of a peak.

Discussion: The correctness of this conclusion can be seen when an examination is made of tables 3, 5, 6, 9 and figures 1, 2, 3. Thus, the conclusion holds true both in the arbitrary as well as in the actual crystal. The applicability of this conclusion does not depend very much upon whether the structure concerned is simple or complex, it depends solely on the condition whether the fundamental assumption mentioned before is true or not in the structure, in other words, whether the unit axial length has been divided properly or not, that is the N has been selected correctly or not.

Conclusion 2. The background in the new synthesis is clearer than that in the classical. The background in the new synthesis, however, is referred to merely the N reference points defined before, all the other points in the fundamental interval being supposed to be free from atoms, in accordance with our fundamental assumption.

Discussion: It is seen in tables 3, 5, 6, and 9 that, whenever $\Sigma Z_\alpha Z_\beta$ or ΣZ_α is zero theoretically, the corresponding P_μ is also very small in comparison with other P_μ in the same table, deviating from zero merely in a few per cents, an amount of probable errors usually occurring in X-ray intensity measurements. Again the conclusion is true for the arbitrary crystal as well as the real crystal NaCl.

Conclusion 3. There is no fear of interference of peaks. If superposition of peaks takes place, this superposition will be known from the numerical P_μ of the peaks; otherwise they should remain distinct from each other no matter how close they crowd together. The clause "no matter how close they crowd together" is referred again to the N reference points alone in conformity with the fundamental assumption. (The writer regrets his forgetting to put this last remark in Yü L[3].)

Discussion: The conclusion is best understood in an examination of the peaks at $\mu=0$ and $\mu=1$ in the original Patterson structure shown in table 3 of the arbitrary crystal. It is seen that the peak at $\mu=0$ alone gives rise a background at $\mu=1$ in the first component structure shown in table 5 and the peak at $\mu=1$ gives rise a background at $\mu=0$ in the second component structure shown in table 6. Both the backgrounds are small in comparison with the peak values at the respective μ in the original Patterson structure, that is, -0.8 compared with 152 and -1.8 compared with 84. This means that the peaks at $\mu=0$ and $\mu=1$ in the original structure do not interfere with each other to an appreciable amount, though they are closest neighbours. As to the question of superposition, let us consider the peak at $\mu=1$ in the original Patterson structure. The peak is due to the superposition of the ends of four interatomic vectors between two of atom 7 to two of atom 3, making up the peak strength $7\times3\times4=84$. The peak strength revealed by the new synthesis shown in table 3, is 70, somewhat too small in comparison with 84. It is true that to arrive at the correct superposition for the peak solely from the number 70 is rather a long way. However, how much this definite numerical datum 70 will be of use in actual structure analysis any experienced X-ray worker may easily be able to realize; and this 70 is the worst datum in comparison with the other P_μ in table 3.

In spite of all the favourable conclusions drawn above, they become untenable unless the fundamental assumption is valid exactly or very approximately, that is to say, the index N is correctly or fairly correctly chosen. To test whether this choice has been correct or not, the following three criteria are proposed:

1. To see whether there are in a synthesis of a given index N for the structure in question, very large negative values of P_μ. According to the theory, P_μ must be always positive if N has been correctly chosen, no matter whether the structure is of the type of Patterson or of the ordinary Fourier.

2. To make a synthesis of index 2N and see if P_μ at the equivalent positions are materially altered or not. If N has been chosen correctly, the alteration must be inappreciable. This test, however, requires the order of an X-ray spectrum to be so high that its maximum H must be equal to or greater than N.

3. If the X-ray spectra have no enough higher order reflections, we can still make a synthesis of 2N or even 4N as proposed in a note in *Nature*[4], or even make a classical Fourier. In all these syntheses, the numerical values of P_μ at the

equivalent points are surely different from those in the original synthesis even N has been chosen correctly in the original one. However, if N is chosen correctly, the positions of the peaks will not be materially shifted.

The performance of the preceding processes involves a new kind of trial and error and so introduces a new type of labour in crystal analysis. This is the first disadvantage in the new method.

Again, for a somewhat complex structure, N most probably cannot be too small; from many different considerations the maximum H of a spectrum cannot probably be smaller than 50 in order to get a useful synthesis[4]. This requirement is not fulfilled yet by a spectrum taken in the usual way. This situation is not permanent though, and will very likely be improved by the recent progress in the technique of weak intensity measurement such as the method developed by de Lange, Robertson and Woodward in the analysis of trans-azobenzene[11]. Still this requirement of high order spectra does restrict the usefulness of the method and so forms the second disadvantage of the method.

The fundamental assumption can be removed, however, and so goes with the two disadvantages.

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11. De Lange, Robertson and Woodward, *Proc. Roy. Soc.* A, **171** (1939), 398.