A NEW METHOD FOR THE STRUCTURE ANALYSIS OF NON-CENTRO-SYMMETRIC CRYSTALS

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NO direct methods are available at present for the determination of the phases of structure factors of a single non-centrosymmetric crystal. If two isomorphous crystals are available and if the positions of the replaceable atoms (A) in the unit cell can be fixed, then the phases of the various reflections can be determined but for an ambiguity between two possible values. This ambiguity is in the sign of the phase θ with respect to the phase of the contribution from the replaceable atom, say, $a_A(hkl)$, so that the phase of the structure factor $F(hkl)$ may be either $a_1 = a_A + \theta$ or $a_2 = a_A - \theta$. In all the determinations made so far, the replaceable atoms are related by a centre of inversion so that the phase $a_A(hkl)$ is either 0 or π and so $a_1 = -a_2$. In such a case, if a Fourier synthesis is calculated using both a_1 and a_2, then the resulting diagram will consist of the structure, duplicated by its inverse at the inversion-centre of the replaceable atoms. If the replaceable atoms do not have a centre of symmetry, then no simple relation exists between the Fourier synthesis calculated by using both a_1 and a_2 and the actual structure.

DETERMINATION OF PHASE FROM ANOMALOUS DISPERSION

It is possible to obtain the phases directly, without the need for an isomorphous pair of crystals by making use of effects of anomalous dispersion. Suppose the crystal contains one atom or a set of atoms, for which the imaginary component of the scattering factor is appreciable, while for all the other atoms, this component is negligible. Such a situation occurs in a large number of organic

compounds, containing a halogen or sulphur or a metal atom, in addition to C, N and O. In such a case, it is possible to find the phase $a(hkl)$ with reference to the phase $a_A(hkl)$ of the anomalous scatterer.

Fig. 1 represents the various components of the structure amplitudes of a reflection hkl and its inverse $\bar{h}\bar{k}\bar{l}$ The latter are indicated by a bar over the symbols. F_A' is that part of the contribution from the anomalous scatterer which depends upon normal dispersion and F_A''
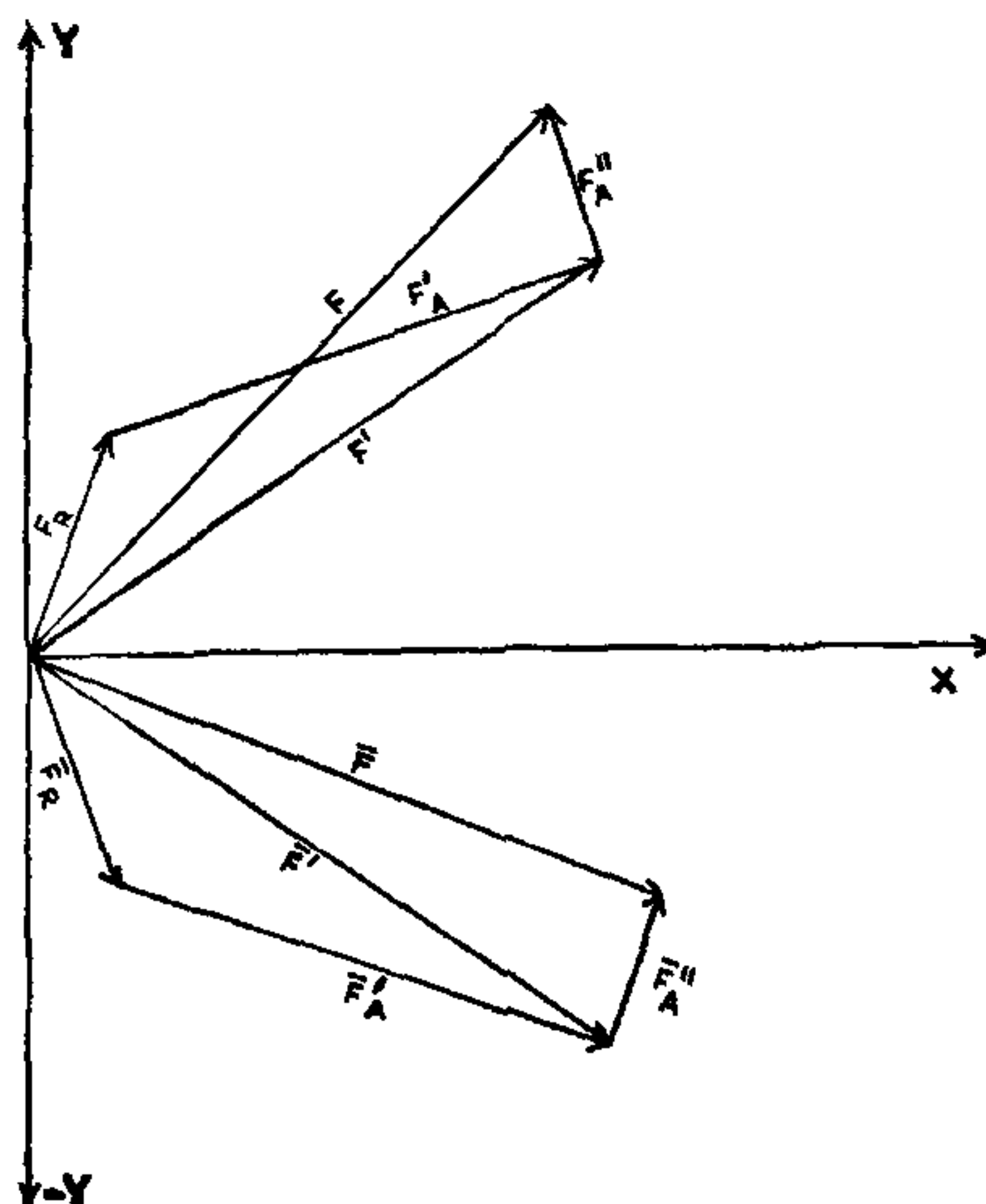

FIG. 1. Diagram showing the relationship between the various components of the structure amplitudes of reflections hkl and $\bar{h}\,\bar{k}\,\bar{l}$.

is the part which is produced by anomalous dispersion and F_R is the net contribution from all the other non-anomalous scatterers. The relationship between F, $\bar{F}$ and F_A'' is particularly brought out in Fig. 2 where the vectors
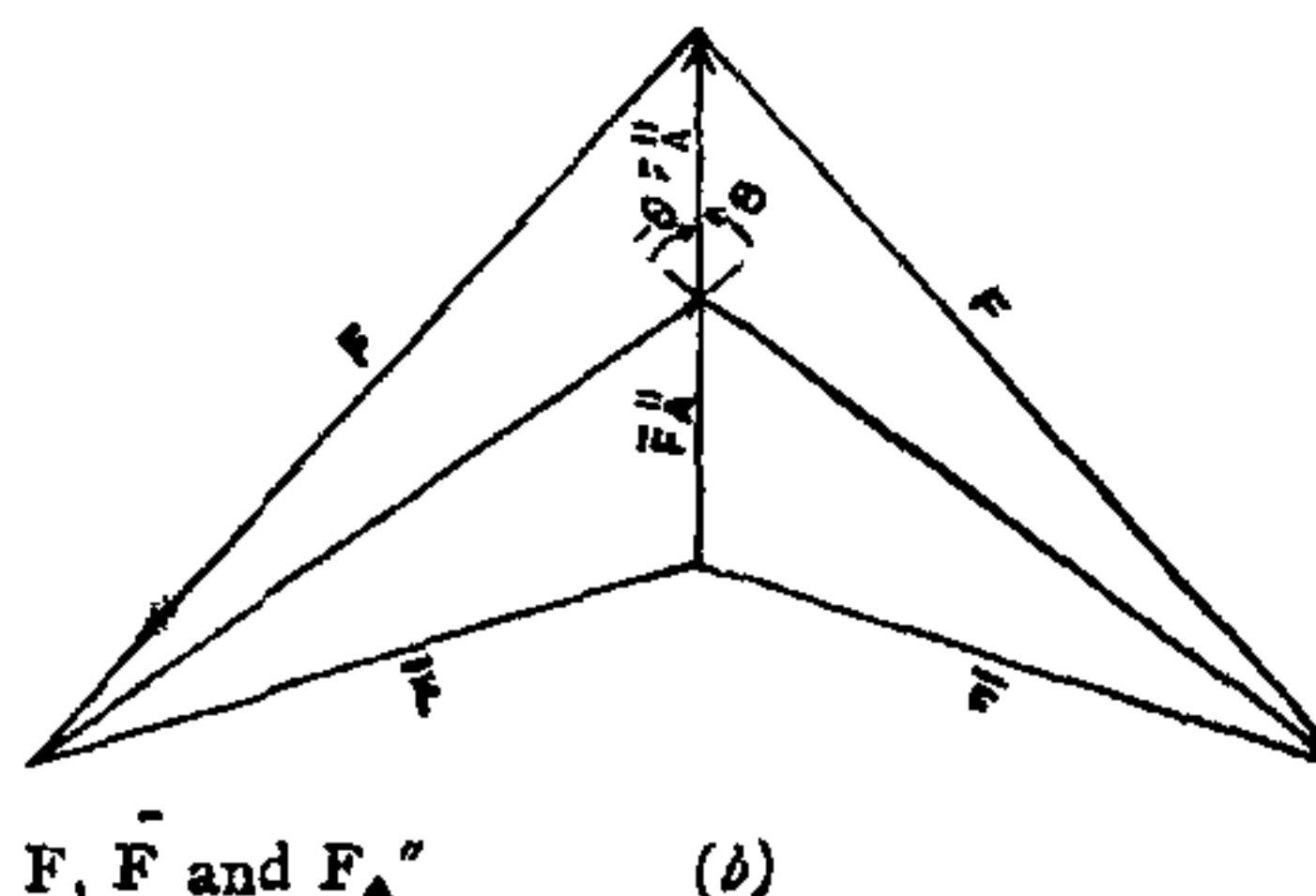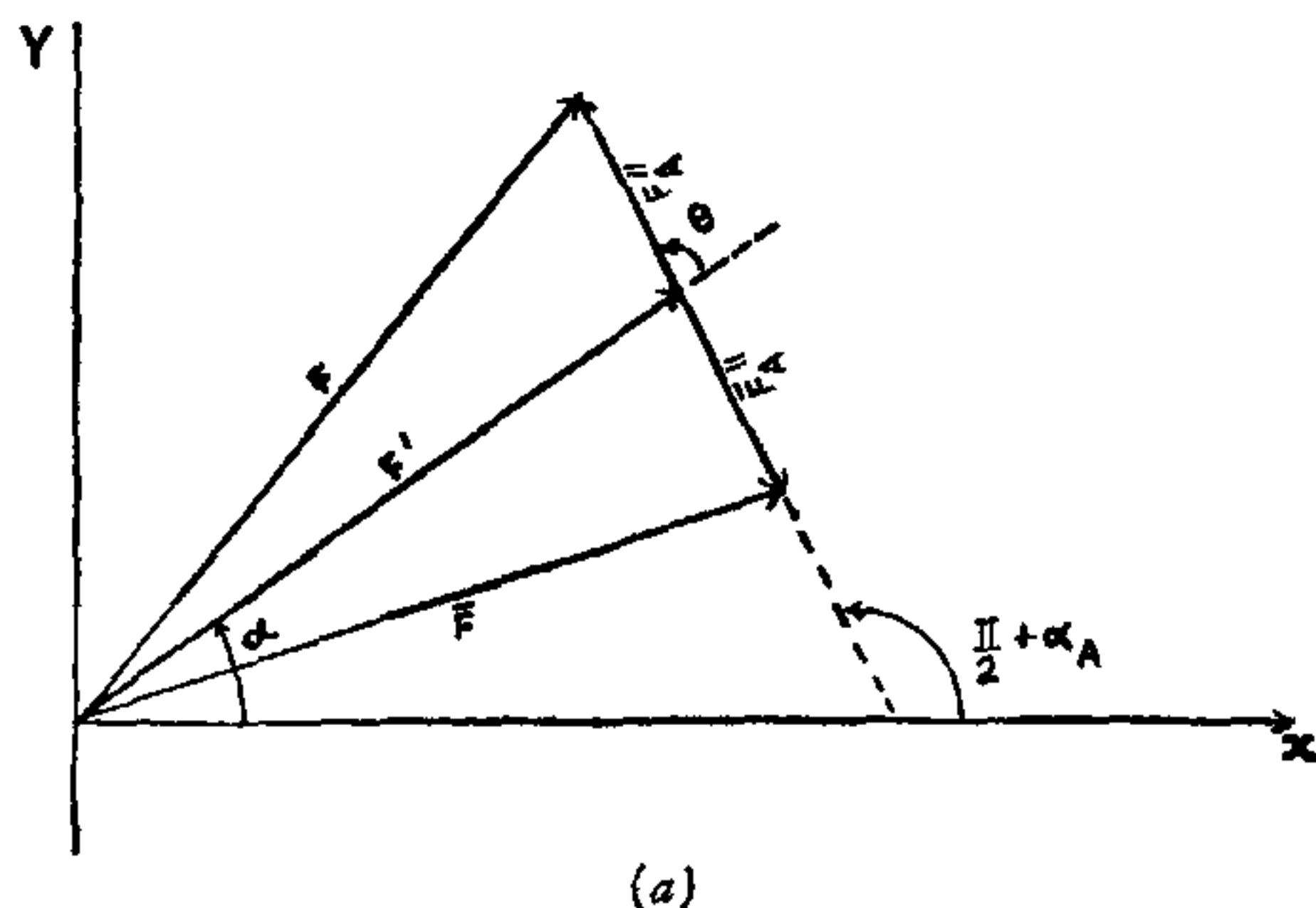

(a)

FIG. 2. Relation between F, $\bar{F}$ and F_A'' (b)

relating to $\bar{h}\,\bar{k}\,\bar{l}$ have been reflected about the real axis. We have from this diagram, since $\overline{F}_A'' = F_A''$ numerically,

$$F^2 = F'^2 + F_A''^2 + 2\,F'F_A''\cos\theta$$

$$\overline{F}^2 = F'^2 + F_A''^2 - 2\,F'F_A''\cos\theta$$

$$F'^2 = \tfrac{1}{2}\,(F^2 + \overline{F}^2) - F_A''^2$$

Thus

$$\Delta F^2 = (F^2 - \overline{F}^2) = 4\,F'F_A''\cos\theta$$

and $\cos\theta = \Delta F^2/4\,F'F_A''$ (1)

If $F_A'' \ll F_A'$, an approximate formula is

$$\cos\theta = \Delta F/2F_A''. \qquad (2)$$

Here θ is the angle made by the non-anomalous part of the structure factor with the anomalous part. The phase of F' is obviously $\alpha = \pi/2 + \alpha_A - \theta$, if all the anomalous scatterers are of the same type, e.g., all chlorines. If not, the phase angle ϕ between F_A'' and F_A' can be worked out from the known positions of the anomalous scatterers alone, and then

$$\alpha = \phi + \alpha_A - \theta$$

In the discussion below we shall confine ourselves to the former case when $\phi = \pi/2$ and the extension to the more general case is obvious.

Experimentally therefore, if the difference in intensity of the reflection hkl and its inverse $\bar{h}\,\bar{k}\,\bar{l}$ is measured accurately, then ΔF^2 can be calculated provided the scale factor is known. F_A'' can be calculated from the atomic co-ordinates of the anomalous scatterers (which can be obtained in most cases from a Patterson synthesis) and the known imaginary component of their atomic scattering factors and therefore θ can be obtained.

However, the solution for θ from $\cos\theta$ is ambiguous, since θ can be either $+\theta$ or $-\theta$ and consequently the phase of F' determined in this way has the ambiguity given by

$$\alpha_{1,2} = \pi/2 + \alpha_A \pm \theta$$

This ambiguity is similar to the one occurring in the determination of phase by the isomorphous replacement method. In fact the scattering factor of the atoms A for the two reflections hkl and $\bar{h}\,\bar{k}\,\bar{l}$ are effectively different and this is made use of in the determination of phase.

Ambiguity and Its Resolution

If the group of anomalous scatterers is centrosymmetric, the phase angle α_A is 0 or π and in this case, the two possible values of the phase of F' are $\alpha_1 = \alpha$ and $\alpha_2 = \pi - \alpha$. It can be shown that if a Fourier synthesis is calculated using both the values of the phase, then the resulting

diagram would contain, in addition to the peaks of the real structure, an equal number of negative peaks, at positions related to the former by an inversion about the inversion centre of the replaceable atoms. This diagram is similar to what one obtains by performing a Patterson synthesis with ΔF^2 which has been utilised by Pepinsky and collaborators for the determination of absolute configuration.[1] However it is superior to the latter in that only one duplication of the structure occurs and this too in the form of negative peaks, while in the ΔF^2 Patterson, a series of images of the structure as seen from each of the atoms in the set A occurs and the whole series is duplicated in the form of negative peaks about the inversion centre.

Experimental Verification

The method has been tested in the case of ephedrine hydrochloride[2] in which there are two chlorine atoms per unit cell. Only CuKα radiation was used and the anomalous dispersion of chlorine for this wavelength ($\Delta f'' = 0.69$) was sufficient to give useful information. The difference in intensity between each pair of inverse reflections was measured accurately with a Geiger counter spectrometer for all the reflections of type $hk0$ and the phases were calculated from expression (2). The measurements were put on an absolute scale by using the reported values of F_c. The values of α as found by experiment are given in Table I together with the values of α calculated from the structure determined by conventional methods. The agreement is seen to be good, the differences rarely exceeding 20°.

Of the two possible values, the one which is nearer to the phase of the chlorine atoms may be chosen for a preliminary synthesis and thus the ambiguity resolved. This assumption is seen to be valid in nearly 75 per cent. of reflections as may be seen from Table I. The phases of those reflections for which the contribution from the chlorine atom is zero are indeterminate and this is a defect of the method. Such reflections are small in number and this difficulty is present even in the isomorphous replacement technique.

Combination of the New Method and Isomorphous Replacement Technique

An interesting possibility arises if a pair of isomorphous substances are available and the replaceable atoms are anomalous scatterers. This is possible for instance with hydrochlorides and hydrobromides

TABLE I

Measurement of anomalous dispersion effect for hk0 reflections of ephedrine hydrochloride. a_1 and a_2 are the two possible values of the phase, and the one which agrees with the phase calculated from the structure is shown in heavy type. The tick mark indicates those reflections for which the correct phase angle is the one which is closer to the phase a_A of the chlorines. The reflections for which the columns beyond the fourth are left vacant are those for which θ is indeterminate, since $F_A'' = 0$.

h	k	l	$\dfrac{\Delta \sqrt{I}}{\sqrt{I}}$	$\Delta F = \dfrac{\Delta \sqrt{I}}{\sqrt{I}} \cdot F_0$	$2F_A''$	θ	a_A	a_1	$a_2 = \pi - a_1$	a from structure	Validity of hypothesis
1	1	0	-0.055	-0.086	-2.02	62	180	**28**	152	61	√
2	1	0	-0.052	-1.487	-2.76	57	180	33	**147**	158	√
3	1	0	-0.012	-0.466	-1.88	76	180	14	**166**	174	√
4	1	0	-0.010	-0.146	0.0	..	..	..	..	..	..
5	1	0	0.103	1.380	2.02	47	0	53	**127**	113	×
6	1	0	0.0	0.0	2.76	90	0	**0**	180	11	√
7	1	0	0.005	0.028	1.88	89	0	**1**	179	4	√
8	1	0	0.0	0.0	0.0	..	..	..	..	--	..
9	1	0	0.064	0.608	-2.02	108	180	342	**198**	225	√
10	1	0	-0.046	-0.409	-2.76	82	180	8	**172**	168	√
11	1	0	0.0	0.0	-1.88	90	180	0	**180**	175	√
12	1	0	-0.016	-0.027	0	..	..	..	..	..	..
0	2	0	0.0	0.0	-2.76	90	180	0	**180**	174	√
1	2	0	-0.025	-0.505	-1.88	74	180	16	**164**	153	√
2	2	0	0.0	0.0	0.0	..	..	..	..	..	..
3	2	0	0.270	1.701	2.02	32	0	58	**122**	116	×
4	2	0	-0.068	-1.292	2.76	118	0	**332**	208	324	√
5	2	0	-0.094	-0.686	1.88	111	0	**339**	209	325	√
6	2	0	0.0	0.0	0.0	..	..	..	..	..	..
7	2	0	-0.067	-0.0549	-2.02	74	180	16	**164**	163	√
8	2	0	0.0	0.0	-2.76	90	180	0	**180**	172	√
9	2	0	0.023	0.276	-1.88	99	180	351	**189**	220	√
10	2	0	-0.038	-0.251	0.0	..	..	..	..	..	..
11	2	0	-0.035	-0.200	2.02	95	0	**355**	195	351	√
12	2	0	0.071	0.511	2.76	79	0	**11**	169	27	√
1	3	0	-0.024	-0.451	2.02	103	0	**347**	193	349	√
2	3	0	0.009	0.156	2.76	87	0	**3**	177	15	√
3	3	0	0.026	0.354	1.88	79	0	**11**	169	10	√
4	3	0	-0.025	-0.315	0.0	..	..	..	..	..	..
5	3	0	0.035	0.371	-2.02	101	180	349	**191**	194	√
6	3	0	0.135	1.053	-2.76	112	180	338	**202**	242	×
7	3	0	-0.060	-0.378	-1.88	78	180	12	**168**	140	√
8	3	0	-0.040	-0.484	0.0	..	..	..	..	..	..
9	3	0	-0.026	-0.086	2.02	92	0	**358**	182	146	×
10	3	0	-0.058	-0.551	2.76	101	0	**349**	191	329	√
11	3	0	0.046	0.179	1.88	85	0	**5**	175	18	√
0	4	0	0.046	0.497	2.76	80	0	**10**	170	22	√
1	4	0	0.007	0.063	1.88	88	0	**2**	178	7	√
2	4	0	-0.012	-0.046	0.0	..	..	..	..	..	..
3	4	0	0.218	0.523	-2.02	105	180	**345**	195	280	×
4	4	0	0.043	0.383	-2.76	98	180	352	**188**	179	√
5	4	0	0.023	0.255	-1.88	98	180	352	**188**	202	√
6	4	0	..	..	0	..	..	..	..	..	..
7	4	0	-0.270	-1.701	2.02	148	0	**302**	238	273	×
8	4	0	0.024	0.250	2.76	85	0	**5**	175	26	√
1	5	0	-0.136	-1.006	-2.02	60	180	30	**150**	124	√
2	5	0	-0.055	-0.798	-2.76	73	180	17	**163**	179	√
3	5	0	-0.122	-0.598	-1.88	71	180	19	**161**	153	√
4	5	0	-0.066	-0.277	0	..	..	..	..	..	..
0	6	0	-0.025	-0.228	-2.76	85	180	5	**175**	161	√

of organic compounds. As already observed, the phase determination by isomorphous replacement is ambiguous. Detailed considerations[3] show that an unambiguous solution for the phases is possible by making use of a double replacement, *i.e.*, when one has two other isomorphous compounds related to the compound under study in which two different groups of atoms are replaced. It is essential that the two groups of replaceable atoms are not centrosymmetric about the same point in the unit cell or about points differing by integral multiples of half the unit translations. Even if these conditions are satisfied, the ambiguity might still occur for some reflections.

The ambiguity in the sign of the phase angle with reference to the phase of the replaceable atoms can however be resolved if the isomorphous replacement method is used in conjunction with the new method. This is so because the latter gives the two values

$$\alpha_1 = \alpha_A + \pi/2 + \theta \text{ and } \alpha_2 = \alpha_A + \pi/2 - \theta$$

while the former gives

$$\alpha_3 = \alpha_A + \phi \text{ and } \alpha_4 = \alpha_A - \phi$$

It is seen that one from each set should agree. Thus if $\alpha_1 = \alpha_3$ the other two are always different, and the choice is obvious. The advantage of this combination is that it requires only one pair of isomorphous compounds, and in such cases, an unambiguous solution for the phase is always possible, irrespective of whether the replaceable atoms have a centre of symmetry or not.

The anomalous dispersion method of determining phases is now being used in the analysis of L-lysine hydrochloride in this laboratory.

1. Pepinsky, R. and Okaya, Y., *Proc. Nat. Acad. Sci. U.S.*, 1956, **42**, 286.
2. Phillips, D. C., *Acta Cryst.*, 1954, **7**, 159.
3. Harker, *Ibid.*, 1956, **9**, 1.

SECOND CONGRESS ON THEORETICAL AND APPLIED MECHANICS

THE Second Congress on Theoretical and Applied Mechanics was held under the auspices of the Council of Scientific and Industrial Research on the 15th and 16th October 1956, at the National Physical Laboratory of India under the Presidentship of Dr. K. S. Krishnan, Director of the Laboratory. About eighty delegates were present including some from Germany, Japan, Poland and the U.S.A. Dr. J. C. Ghosh, Member, Planning Commission, who delivered the inaugural address, expressed the hope that the Indian society would soon establish direct contact with the International Union of Theoretical and Applied Mechanics. He also discussed the construction of a suitable model for the separation of diffusion and kinetic processes in gaseous catalytic reactions.

Dr. Krishnan in his presidential address explained the part played by the polarisation field in determining the observed resonance frequencies of the medium with particular reference to alkali-halides where the dispersion of the dielectric constant may also be regarded as exercised indirectly through its influence on resonance frequencies. Dr. P. Nilkantan gave a technical talk on 'The Origin of Ripples on Sand and Allied Phenomenon' where he suggested that the wave pattern was not due to 'saltation' of sand particles, but corresponded to the hydrodynamical effect of a fluid moving over another highly viscous fluid.

The Congress received eighty-six communications from many parts of the world including China, Czechoslovakia, Egypt, Japan, Poland, U.S.S.R. and the U.S.A. Forty-eight of these were presented before the Congress relating broadly to finite deformation, elasticity theory, vibration and stability, fluid flow, heat-transfer, ballistics and statistics.

The Society accepted an invitation to hold the Third Congress in October-November 1957 at the Indian Institute of Science, Bangalore. Dr. S. R. Sen Gupta, Director, Indian Institute of Technology, Kharagpur, was elected President for the sessions 1957-59.

The following other Office-bearers were elected : *Vice-Presidents* : Sri. V. Cadambe and Prof. N. R. Sen; *Secretary-Treasurer* : Prof. B. R. Seth, Indian Institute of Technology, Kharagpur; *Members of the Council* : Sri. C. V. Joga Rao, Dr. G. P. Chatterjee, Prof. B. M. Belgaumkar, Dr. S. K. Roy, Dr. Ram Ballabh, Prof. V. Lakshminarayan, Sri. S. Krishnan, Dr. K. L. Rao and Dr. A. K. Gayen.