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Use of the Tangent Formula to Resolve the Phase Ambiguity in the Neutron Anomalous-Dispersion Method

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It is proposed that the tangent formula can be used to resolve the phase ambiguity arising in the neutron anomalous-dispersion method. This is checked by calculations on the structure of L-aspartatocadmium (II) trihydrate.

Ramachandran & Raman (1956) have shown that the phase φ of F' for a crystal containing some atoms which scatter the radiation anomalously is given by

$$\varphi=\varphi_A+\frac{\pi}{2}+\theta$$

where

$$\cos\theta=\frac{|F|^2-|\bar{F}|^2}{4|F'|\,|F_{A''}|}\,.$$

The uncertainty in the sign of θ gives rise to the two possible values φ_1 and φ_2 (see Fig. 1) for the phase of each reflexion. In the X-ray case, this ambiguity is resolved or circumvented by (*a*) the heavy atom method (Ramachandran & Raman, 1956), (*b*) the double-phase Fourier-synthesis method (Ramachandran, 1964) (*c*) the sine–Patterson method (Okaya, Saito & Pepinsky 1955) and (*d*) the two-wavelength method (Raman, 1959). For neutron diffraction, MacDonald & Sikka (1969) have pointed out that the heavy-atom method cannot be used since there are no heavy atoms from the scattering point of view. Methods (*b*) and (*c*) were successfully applied by them in the structure determination of $Cd(NO_3)_2.4D_2O$. The relative ease in solving this structure by these methods depended partly, perhaps, on the fact that deuterium atoms had been substituted for hydrogen atoms. This not only avoided the confusion between positive and negative peaks (note that the neutron-scattering amplitude of hydrogen is negative and that of deuterium is positive) but also the cancellation of some atomic positions by possible overlap of these positive and negative peaks, which arise in the maps for methods (*b*) and (*c*). The limitations of the two-wavelength method have been examined by Sikka (1969). If the phase ambiguity has to be resolved then the two wavelengths chosen for data collection have to be on opposite sides of the resonance. The best choice seems to be, for ^{113}Cd ($\lambda_1=1\cdot00$ and $\lambda_2=0\cdot55$ Å, $\lambda_0=0\cdot68$ Å) and for ^{149}Sm ($\lambda_1=1\cdot30$ and $\lambda_2=0\cdot75$ Å, $\lambda_0=0\cdot93$ Å). For Cd, the value 0·55 Å is not practicable unless a hot source coupled with the reactor is used. For ^{149}Sm, the wavelengths are suitable but the larger absorption of Sm compared with Cd will make the measurement of four sets of data $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ at λ_1, λ_2 time consuming.

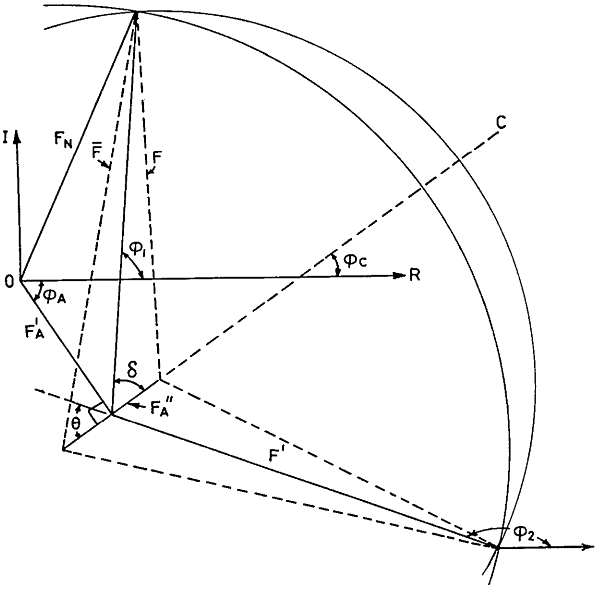

Fig. 1. Amplitude–phase diagram for anomalous-dispersion scattering. F and $\bar{F}$ are the structure factors for Bijvoet pairs, F' is the mean structure factor, $F_{A'}$ and $F_{A''}$ are the real and imaginary structure factors of the anomalous scatterer of phase φ_A.

Hazell (1970) has suggested that direct methods can be used to choose the correct phase in the anomalous-dispersion method. Since the applicability of direct methods in neutron diffraction has already been demonstrated by us (Sikka, 1969*b*, 1970*a*), we have examined the possibility that the tangent formula (Karle & Karle, 1966) can be used to circumvent the phase ambiguity in the neutron resonance-scattering case. This note presents the results of this study.

Experience has shown that in a tangent-formula calculation, if any input phase is within about 45° of its true value then it will be useful in determining the phases of other reflexions. Also the error in this phase will probably be reduced during the course of refine-

Table 1. *Tangent formula refinement results**

Set number	Input set	Number of reflexions in the set	δ limit	Weight assigned in first cycle	$\langle\lvert\varphi_o-\varphi_{\rm TAN}\rvert\rangle$ for acentric reflexions	Number of centric reflexions with wrong phase
1	φ_o	144	—	1	22·4°	2
2	φ_c	88	90°	$\lvert\cos\delta\rvert$	24·5	3
3	φ_c	88	90	$\lvert\cos\delta\rvert^2$	22·5	1
4	φ_c	17	20	$\lvert\cos\delta\rvert$	24·7	4

* φ_o is the true value of phase and $\varphi_{\rm TAN}$ is the one calculated by the tangent formula. Out of 144 reflexions, 90 were acentric. $\langle\lvert\varphi_o-\varphi_{\rm TAN}\rvert\rangle$ is the average error after 7 cycles of refinement.

ment.* Now one can get an input set of phases with errors less than 45° from the Bijvoet differences as follows. In Fig. 1, we have defined the centroid of φ_1 and φ_2 to be φ_c and δ is the half angle of this ambiguity. It is easy to see that if φ_c is chosen to be the starting phase then the error will be δ, which varies from 0 to 90°; there will be a reasonable number of reflexions with δ less than 45°. In practice one may take all the φ_c's above a certain $\lvert E_{\rm min}\rvert$ as input and then weight them by a suitable function of δ.

For checking the above approach we have carried out calculations for the hypothetical structure of L-aspartatocadmium (II) trihydrate, $\rm Cd(NH_2CH(CH_2COO)COO)3H_2O$. This crystal has been assumed to be isomorphous with the Zn compound ($P2_12_12_1$, $a=9{\cdot}38$, $b=7{\cdot}92$ and $c=11{\cdot}53$ Å), the heavy atoms of which have been located by Doyne, Pepinsky & Watanabe (1957), using X-rays. The hydrogen atom coordinates were calculated by assuming reasonable bond distances and angles and then from these, the values of E's, φ_1, φ_2, φ_c and δ were computed up to $\sin\theta/\lambda=0{\cdot}70$ Å^{-1}. The neutron scattering factors used were: $b_{\rm N}=0{\cdot}94$, $b_{\rm C}=0{\cdot}66$, $b_{\rm O}=0{\cdot}58$, $b_{\rm H}=-0{\cdot}38$ and $b_{\rm Cd}=(0{\cdot}33+0{\cdot}10i)\times10^{-12}$ cm.

Weighted tangent-formula calculations with inputs as discussed above were performed for 144 reflexions ($\lvert E_{\rm min}\rvert=1{\cdot}5$), with the program *TANFMULA* (Sikka, 1970*b*). The results of these are given in Table 1.

It was found that all the output phases for the different input sets were similar with the one for φ_o as input. This is also shown by the average errors $\langle\lvert\varphi_o-\varphi_{\rm TAN}\rvert\rangle$. This confirms that the tangent formula can be successfully used to derive the correct set of phases, starting from φ_c's. An obvious bonus of this is the phases of centric reflexions. The weighting scheme seems to be having very little effect although the agreement of set 3 is marginally better than others. Hazell (1970) has suggested that one can take the starting set of reflexions for which $\varphi_1=\varphi_2$.† This approach may have limited application since there will be few reflexions of this type and still fewer reflexions with $\lvert E\rvert$ values also greater than, say, 1·3.‡ For example in our neutron study of $\rm Cd(NO_3)_2.D_2O$ there were 32 reflexions with $\varphi_1=\varphi_2$, of which only 13 had $\lvert E\rvert$ values greater than 1·3 ($6\geq1{\cdot}5$). The refinement 4 in Table 1 is similar to Hazell's approach. It yields the correct set but the errors are a little higher than others. Our results support the view that larger errors can be tolerated in the starting set for tangent calculation if it consists of a large number of reflexions (Dewar, 1968).

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* This is the basis of quadrant permutation method of Germain & Woolfson (1968).

† This can happen if $\lvert\cos\theta\rvert\geq1$ due to errors in measurements or due to wrong scaling of observed F_o's.

‡ Unlike the X-ray case, the tangent formula is not applicable for all E values in neutron diffraction if the crystal contains hydrogen atoms.

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