Short-Range Order in N-oxyphenazine and in Mixed Crystals of Phenazine-N-oxyphenazine

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VI. SHORT-RANGE ORDER IN N-OXYPHENAZINE AND IN MIXED CRYSTALS OF PHENAZINE–N-OXYPHENAZINE

By A. M. GLAZER

[Plates 13 and 14]

CONTENTS

Disorder diffuse scattering has been observed for N-oxyphenazine which indicates the existence of domains of short-range order in (100) planes, of average size 13 Å (along b) by 50 Å (along c). Along a the alternation of centrosymmetrically arranged molecules is random. Mixed crystals with phenazine show diffuse scattering which indicates that up to about 60 mole % of phenazine can occur in the structure without disrupting these short-range-order domains. Mixed crystals of low N-oxyphenazine content have these molecules arranged randomly in the phenazine matrix. Between these two phases there appears to be a miscibility gap. It is probable that two components, one of which is ordered and the other showing only short-range order cannot form a continuous mixed-crystal series.

INTRODUCTION

Diffuse scattering due to static or dynamic disorder occurs as a background to every well-exposed X-ray diffraction pattern but is most easily recognized and measured using a stationary crystal and white + characteristic radiation. If the diffracted intensity is sufficient it is better to filter or even monochromatize the incident beam, since the diffuse scattering is mainly due to the characteristic component; but Laue spots may be useful for a determination of crystal orientation. Diffuse scattering due to short-range order occurs between the normally sharp layer-lines in anthrone (Flack, part III, above), 9-bromo-10-methylanthracene (Prat 1961) and lead n-butyl xanthate (Hagihara, Watanabe & Yamashita 1968).

EXPERIMENTAL OBSERVATIONS

Large crystals of phenazine and N-oxyphenazine were selected and mounted on glass fibres on goniometer arcs, each with [010] vertical. A series of stationary-crystal photographs was taken at 5° intervals about [010], using CuK radiation, unfiltered. Exposure times were 1 h for phenazine, 2 h for N-oxyphenazine. Examples of these photographs are shown in figure 1, plate 13.

It is evident that the thermal diffuse scattering is very similar for phenazine and N-oxyphenazine, but that for the latter there are extra diffuse spots in the $h\frac{1}{2}l$, $h\frac{3}{2}l$, $h\frac{5}{2}l$, etc. positions, that is, half-way between the normal k integral layer-line positions. Photographs taken at $-90\,^{\circ}\mathrm{C}$ confirmed that these are due to short-range order, since they are, if anything, enhanced in

intensity at the lower temperature, whereas the thermal diffuse scattering is greatly diminished (Flack, part II, above).

Stationary-crystal and oscillation photographs of N-oxyphenazine taken with [001] vertical (along the axis of the cylindrical camera) showed $l = \frac{1}{2}, \frac{3}{2}$, etc. inter-layer diffuse scattering also.

Similar X-ray diffraction photographs were taken of mixed crystals containing 8, 25, 35 and 52 mole % N-oxyphenazine. One example is shown in figure 2, plate 14. Short-range-order diffuse scattering was observed for crystals containing between 25 and 100 mole % N-oxyphenazine, although at 25 % it is only just visible.

Conversion of observed diffuse scattering to reciprocal space

For comparison with calculations made on the basis of Flack's theory (part II) it was decided to plot the sections $h\frac{1}{2}l$, $h\frac{3}{2}l$ and $hk\frac{5}{2}$. This was done as follows, using the complete sets of photographs taken at 5° intervals.

(1) A circle of paper was cut, radius $(1-\zeta)^{\frac{1}{2}}$ where ζ is the reciprocal lattice coordinate as defined on p. 175 of the *International tables for X-ray crystallography*, vol. 2.

(2) On this circle, which represents the circle of reflexion, lines of constant ξ were drawn at intervals of 0.1 reciprocal unit.

(3) The circle was then placed on a suitably scaled drawing of the reciprocal lattice, so that its diameter coincided with the direction of the incident beam for the first stationary-crystal photograph.

(4) By reference to a Bernal chart, the ξ coordinates covering the full extent of each diffuse peak were read off and then marked on the reciprocal lattice by drawing an arc around the edge of the cut-out circle of reflexion (see figure 3). This was repeated for each diffuse maximum in the selected layer for one photograph.
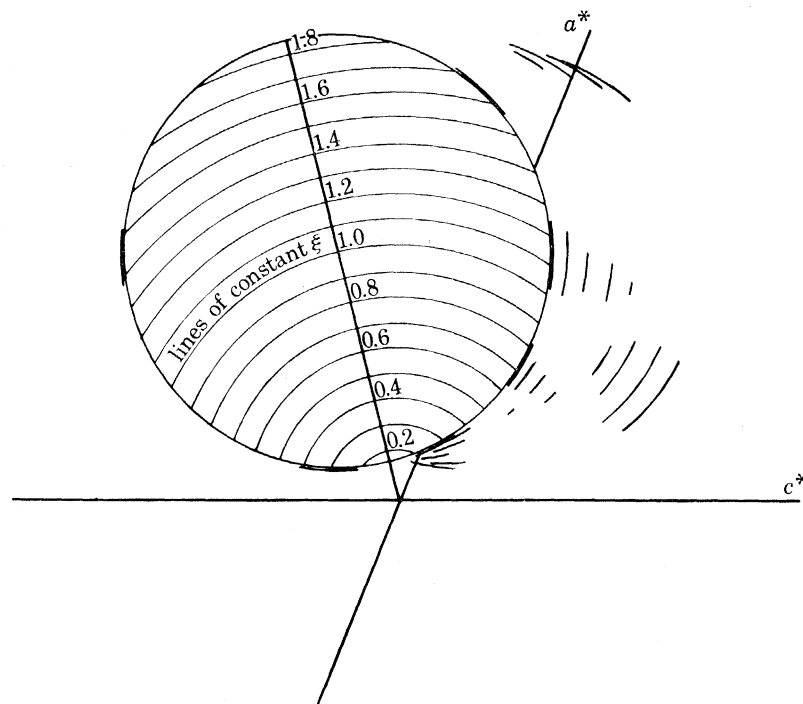

FIGURE 3. Construction to convert observed diffuse scattering data to reciprocal space.
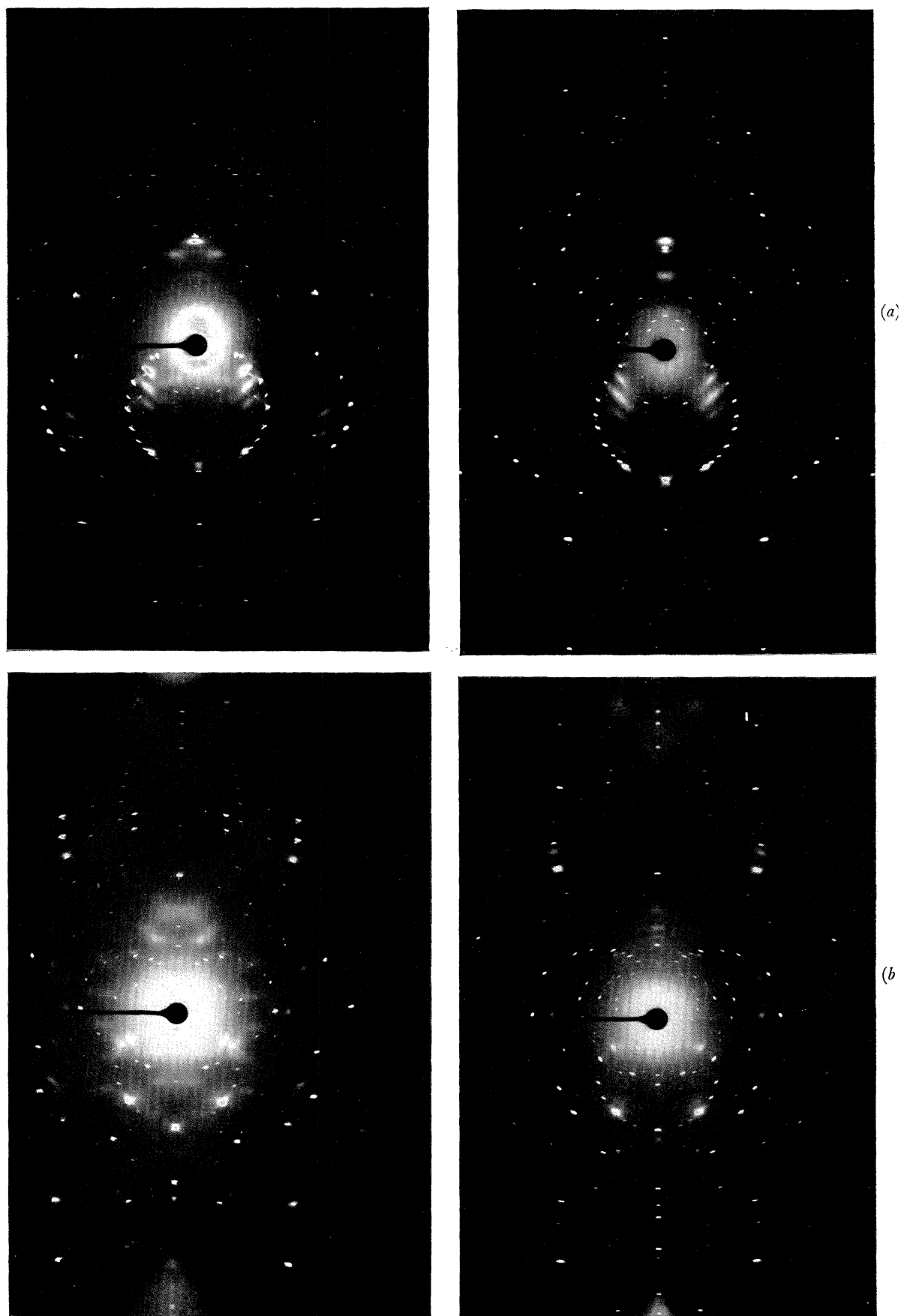
FIGURE 1. Stationary-crystal photographs, [010] along cylindrical camera axis, white + CuK (unfiltered) X-radiation: (right) phenazine, (left) *N*-oxyphenazine. (*a*) [001] approximately 30° from incident beam direction. (*b*) [001] approximately 95° from incident beam direction. Short-range-order diffuse scattering can be seen arranged in $h \frac{1}{2}(2n+1) \, l$ and $h \, k \, \frac{1}{2}(2n+1)$ layers.
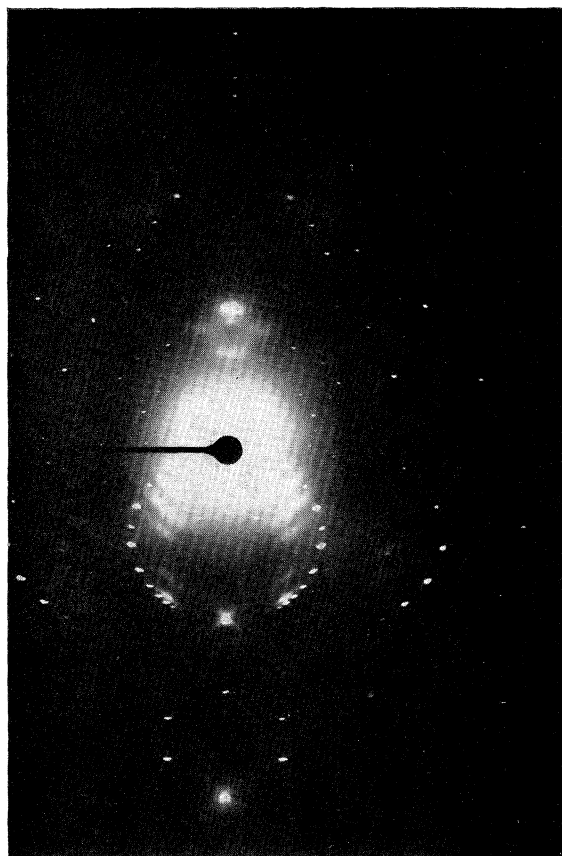
FIGURE 2. Stationary crystal photograph of mixed crystal (52 mole % *N*-oxyphenazine), [010] a long cylindrical camera axis, white + Cu K (unfiltered) X-radiation, [001] approximately 30° from incident beam direction. (C.f. figure 1 (*a*)).
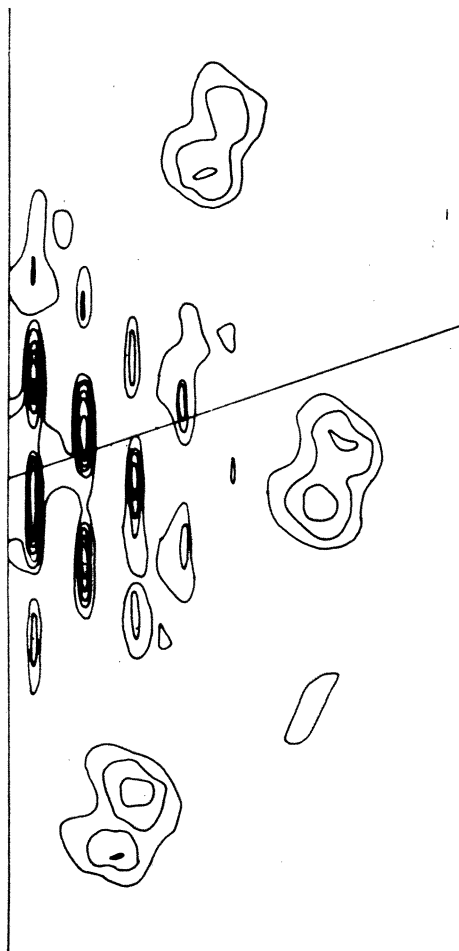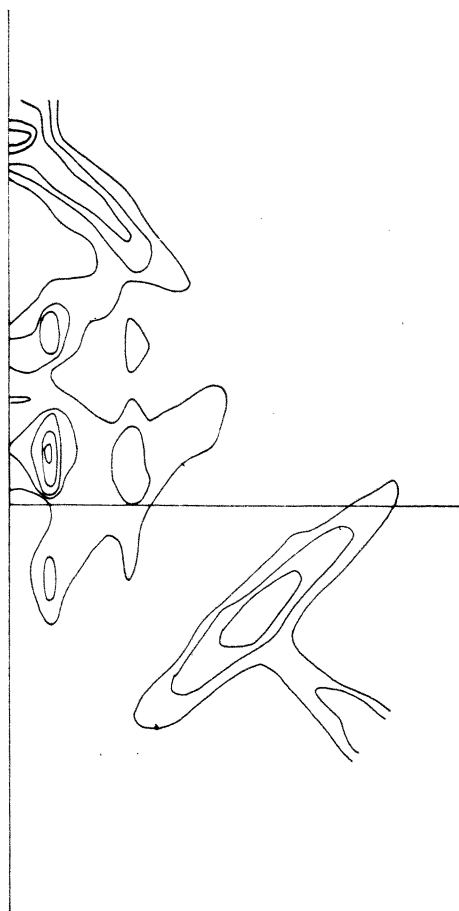
FIGURE 4 (*b*)

FIGURE 5 (*b*)

(5) The circle of reflexion was then rotated by 5° about the origin of the reciprocal lattice and the positions and extent of the diffuse spots on the next photograph were then similarly recorded.

Figures 4*a* and 5*a* show the resultant 'observed' distributions of diffuse scattering in $h\frac{1}{2}l$ and $hk\frac{5}{2}$ respectively. No patterned diffuse scattering was observed normal to [100].
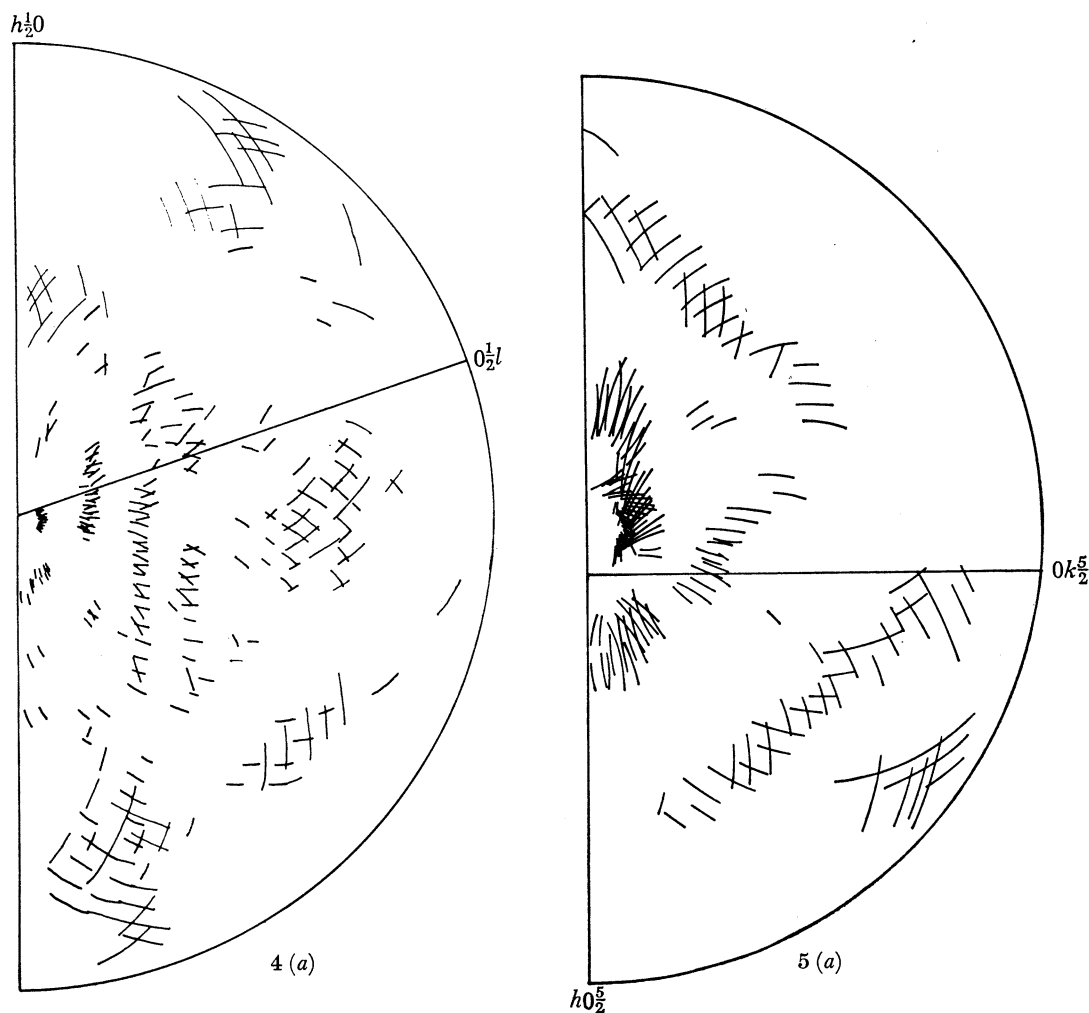

FIGURE 4. (*a*) Distribution of observed diffuse scattering in $\{h\frac{1}{2}l\}$ section of reciprocal space. (*b*) (Overlay) Theoretical distribution of diffuse scattering in $\{h\frac{1}{2}l\}$ derived from deduced α, β, γ values.

FIGURE 5. (*a*), (*b*) The same for $\{hk\frac{5}{2}\}$.

COMPARISON WITH THEORY

By measurement of the breadths of the diffuse maxima, using Flack's theory (part II) it has been estimated that for *N*-oxyphenazine

$$\alpha = 0.50, \quad \beta = 0.65, \quad \gamma = 0.85.$$

The value chosen for α corresponds with complete randomness of molecular orientations along [100] as between either of the two possible directions which together produce pseudo-centrosymmetry.

(5) The circle of reflexion was then rotated by 5° about the origin of the reciprocal lattice and the positions and extent of the diffuse spots on the next photograph were then similarly recorded.

Figures 4a and 5a show the resultant 'observed' distributions of diffuse scattering in $h\frac{1}{2}l$ and $hk\frac{5}{2}$ respectively. No patterned diffuse scattering was observed normal to [100].
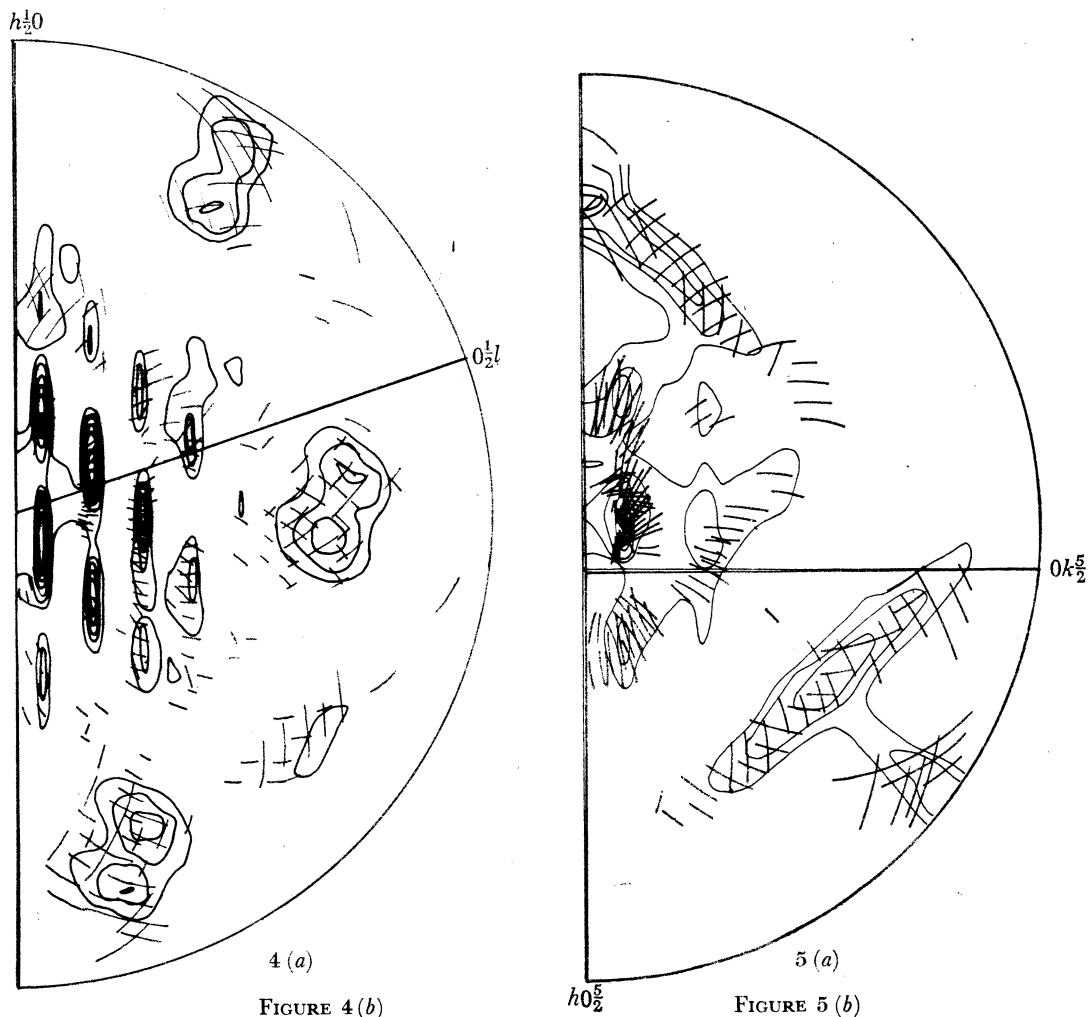

FIGURE 4 (b)   FIGURE 5 (b)

FIGURE 4. (a) Distribution of observed diffuse scattering in $\{h\frac{1}{2}l\}$ section of reciprocal space. (b) (Overlay) Theoretical distribution of diffuse scattering in $\{h\frac{1}{2}l\}$ derived from deduced α, β, γ values.

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In calculating the intensity of diffuse scattering corresponding to the above α, β, γ values, only the oxygen atoms had to be taken into account since the remainder of the molecule is effectively centrosymmetrical. As Flack (part III) has explained, the calculation must also include an allowance for the thermal diffuse scattering, which must interact with the short-range-order effects. The calculation of disorder scattering is given by equation (14) of Flack (part II) using the oxygen atoms, and the difference Fourier transform (d.F.t.) gives the thermal scattering. Using both these, the calculated total diffuse scattering patterns for $h\frac{1}{2}l$ and $hk\frac{5}{2}$ are as shown in figures 4b and 5b. The qualitative agreement with observation is good, which implies that the values of α, β, γ deduced for the short-range order must be essentially correct.

It seems, therefore, that the N-oxyphenazine crystal consists of small ordered areas or domains, separated by regions of disorder, the domains being of the type

$$
\begin{array}{ccccccc}
A & B & A & B & A & B & \ldots \\
B & A & B & A & B & A & \ldots \\
A & B & A & B & A & B & \ldots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots
\end{array}
$$

where the average size is $b/(1-\beta)$ by $c/(1-\gamma)$, i.e. approximately 13 Å along [010] by 50 Å along [001] (rather less than 3 molecules along b by 7 molecules along c), with random disorder along [100].

Interpretation of observations for mixed crystals

Although the disorder scattering became relatively weakened, as compared with that for pure N-oxyphenazine, as the mole percentage of phenazine was increased, the actual shapes and distribution of the maxima seemed not to change very much. This suggests that the phenazine molecules take up positions between the short-range-ordered domains, but do not break up the domains themselves.

The growth of the mixed crystal may be pictured as follows. There is an alternation of N-oxyphenazine molecules (figure 6) to the point where the probability distribution indicates a break. In the figure this occurs for an orientation B, after which either another molecule of N-oxyphenazine (also in orientation B) or a molecule of phenazine (P) may be added, each of these presenting the same type of intermolecular contact to the end molecule of the row. The likelihood of such a choice occurring at each break in the short-range order would explain why phenazine can form a solid solution with N-oxyphenazine even up to about 60 mole % phenazine (see part V, preceding). Beyond this point the proportion of phenazine present would be high enough to disrupt the short-range-ordered domains. At the other extreme, when N-oxyphenazine molecules are only present to a few per cent they may substitute for phenazine molecules at random. There are therefore two phases in the system: (1) N-oxyphenazine substituted at random in the phenazine matrix; (2) phenazine substituted randomly between small ordered domains of centrosymmetrically arranged N-oxyphenazine.

The miscibility gap corresponds with the transition between these two phases.

It is difficult to pinpoint the exact composition at which short-range order breaks down, because high background scattering due to general disorder tends increasingly to mask the diffuse scattering typically due to short-range order. However, the observations made both on the phenazine–N-oxyphenazine and on the anthrone–anthraquinone mixed-crystal series (Flack
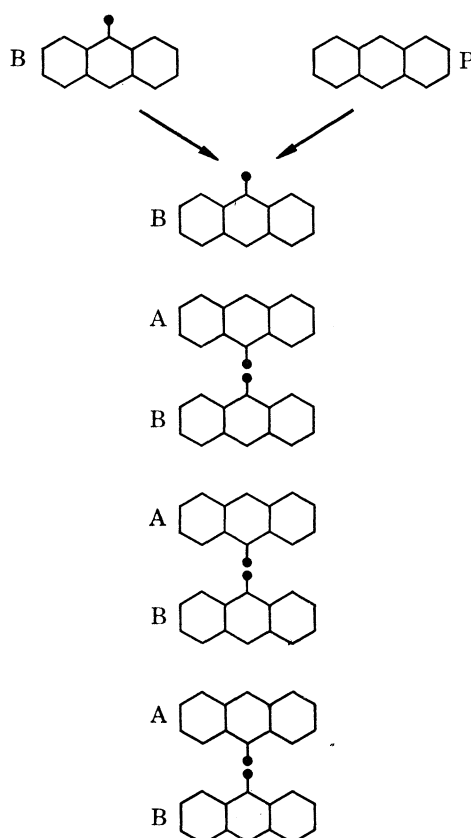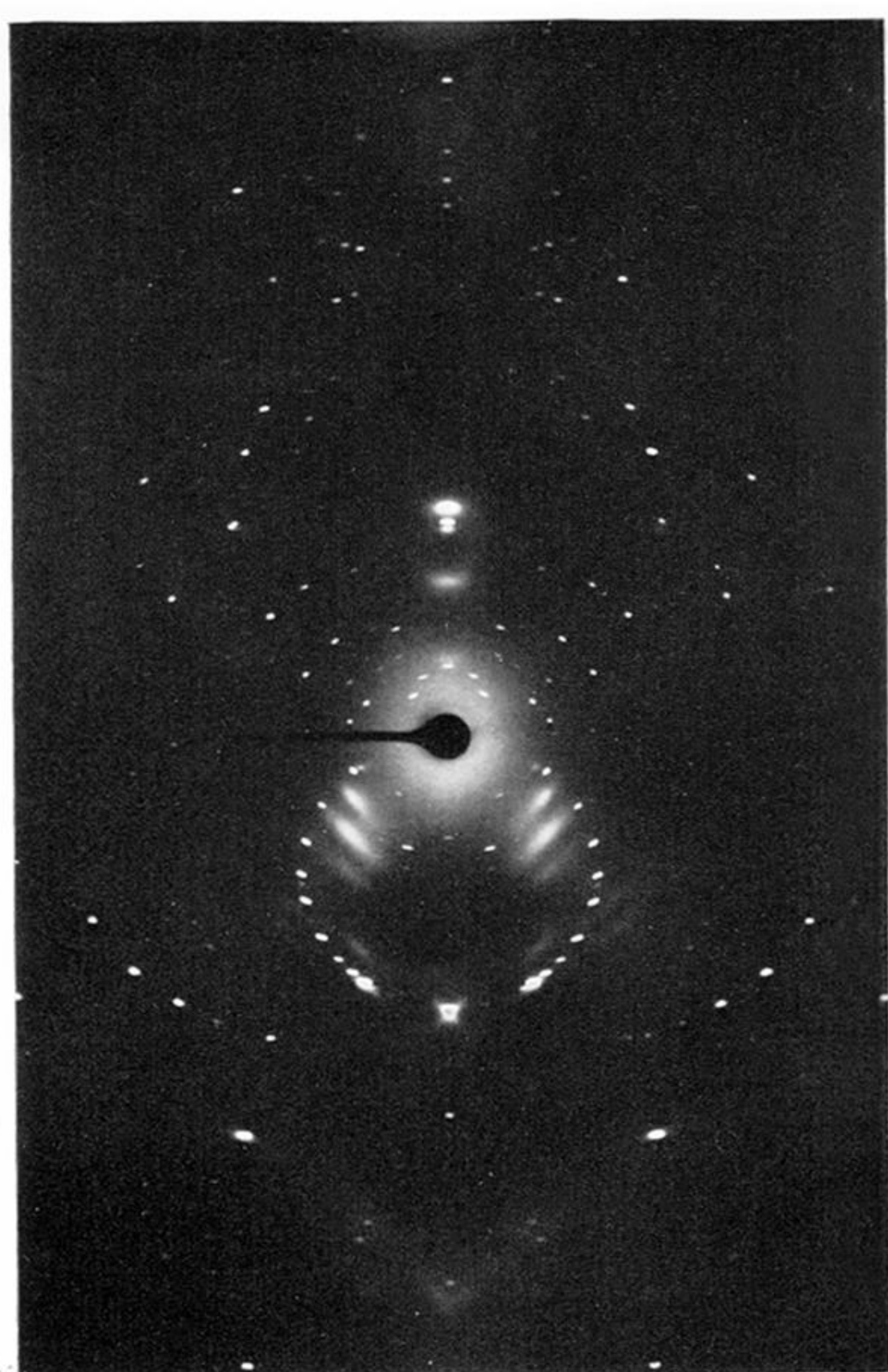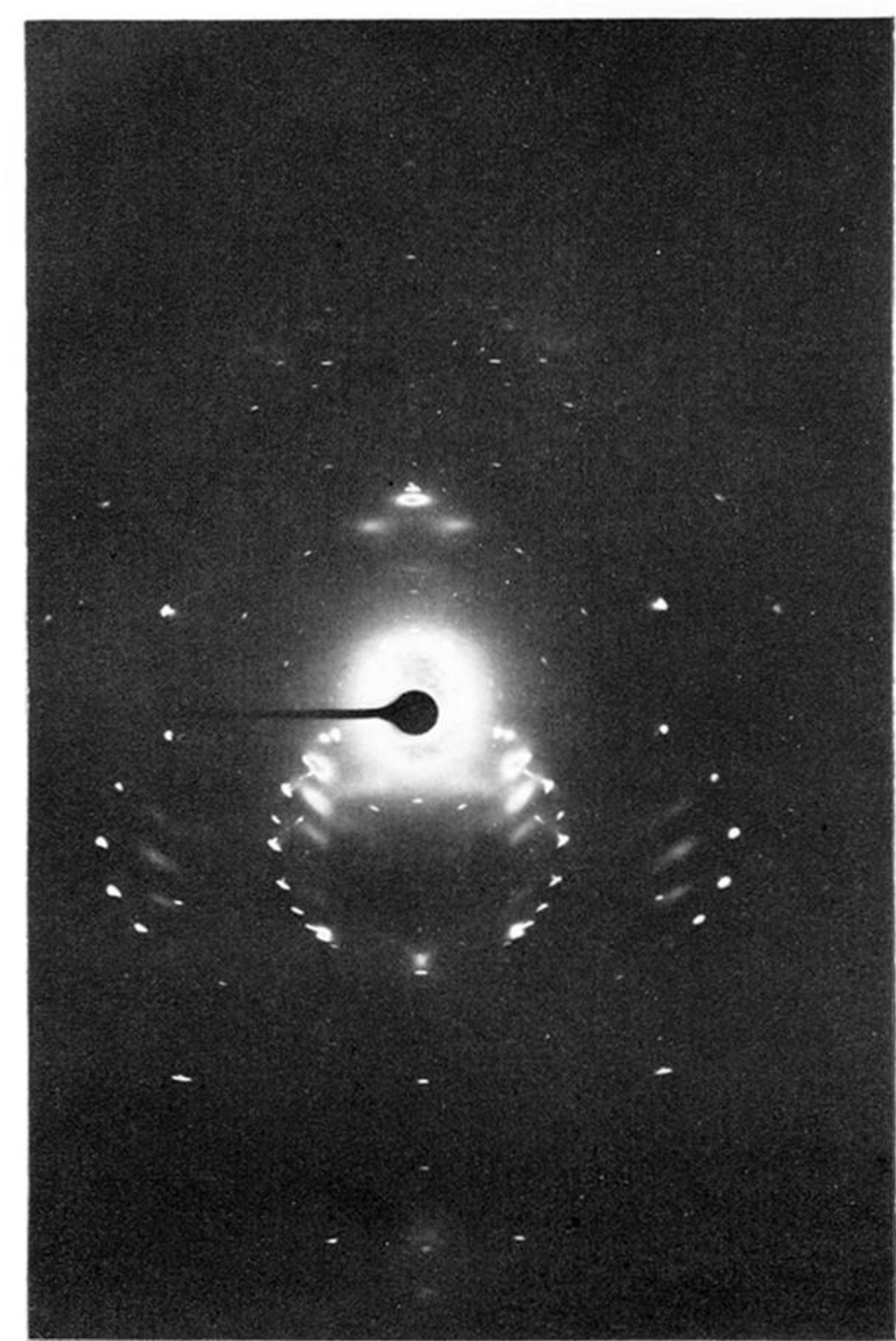
FIGURE 6. Diagrammatic representation of the formation of an 'interblock' solid solution
of phenazine in partially ordered *N*-oxyphenazine.

1968) imply that, in addition to the rules given by Kitaigorodskii (1957) there is one further condition for solid state solubility, namely that complete miscibility is unlikely between two components one of which is fully ordered, whereas the other possesses limited short-range order only.
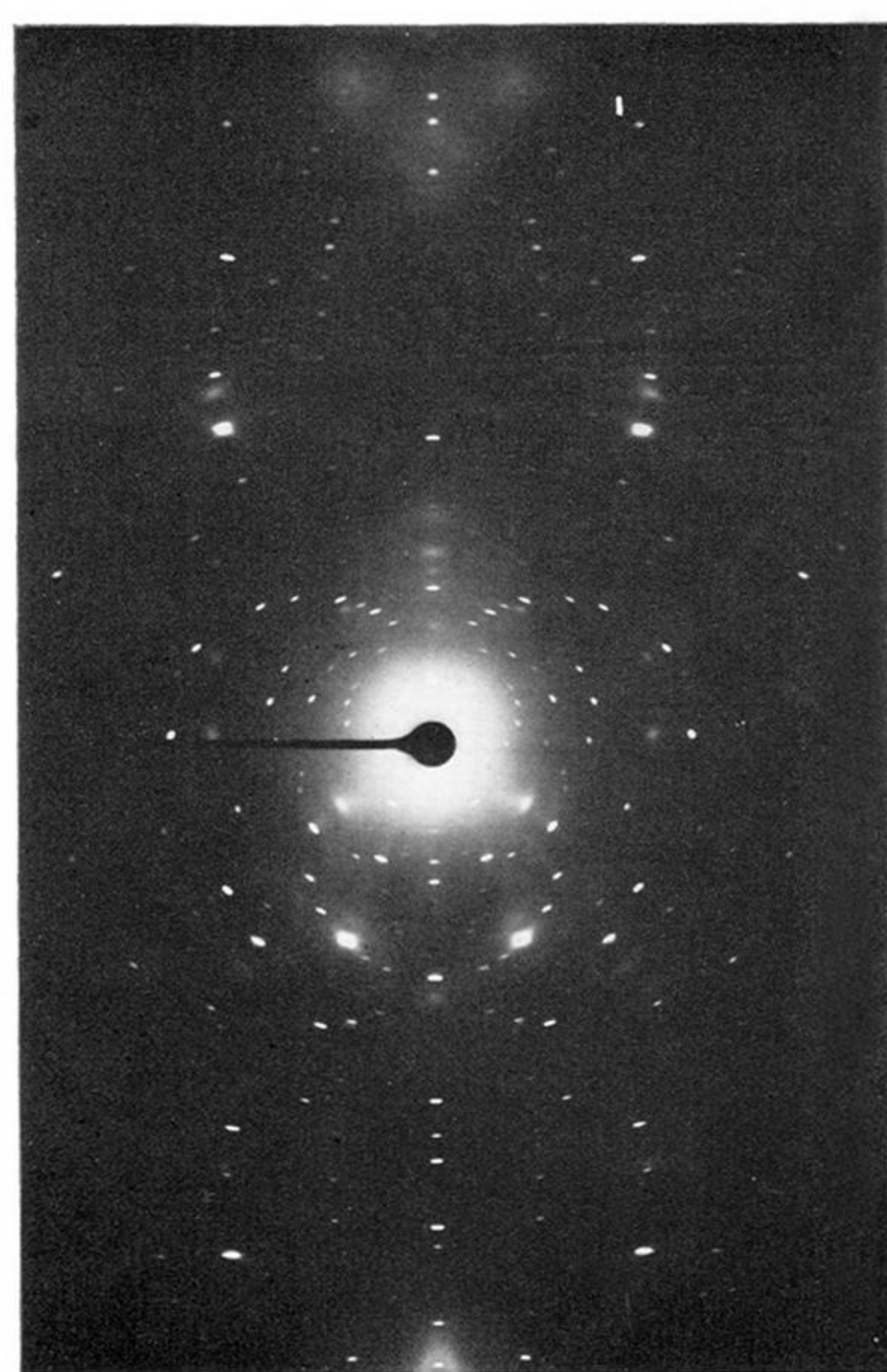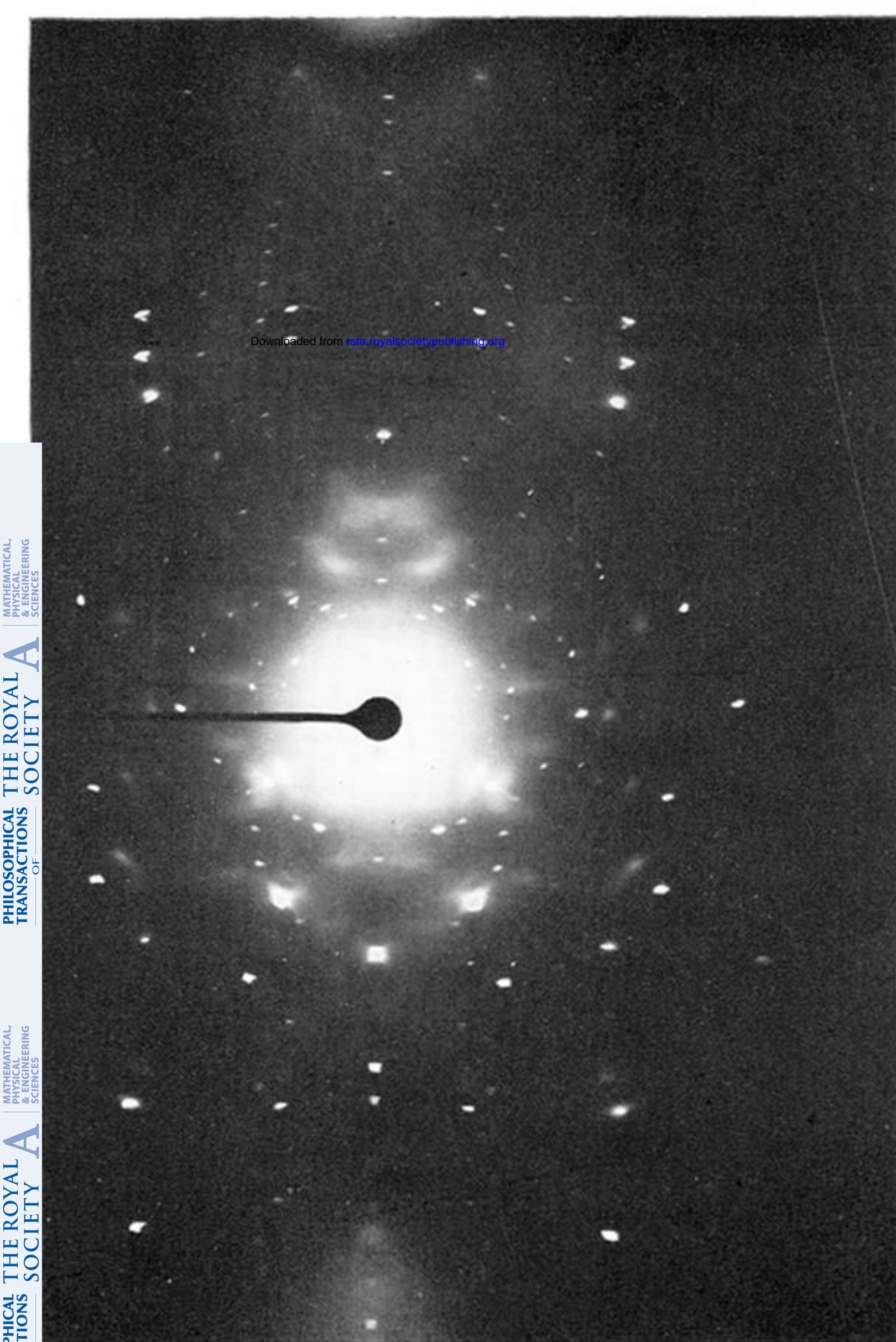
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Kitaigorodskii, A. I. 1957 *Kristallografiya* **2**, 456; also *Dokl. Akad. Nauk. SSSR* **113**, 604.
Prat, M. T. 1961 *Acta crystallogr.* **14**, 110.

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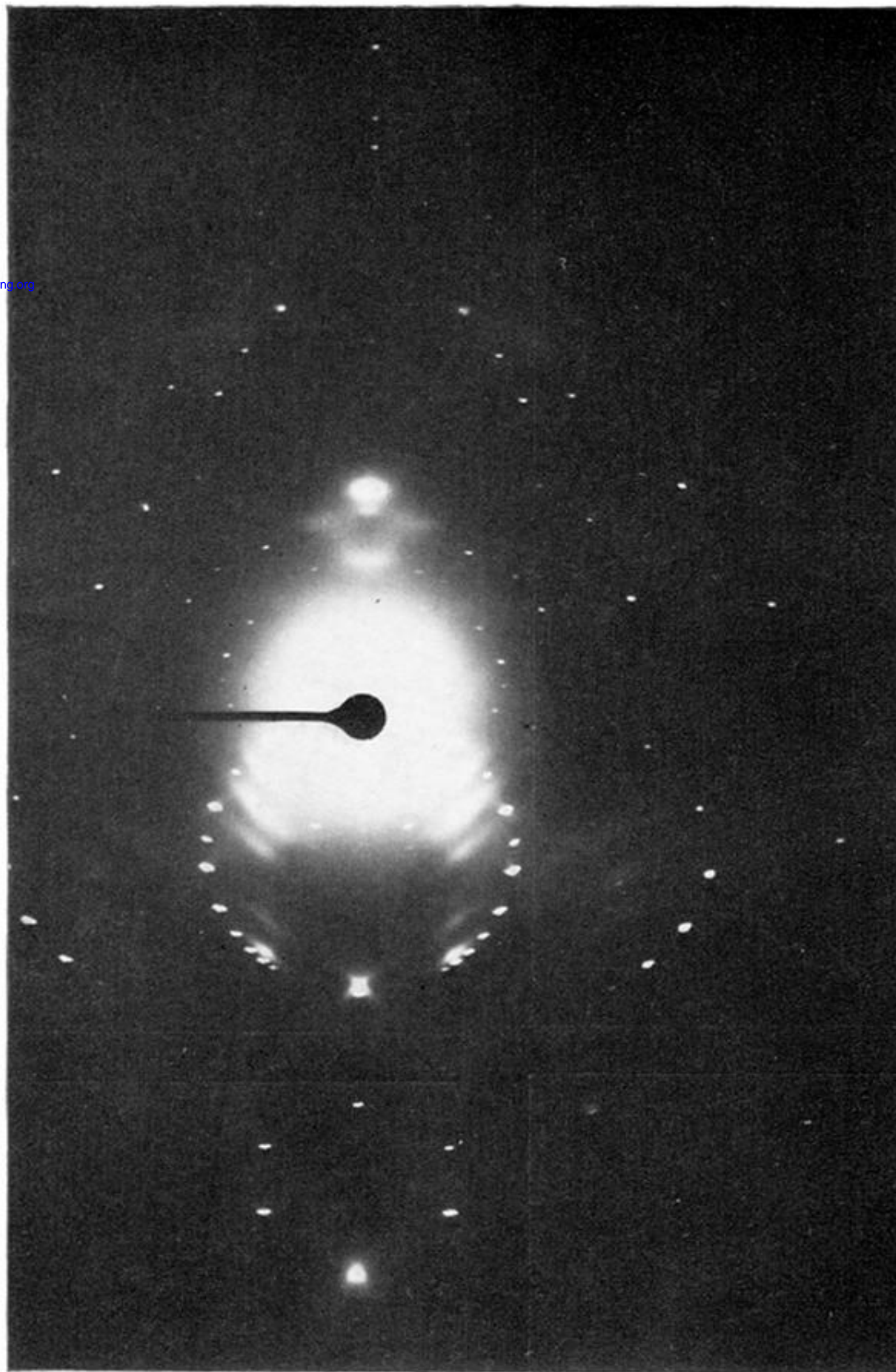
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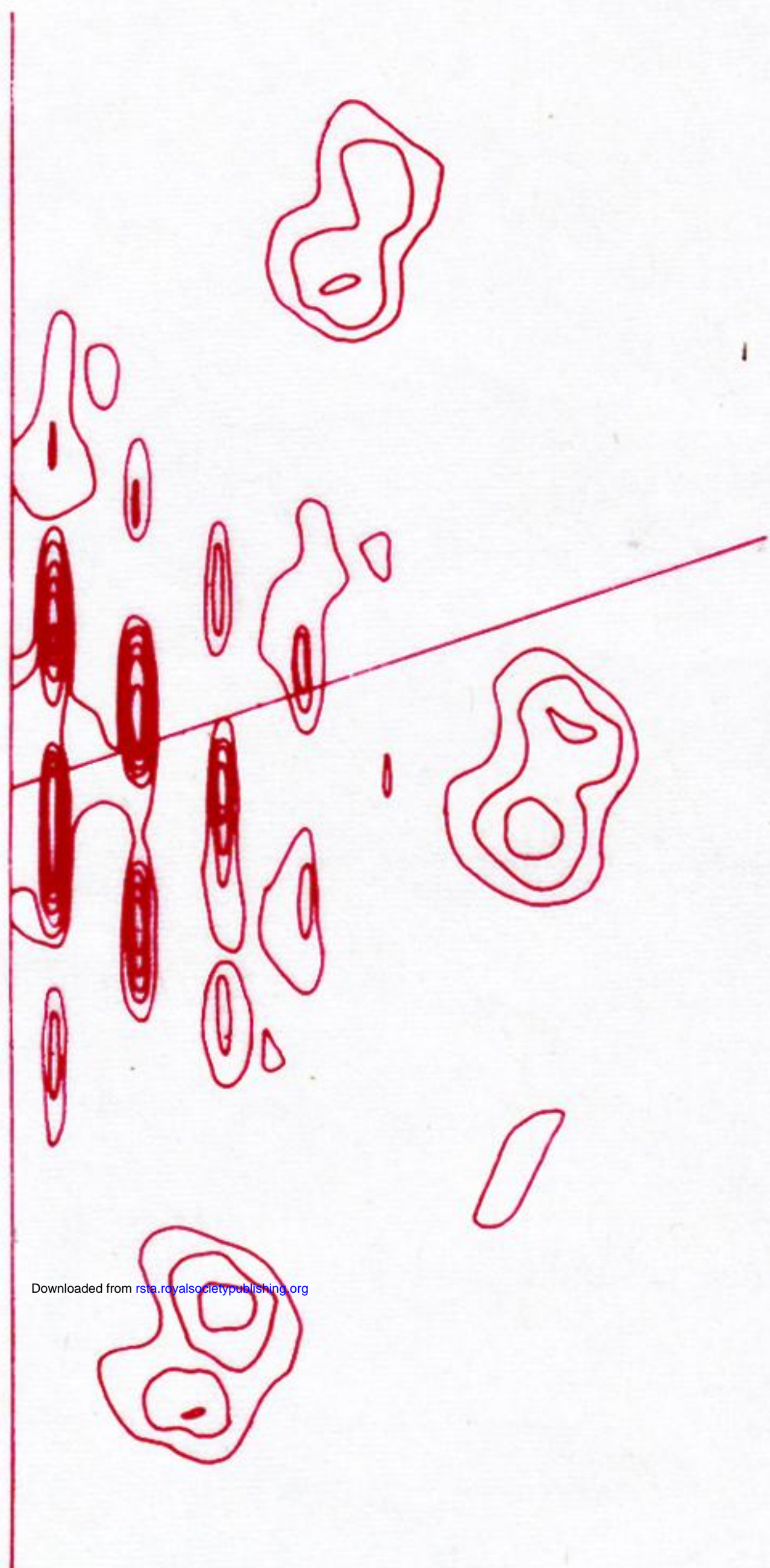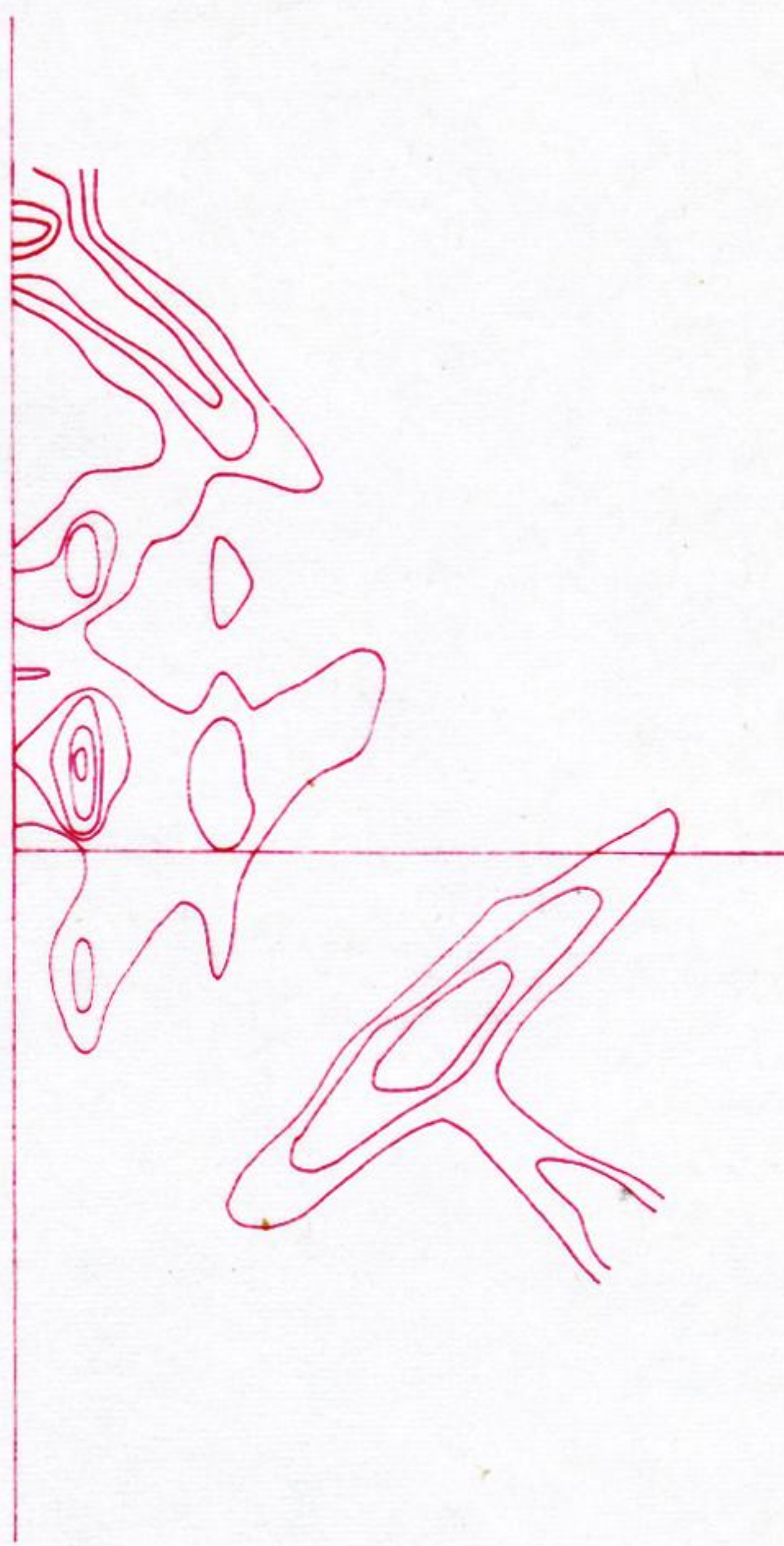
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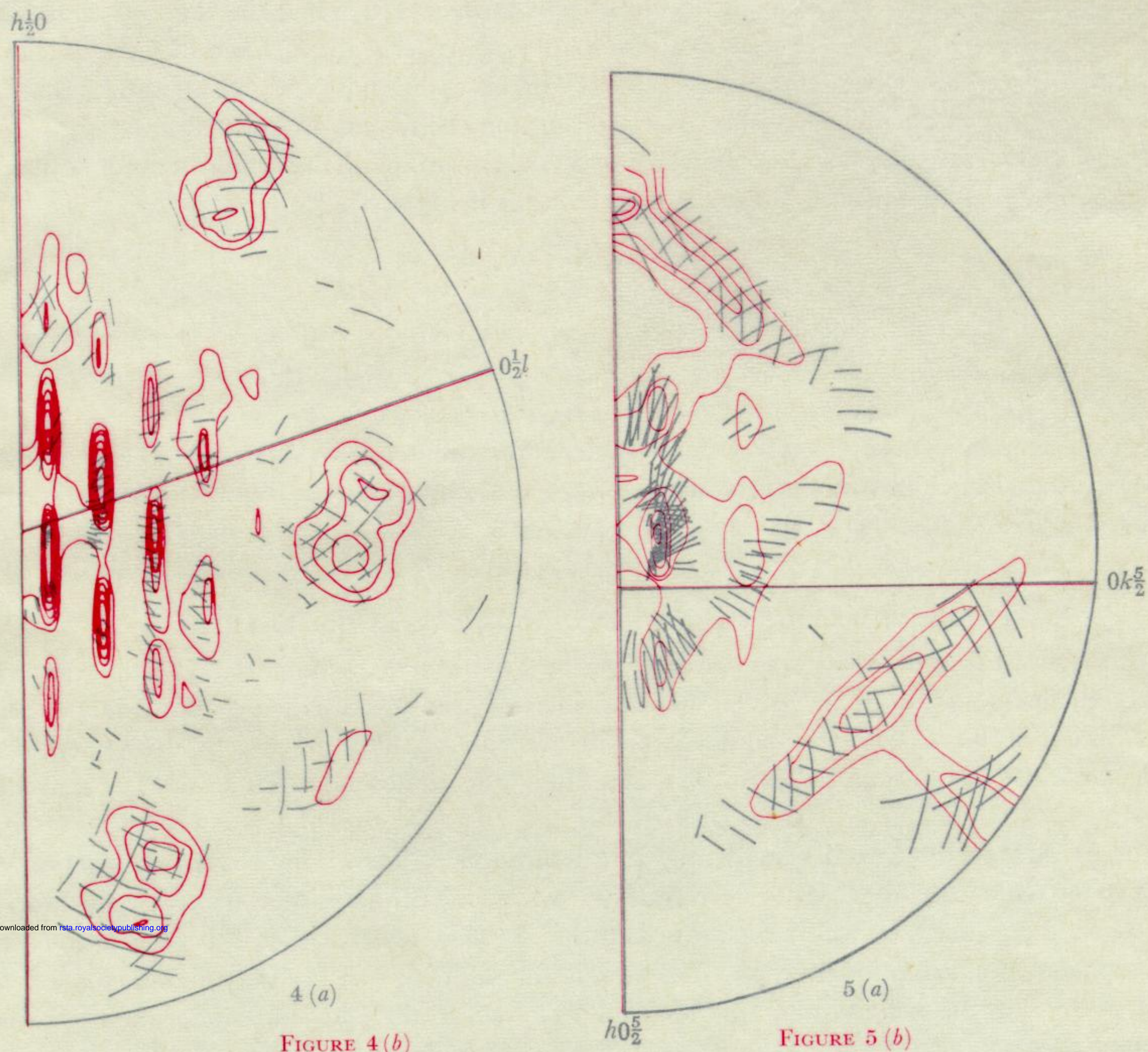
4 (*a*)   5 (*a*)

FIGURE 4 (*b*)   FIGURE 5 (*b*)

FIGURE 4. (*a*) Distribution of observed diffuse scattering in $\{h\frac{1}{2}l\}$ section of reciprocal space. (*b*) (Overlay) Theoretical distribution of diffuse scattering in $\{h\frac{1}{2}l\}$ derived from deduced α, β, γ values.

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[*Overlay to p.* 637]