$$\mu_K^{D,O} = \frac{2\mu_K^D}{5} \left(\frac{\lambda_c}{\lambda}\right) [1 - 2\lambda/\lambda_1] \qquad (A5)$$

where D means dipole, O octupole and D,O mixed dipole-octupole. The two terms for μ_K^Q correspond to the two different possible final states (angular momentum $l=1$ or $l=3$). λ_1 is defined by $\lambda_1 = [(Z-s)^2R]^{-1}$ where R is the Rydberg constant and s is a screening constant. Further $n' = [\lambda/(\lambda_1-\lambda)]^{1/2}$. For references on the steps leading to equations $(A1)-(A5)$ see Wagenfeld's paper. Hönl (1933) has made essentially the same analysis. However, he uses the fact that for $1 \lesssim z \lesssim 4$, it is a good approximation (better than 1·5%) to replace the last factors in equation $(A1)$ by a series expansion, using that

$$e^{-\frac{4}{\sqrt{z-1}} \text{ arc tg } \sqrt{z-1}} \Big/ 1 - e^{\frac{-2\pi}{\sqrt{z-1}}} \simeq e^{-4}(4z-1)/3 . \qquad (A6)$$

Also, Hönl introduces a quantity

$$\delta_K = 1 - (hc/\lambda_K)/E_{K,\text{Som}}$$

where $E_{K,\text{Som}}$ is the energy eigenvalue of the K-electrons using Sommerfeld's fine structure formula. Hönl then arrives at the expression of equation (9). If we neglect the fine structure terms we have $\delta_K = 1 - \lambda_1/\lambda_K$ and there is agreement between Hönl's and Wagenfeld's expressions except for the series expansion mentioned. For germanium, we have calculated $\delta_K = 0.197$.

From equations $(A1)-(A5)$ it is easy to estimate the relative importance of terms higher than the dipole type. Fig. 5 gives results for germanium in the range of wavelengths of interest to us.

First we want to thank Professor G. Brogren and Dr O. Efimov, whose knowledge of the experimental technique has been of invaluable help. We also want to thank Professor S. Lundqvist for a discussion on many-
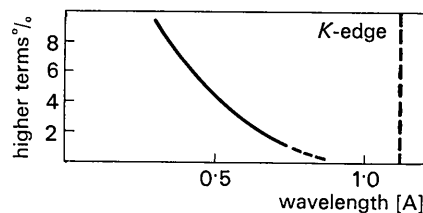

Fig. 5. Relative contribution to the absorption by the K-electrons from terms higher than the dipole type.

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The Twinning in 1-p-Nitrobenzeneazo-2-naphthol (Para Red)

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Crystals of Para Red have been studied by photographic X-ray methods. Cooling the crystals produced reversible splitting of the diffraction spots. This was traced to the use of crystals twinned by pseudo-merohedry, in association with anisotropic thermal contraction. At room temperature the twin obliquity was only 0° 22′ and the diffraction spots of the two twin individuals were not resolved.

Introduction

In the course of an X-ray study of 1-p-nitrobenzeneazo-2-naphthol, a red paint pigment commonly known as Para Red, some intriguing phenomena were observed when the crystals were cooled. At first these were attributed to some type of phase transformation, and it was not until the structure at room temperature failed

to refine properly that the phenomena were fully investigated and finally elucidated as being the result of the use of crystals twinned by pseudo-merohedry. This is not the first time that the effects of this type of twin have been temporarily unrecognized (Herbstein, 1964), but here a very small twin obliquity angle added to the difficulties. It would not be surprising if some alleged phase transformations were in fact due to similar circumstances. However, if one knows in advance the characteristics of this type of twinning and employs a chart of suitable type (Grainger, 1969*b*), early recognition should present no obstacle.

It is the purpose of this paper to describe the phenomena encountered in Para Red and how these were elucidated. Methods of treating overlapped reflexion data such as were encountered owing to the small obliquity angle are described elsewhere (Grainger 1969*a*).

The crystal lattice of Para Red

At room temperature the lattice at first appeared to be orthorhombic with approximate cell dimensions $a = 3.8$, $b = 24.6$, and $c = 7.2$ Å, but the symmetry of the intensities was that appropriate to the monoclinic system with c as the axis of symmetry. The above cell could still have been used, but for reasons which are here irrelevant a unit cell having $\gamma \simeq 115°$ and $b \simeq 27.0$ Å was selected, with a and c as above, the space group being then Pb (second setting).

Characteristics of the splitting of the diffraction spots at low temperature

It was found that when the crystals of Para Red were cooled, splitting of many of the diffraction spots occurred on Weissenberg photographs taken with the unique axis as rotation axis, but not using other axes. The following preliminary points were noted (see Fig. 1):

(i) The two components of an affected spot separated *along* the festoon of the Weissenberg film.

(ii) Photographs at different temperatures revealed that splitting increased progressively as the temperature fell and appeared to be reversible.

(iii) It was difficult to see any pattern in either the occurrence or the nature of the splitting: many spots, including strong ones, did not split at all, and of those which did, sometimes the left-hand component was stronger and sometimes the right. These was no obvious relationship between the intensities of the two components.

A variety of $hk0$ photographs taken at about $-140°$C and at room temperature were compared in various ways to determine the characteristics of the splitting in more detail. Most were taken with copper radiation but chromium was also used. For most of the photographs the crystal was coated with silicon powder to provide calibration lines as reference points for measurements, this being especially important at low temperatures where only half-films were taken with the usual 'Nonius' apparatus.

The following further facts were discovered (see Fig. 2):

(iv) At $-140°$C on an $hk0$ film, the separation of the two split components, measured in reciprocal lattice units, is proportional to the value of h. Thus the separations parallel to the b^* axis of the components of the $1k0$, $2k0$, $3k0$ ... split spots were approximately 0.18 b^*, 0.36 b^*, 0.54 b^*... respectively. $0k0$ spots were not split.

This was found by use of an equatorial Weissenberg chart to plot the rectangular coordinates of all the spots, split or not. This method did not give the absolute positions of the reflexions to very high accuracy, especially since the film measured was the uppermost of a pack of four films, but the separation of the components could be measured well enough to establish the above relations.

(v) Examinations of the positions of all the split components (irrespective of their intensities) revealed that the plane through the origin of the reciprocal lattice perpendicular to the b^* axis is a mirror plane. This was verified by accurate measurements of the diffraction angles relative to the silicon calibration lines: when the two mirror-related reflexions both split into two visible components, the 'left-hand' split component of one reflexion and the 'right-hand' component of the other were found to have equal diffraction angles. The sensitivity of this method is greater for reflexions on the more nearly 'vertical' parts of a festoon, and is also greater at high angles.

(vi) Thermal contraction is highly anisotropic. This was determined by comparing two $hk0$ photographs calibrated by silicon powder lines, one taken at room temperature and the other at about $-140°$C. Contraction along the b^* axis was easily measured since no splitting of $0k0$ reflexions occurred. Thus the $0,30,0$ reflexion ($\theta = 71.1°$ at room temperature) moved upwards about 0.5 mm ($\Delta\theta = 0.5°$) during cooling, relative to the nearby 533 $K\alpha$ silicon line, corresponding to a mean thermal expansion coefficient of about 25×10^{-6} (C deg)$^{-1}$ in this direction, after allowing for the contraction of silicon.

In general, the presence of splitting complicates the measurement of thermal expansion in other directions. However, in the perpendicular direction, corresponding to the bottoms of the festoons, measurement is possible because the effects of splitting and of thermal expansion take place in perpendicular directions. By considering a reflexion near the bottom of a festoon, the thermal expansion coefficient parallel to the a axis was calculated to be about 90×10^{-6} (C deg)$^{-1}$.

(vii) Examination of a room-temperature photograph taken with chromium radiation revealed slight splitting in a few of the high-angle spots. Evidence of splitting was not immediately detected on photographs using copper radiation at room temperature, but traces were revealed later by a detailed examination with use of the appropriate chart (Grainger, 1969*b*).
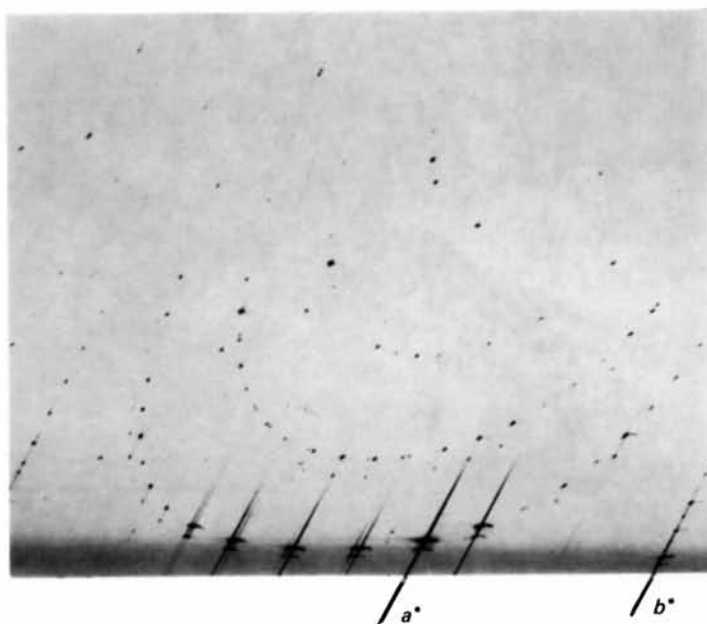
Fig. 1. $hk0$ Weissenberg film taken at $-140\,^\circ$C showing splitting of spots along festoons. (Unfiltered copper radiation).

The geometry of splitting was now clear. In Fig.2 the *hk*0 reciprocal lattice points are represented as unsplit at room temperature (open circles) although it is probable they are slightly split. When the crystal is cooled the reciprocal lattice expands outwards in all directions, but in the Figure, for simplicity, the smaller expansion parallel to the *b** axis is not shown. Splitting occurs at the same time, and the positions occupied by the components in the expanded lattice are represented by filled circles. Often only one of a pair of sites is occupied, the spot then appearing to be unsplit.

It was apparent that the crystal contained two components whose reciprocal lattices practically coincided at some temperature slightly above room temperature, possibly at the temperature of crystallization, and which moved in opposite directions on cooling.

Explanation of splitting

Para Red was known (Grainger & McConnell, 1969) to consist of almost planar molecules roughly parallel to the (100) planes, and could be expected to possess anisotropic thermal expansion with the largest coefficient normal to this plane (along the *a** axis), and much smaller coefficients in other directions, as is the case for napthalene and *p*-nitroaniline (*International Tables for X-ray Crystallography*, 1962). Anisotropic contraction of this kind would be expected to distort the unit cell in such a way as to increase the cell angle γ (or decrease the angle γ* of the reciprocal cell) when cooling took place. In Fig.3, *ABCD* represents (not to scale) a cross-section of the unit cell drawn on a surface which is allowed to shrink anisotropically in such a way that fractional shrinkage is greatest perpendicular to *BC* and least parallel to *BC*, which represents the face (100). The shape will be changed to *A'B'C'D'*, increasing the cell angle γ. For a small temperature change ΔT, the angle is changed to γ', where

$$\tan(\gamma' - \gamma) = \frac{\Delta T}{2}(\alpha_1 - \alpha_2)\sin 2\gamma , \qquad (1)$$

and α_1 and α_2 are principal thermal expansion coefficients respectively perpendicular and parallel to *BC*.

If one considers the behaviour of the reciprocal lattice of a crystal containing such cells during cooling, one finds that the distortion gives rise to motion of the lattice points which is identical with the observed behaviour of either one of the postulated component lattices of Para Red.

It appeared at this stage (Fig.4) that the crystals of Para Red contained two types of cell, mirrored in the (010) plane whose reciprocal lattice practically coincided at room temperature. These distorted in mirror fashion when cooled, separating their reciprocal lattices and giving rise to splitting as observed. The heavy lines in Fig.4 represent the reciprocal cells of the two types *A* and *B* at room temperature; the dashed lines refer to low temperatures. On cooling, the lattice points for which *h* = 1 due to *A* (circles) move to the right, and
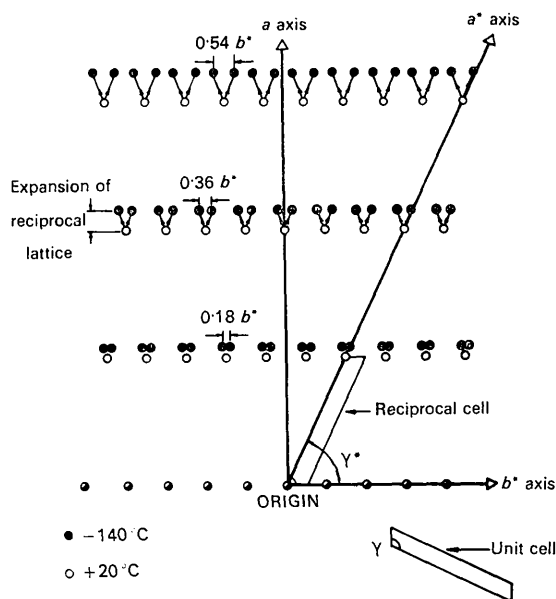

Fig.2. Diagram showing how splitting occurs when Para Red is cooled. Reflexions having *k* odd are absent from this *hk*0 reciprocal level. The diagram is not drawn to scale.
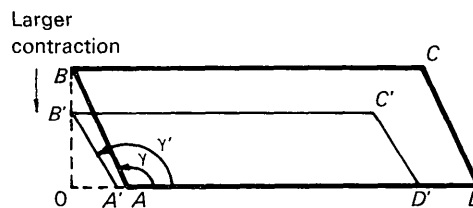

Fig.3. Distortion by anisotropic thermal contraction. The cell *ABCD* is distorted to *A'B'C'D'*, increasing the cell angle.
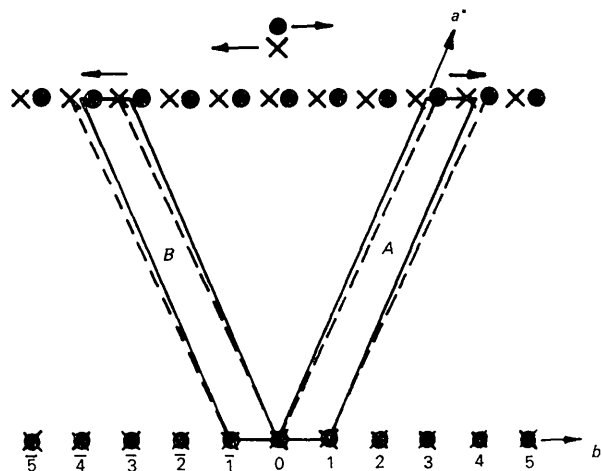

Fig.4. Explanation of splitting. Two types of reciprocal cell, *A* and *B*, distort in opposite directions when cooling takes place, causing splitting.

those due to B (crosses) to the left, as indicated by arrows. For simplicity, lattice thermal expansion is not shown. This diagram applies to any c-axis level other than $hk0$ (for which the reflexion condition is $k = 2n$).

When it was realized that this description applied perfectly to a crystal twinned on (010), the split-lattice low temperature photographs were examined more closely, especially with regard to the intensities of the components of 'related' or mirror-image reflexions. Now that the geometry of splitting was clear the intensity pattern, too, became obvious. In the first $hk0$ photograph examined, the spots due to one of the component lattices were all approximately one-tenth as intense as those belonging to the other, the two lattices being, of course, related by a mirror plane. This crystal thus contained twin components in the ratio of about 1 to 10 parts by volume. Similar effects have been found in photographs using other crystals except that the ratio of the two components differs.

Splitting was thus due first to the use of twinned crystals and secondly to anisotropic thermal contraction.

The previous measurements of thermal contraction were, in effect, taken only in directions for which the contraction of the two individuals of the twin lattice were identical, these directions being respectively parallel and perpendicular to the a axis. Knowing these figures, and the geometry of the splitting, one can ignore the weaker of the superimposed reciprocal lattices and calculate the expansion coefficient of the main part of the crystal in any direction in the $(hk0)$ plane. The result of such a calculation was that the expansion coefficient would have its maximum value, 112×10^{-6}

Fig. 5. The axes of the two individuals in a twinned crystal of Para Red.

Fig. 6. Scale drawing at $-140\,^{\circ}C$ of the (001) lattice of a twinned crystal of Para Red. The contact plane between the two individuals A and B is taken to be (010).

(C deg)$^{-1}$, at an angle of about $28\,^{\circ}$ to the a axis, which is within $3\,^{\circ}$ of the normal to the (100) plane. The excellent agreement with the expected direction is much better than could be hoped in view of the accuracy of the figures employed. The minimum coefficient was calculated to be 6×10^{-6} (C deg)$^{-1}$ in a direction perpendicular to that of maximum expansion.

Expansion in the direction of the normal to (100) was also determined directly by measurement of the upper component of the split $\overline{4}00$ reflexion and this resulted in a figure 113×10^{-6} (C deg)$^{-1}$, in remarkable agreement with that calculated. A suitable reflexion for the experimental determination of the minimum coefficient was not available.

It is interesting to note that if the maximum and minimum thermal coefficients are substituted in equation (1) the calculated increase in the unit-cell angle is $0\,^{\circ}22'$ when cooled from 20 $^{\circ}$C to $-140\,^{\circ}$C. This compares with $0\,^{\circ}24'$ calculated directly from the known geometry of splitting at these two temperatures, without the use of expansion coefficients.

Thus the progressive splitting of reflexions of Para Red when the temperature is lowered has been elucidated in terms of the anisotropic contraction of twinned crystals.

Nature of the twinning in Para Red

The twinning in Para Red is classified by Friedel (Cahn, 1954) as twinning by pseudo-merohedry. A merohedral structure is one having a lower symmetry than the symmetry of its lattice. The Para Red structure is pseudo-merohedral in the sense that being monoclinic it has a lower symmetry than its lattice which is pseudo-orthorhombic. We may assign right-handed axes, distinguished by subscripts 1 and 2 for the two components, as shown in Fig. 5. Geometrically, one lattice can be made to coincide with the other by a $180\,^{\circ}$ rotation about the common a axis or by reflexion across the (010) plane, or by a $180\,^{\circ}$ rotation about the b^* axis, that is about the normal to the (010) plane. It should be noted that although these are all distinct arrangements as far as the cell contents are concerned, they cannot be distinguished by considering the diffraction symmetry of the two components of the lattice. This follows because the diffraction symmetry of each component is $2/m$, with c the twofold axis. If one takes the diffraction pattern of either of the two components and operates on it in any of the three ways mentioned above, one obtains the same pattern in each case, which has the appearance of being related to the first by a mirror plane through (010), which, as previously noted, is what is actually observed.

If there is a $180\,^{\circ}$ rotation about the a axis, then [100] is the twin axis, and Para Red is a rotation twin. If the operation is a reflexion across (010), then Para Red is a reflexion twin, with (010) as the twin plane. If there is a $180\,^{\circ}$ rotation about the normal to (010) then Mallard's Law is not obeyed, since this is not the direction of a lattice row, and Para Red would be a
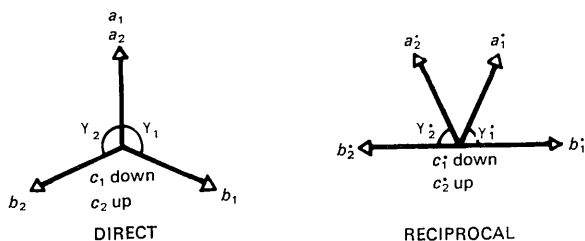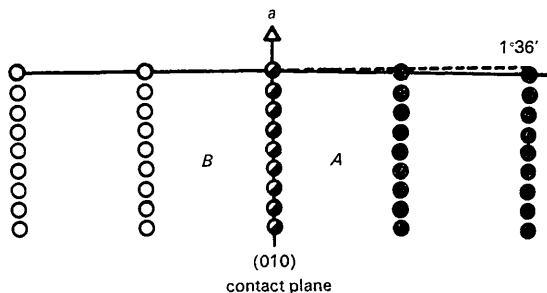
twin of a type not classified. The last possibility might be considered unlikely were it not for the fact that this is the only one in which the molecules in the two individuals comprising the twin do not 'point' in contrary directions.

The fact that (010) is merely a plane of pseudo-symmetry, and that [100] is an axis of pseudo-symmetry of either individual separately, is illustrated in Fig. 6 which shows the direct lattices with (010) as the contact plane. The drawing is to scale at -140° C, when the departure from orthorhombic (called the 'twin obliquity') is about $0^\circ 48'$.

At room temperature the twin obliquity is only $0^\circ 22'$. This figure was calculated from the separation of the split components of a particularly suitable reflexion, $2,\overline{22},0$, on a photograph taken with chromium radiation. Owing to the small obliquity, the large thermal vibration, and other accidental factors, virtually no splitting was detectable on the room temperature photographs with copper radiation, so that all reflexions could be regarded as overlapped.

With the choice of axes given in Fig. 5, reflexions $h_1 k_1 l_1$ and $h_2 k_2 l_2$ arising from the two individuals superimpose at room temperature in most cases if $h_2 = h_1$, $k_2 = -(6h_1 + k_1)$, $l_2 = -l_1$, since these two are related by the (010) mirror plane. It follows that overlapping affects reflexions in pairs which, referred to one set of axes, are of the form hkl and $h, -(6h+k), l$ for Para Red. Each, in effect, contains an admixture of the other. We refer to each as being 'related' to the other. However, this choice is not unique: because the data were in levels parallel to (001), the (010) mirror plane twin-law was the most convenient to use, but it would make no difference if either of the other two twin-laws was assumed. The symmetry is such that one can regard hkl as 'related' also to any of the three reflections equivalent to $h, -(6h+k), l$.

Discussion

Crystals of Para Red crystallized from pyridine solution are found to be twinned by pseudo-merohedry.

A polarizing microscope reveals irregularly shaped inclusions: a powerful light source is necessary to counteract the strong absorption of crystals of the size required for X-ray purposes. At room temperature most reflexions of the twin individuals are overlapped, but on cooling the crystal they are progressively resolved as a result of anisotropic contraction.

An obvious way of collecting intensity data is, therefore, to take all the photographs at low temperatures and so separate the reflexions to be measured from the unwanted twin components. This would have the usual advantage of reducing thermal vibration, but unless temperatures much lower than -140°C could be employed, there would be difficulty in indexing reflexions, and in some cases, of reading the intensity of a reflexion barely resolved from the unwanted twin component, the latter possibly being much stronger.

An alternative procedure, and this is the one adopted, is to use the room-temperature data despite the overlapping of reflexions. The decision to do this was influenced by the fact that the structure had already been solved despite the twinning, and only required refinement.

The methods developed along these lines, an analysis of their success, and an account of the structure of Para Red, are reported elsewhere (Grainger, 1969*a*; Grainger & McConnell, 1969)

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