

Some Procedures in the Determination of the Absolute Configuration of Crystals

S. N. VAIDYA AND S. RAMASESHAN

*Department of Physics, Indian Institute of Science,
Bangalore 12, India and Department of Physics,
Indian Institute of Technology, Madras 36, India*

ABSTRACT

This paper attempts to outline the routine procedures necessary in the determination of the absolute configuration of a crystal by the Bijvoet method using anomalous scattering and employing photographic techniques. The method due to Peerdeman and Bijvoet for assigning correct indices to the reflections recorded by the equi-inclination Weissenberg method has been restated to include trigonal, monoclinic and triclinic classes. The pairs of reflections—named Bijvoet pairs—whose intensities are to be compared for the determination of the absolute configuration have here been listed for all the enantiomorphous space groups. The problem of the determination of the absolute configuration of a crystal when only one crystallographic mounting is possible (as in the case of liquids crystallized at low temperatures), has been discussed. A simple double-layer method of recording reflections of the type hkL and $h\bar{k}L$ has been evolved and its application to various crystal classes given.

1. INTRODUCTION

After the classical paper of Bijvoet (1954), the anomalous scattering of X-rays has been used for the determination of the absolute configuration of a good number of crystals. The increased experimental activity in this field is also due to the discovery that there is considerable anomalous scattering with phase change even when the frequency of the K absorption edge is quite far from that of the incident radiation (Peterson, 1955; Dauben and Templeton, 1955). Indeed, this effect is so large that when a suitable atom like iodine is present in the structure as the anomalous scatterer and $Cu K\alpha$ is used, then the simple photographic technique is quite sufficient for establishing the absolute configuration.

In low-temperature cameras using the Fankuchen-Lipscomb type of cooling (Kaufman and Fankuchen, 1949; Abrahams *et al.*, 1950; Singh and Ramaseshan, 1963) the crystal almost invariably grows with a particular crystallographic axis coinciding with the axis of the thin cylindrical capillary tube. It is practically impossible to mount the

crystal on any other axis. Hence, techniques are here presented for the determination of the absolute configuration of a crystal (belonging to any crystal system) using only one mounting on an arbitrary axis. In the course of recent investigations by one of the authors and his collaborators on the absolute configurations of orthorhombic, trigonal and triclinic crystal structures (Manohar and Ramaseshan, 1961; Singh *et al.*, 1962) the necessity was again realized of the need to be able to index the diffraction photographs without any reference whatever to the mounting of the crystal.

It was thought that the knowledge gained by these investigations was worthy of record so that the photographic technique could be used as a routine procedure by the X-ray crystallographer for determining the absolute configuration in any crystal system. In each space group, the pairs of reflections that are to be compared are here listed. The indexing procedure given by Peerdeman and Bijvoet (1956) have been extended to cover the monoclinic and triclinic classes, and finally some special but convenient techniques are discussed which facilitate the determination of the absolute configuration of a crystal.

2. THE BIJVOET INEQUALITY AND THE "BIJVOET PAIRS"

In the absence of anomalous scattering, the reflections hkl and $\bar{h}\bar{k}\bar{l}$ from each of two enantiomorphous crystals A and B are related by

$$\alpha_A(hkl) = \alpha_B(\bar{h}\bar{k}\bar{l}) \quad (1a)$$

$$I_A(hkl) = I_B(\bar{h}\bar{k}\bar{l}) \quad (1b)$$

However, when they are from one and the same crystal, say A ,

$$\alpha_A(hkl) = -\alpha_A(\bar{h}\bar{k}\bar{l}) \quad (2a)$$

$$I_A(hkl) = I_A(\bar{h}\bar{k}\bar{l}) \quad (2b)$$

If among the atoms there is an anomalously scattering atom, Eqs. (2a) and (2b) are violated while, however, Eqs. (1a) and (1b) are still valid.

From the intensity of the one reflection relative to the other in the inequality $I(hkl) \neq I(\bar{h}\bar{k}\bar{l})$, the absolute configurations of structures belonging to the enantiomorphous space groups may be determined.

The phase relations among all those reflections that are equivalent to one another under normal scattering can be one of the following:

$$(a) \alpha = \beta$$

$$(b) \alpha = \pi/2 - \beta$$

$$(c) \alpha = \pi/2 + \beta$$

$$(d) \alpha = \pi - \beta$$

$$(e) \alpha = \pi + \beta$$

$$(f) \alpha = 3\pi/2 - \beta$$

$$(g) \alpha = 3\pi/2 + \beta$$

$$(h) \alpha = -\beta$$

TABLE I. Table of Bijvoet pairs in different point groups†

Axis of rotation	Point group	Zero layer WEP				Higher layer WEP				Double layer method		
		$0k0$	$0k\bar{l}$	$0k\bar{l}$	$0k\bar{l}$	$h0l$	$h\bar{k}0$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$
a	1	$00l$	$0k\bar{l}$	$0k\bar{l}$	$0k\bar{l}$	$h0l$	$h\bar{k}0$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$
	2, 4, 6	$00\bar{l}$	$0k0$	$0k\bar{l}$	$0k\bar{l}$	$h0\bar{l}$	$h\bar{k}0$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$
	222, 432	$00l$	$0k0$	$0k\bar{l}$	$0k\bar{l}$	$h0\bar{l}$	$h\bar{k}0$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$
	23, 432	$00\bar{l}$	$h00$	$h0\bar{l}$	$h0\bar{l}$	$0k\bar{l}$	$h\bar{k}0$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$
	3	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$
	32	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$
c	1	$h00$	$h\bar{k}0$	$h\bar{k}0$	$h\bar{k}0$	$h0\bar{l}$	$h\bar{k}0$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$
	2, 4, 6	$h00$	$h\bar{k}0$	$h\bar{k}0$	$h\bar{k}0$	$h0\bar{l}$	$h\bar{k}0$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$
	222, 432	$h00$	$h\bar{k}0$	$h\bar{k}0$	$h\bar{k}0$	$h0\bar{l}$	$h\bar{k}0$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$
	23, 432	$h00$	$h\bar{k}0$	$h\bar{k}0$	$h\bar{k}0$	$h0\bar{l}$	$h\bar{k}0$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$
	3	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$
	32	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$
c	1	$h00$	$h\bar{k}0$	$h\bar{k}0$	$h\bar{k}0$	$h0\bar{l}$	$h\bar{k}0$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$
	2, 4, 6	$h00$	$h\bar{k}0$	$h\bar{k}0$	$h\bar{k}0$	$h0\bar{l}$	$h\bar{k}0$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$
	222, 432	$h00$	$h\bar{k}0$	$h\bar{k}0$	$h\bar{k}0$	$h0\bar{l}$	$h\bar{k}0$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$
	23, 432	$h00$	$h\bar{k}0$	$h\bar{k}0$	$h\bar{k}0$	$h0\bar{l}$	$h\bar{k}0$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$	$h\bar{k}l$
	3	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$
	32	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$	$+$

† + represents that the Bijvoet pair at the head of the column exists. The $0m0$ axis is the $h\bar{h}0$ axis perpendicular to the $h00$ axis. Since the Bijvoet pairs are symmetrically disposed about this axis the film is indexed using $h00$ and $0m0$ axes. In 432 and 432 Bijvoet pairs with $h = k$ have equal intensity. In 622 Bijvoet pairs with $h = \pm k$ have equal intensity.

‡ Parallel to c -axis.

With an anomalously scattering atom present, those reflections for which (a), (c), (e) and (g) hold will still be of equal intensity; likewise the reflections for which (b), (d), (f) and (h) hold will be equally intense. Whereas both sets were of the same intensity under normal scattering, they will now differ in intensity.

Two reflections which are of equal intensity under normal scattering, and may become unequal when anomalous scattering is present, are named a "Bijvoet pair". Intensity of Bijvoet pairs must be compared to determine absolute configuration. Under conditions which are easily worked out, the reflections of a possible Bijvoet pair may be accidentally of equal intensity, even when anomalous scattering is present. Again, for certain types of reflections in certain space groups, a Bijvoet pair (in the sense that the pair belongs one each to the two sets of phase relations mentioned above) may not show any difference in intensity. The Bijvoet intensity difference vanishes systematically for them.

3. THE BIJVOET PAIRS IN EQUI-INCLINATION PHOTOGRAPHS FOR VARIOUS SPACE GROUPS

On the above principles, and using the expressions for the structure amplitudes and phases given in the *International Tables for X-ray Crystallography*, Vol. I, it is easy to write down the Bijvoet pairs for the various enantiomorphous space groups. As it is usual to employ the Weissenberg equi-inclination photographs (WEP) for the collection of intensity data, the Bijvoet pairs occurring in the WEP's of the different levels are listed in Table I.

Any WEP may become useless for the purpose of determining absolute configuration owing to any of the following reasons.

- (a) There may be no two equivalent reflections in that layer even under normal scattering.
- (b) If such a pair exists the reflections may be of equal intensity both under normal scattering and anomalous scattering.
- (c) The reflections of a Bijvoet pair may not be recorded on the same side of the central line of the WEP. This is an important consideration since reflections recorded in different halves of the equi-inclination photograph undergo different elongations and are then unsuitable for comparison if intensity is measured visually.

For triclinic crystals of point-group 1, and trigonal crystals of point-group 3 mounted on the unique axis, there are Bijvoet pairs only in the zero-level Weissenberg, and none in the other layers. But for crystals belonging to the point-group 32 there are Bijvoet pairs in any layer, every Bijvoet pair lying symmetrically on either side of the $h\ h\ 2h$ L row of reflections.

For crystals of the point-groups 2, 4 and 6, Weissenberg photographs of any layer taken about the unique axis do not contain Bijvoet pairs to be compared. But in the zero-layer Weissenberg and the higher level WEP's about a non-unique axis, say a , the Bijvoet pairs lie symmetrically about the $Hk0$ row of reflections. If b were the axis of rotation, they lie symmetrically about the $hK0$ row.

For crystals of the point-groups 222, 422, 622, 23 and 432, while the zero-layer Weissenberg about any crystallographic axis does not contain a Bijvoet pair, the higher layer WEP's about any axis have Bijvoet pairs situated symmetrically about the central axial rows; only, for a crystal of point-group 622, and mounted on the hexagonal axis, the Bijvoet pairs in a higher layer WEP are symmetrical about the $h\ k\ \bar{2}h\ L$ row.

4. THE METHOD OF UNIQUE INDEXING

The correct indexing of the diffraction photographs is extremely important for the determination of the absolute configuration by the Bijvoet method. Since the formulae for the structure amplitudes for any space group are given for a right-handed system of co-ordinates in the International Tables, they can be used only if the right-handed system is also chosen for indexing the photographs. Peerdeman and Bijvoet (1956) have clearly laid down the procedure for indexing the reflections from an orthorhombic crystal, and have indicated how they are to be applied to the monoclinic system also. We shall extend them to all the general cases here.

Figure 1 (a) shows the arrangement in a right-handed camera like the Unicam single crystal goniometer S-35, where the clockwise rotation of the graduated drum-head causes the film cassette to move along the axis in the direction of advance of a right-handed screw. The positive direction of the crystallographic axis on which the crystal is mounted and about which it is rotated is taken to point away from the drum-head. The position of the camera with respect to the incident beam of X-rays, and the cut usually made to denote the position of the film in the cassette (at the right-hand top corner as an observer facing the incident beam sees it) are also shown in the figure.

When one uses a right-handed camera (Fig. 1 (a)) and a right-handed system of co-ordinates (Fig. 1 (b)) the indexing of the Weissenberg photographs is quite straightforward and may be done without reference to the crystal or its morphological characteristics. It may be easily verified that the sequence from *right to left* of the axial rows will be a cyclic permutation of the sequence $h00$, $0k0$, $\bar{h}00$ and $0\bar{k}0$ assuming of course that the crystal is rotated about the c -axis. When the axial rows have been identified in this sequence the reflections may all be uniquely

indexed (Fig. 1 (c)). The same sequence will obtain in the higher layers as in the zero layer. To obtain the WEP of a particular layer L , the camera has to be turned through a definite angle ν . Depending on the sense of the rotation, one would photograph either the L or the \bar{L} layer. Given

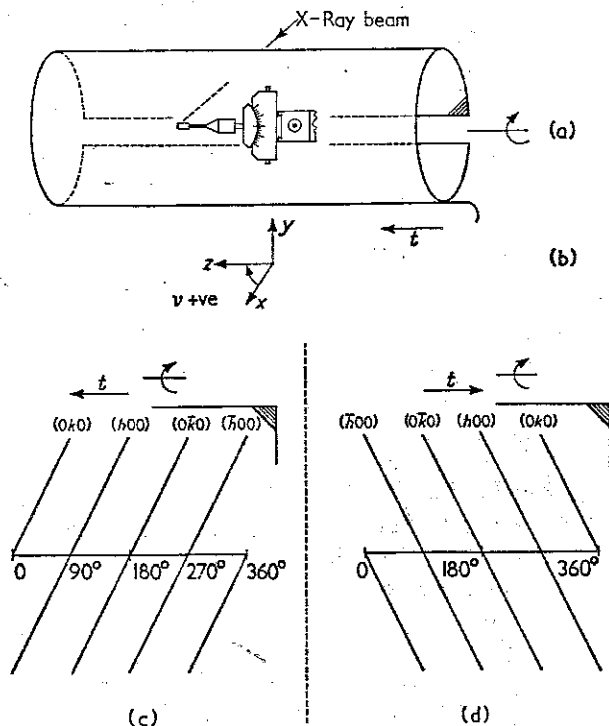


FIG. 1. (a) The direction of the rotation and the translation in a right-handed Weissenberg camera. The direction of the X-ray beam and the position of the cut on the film are also shown. (b) The right-handed system of co-ordinate axes used for indexing. The direction of ν for obtaining positive L layers is also shown. (c) and (d) The sequence of axial reflections as recorded on a film with a right-handed system of co-ordinates using (c) a right-handed camera and (d) a left-handed camera. The actual case illustrated is for an orthorhombic crystal, including all the axial rows for a rotation of 360° .

a right-handed system of co-ordinates, the sense of rotation in a right-handed camera to photograph the layers with positive values of L is apparent from Fig. 1 (b). If a right-handed camera is used, the sequence of the axial rows chosen above (Fig. 1(c)) immediately fixes a right-handed system of co-ordinates (Fig. 1 (b)). This is true, whatever be the symmetry of the crystal, and holds in the zero-level Weissenberg or the higher level WEP.

The appearance of the zero-level Weissenberg photograph from a crystal of any crystal system rotated about its c -axis is as shown in Fig. 2 (a), where γ^* has been chosen acute. In monoclinic, trigonal, tetragonal and hexagonal crystals mounted on the unique c -axis, the

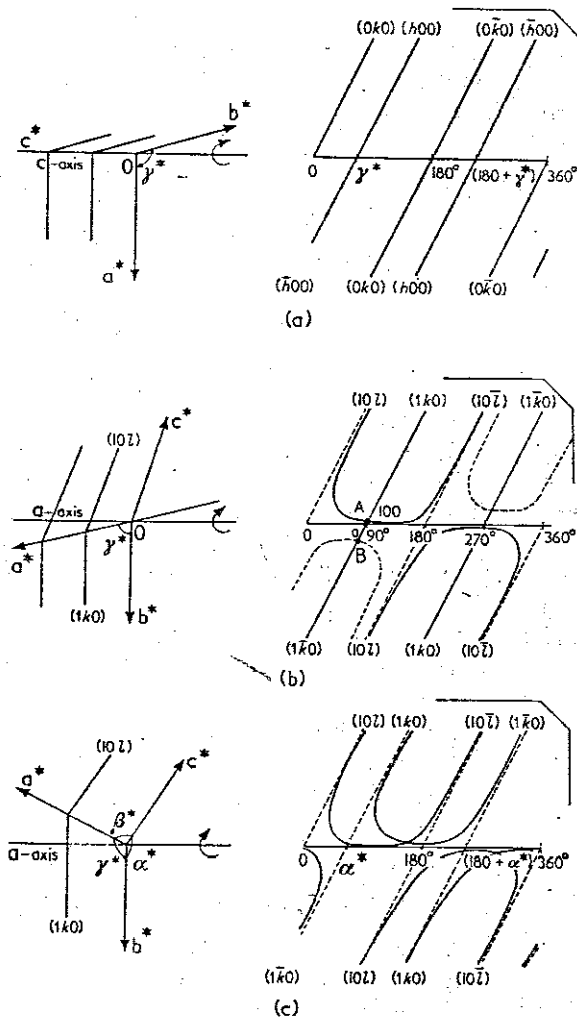


Fig. 2. (a) The zero-layer Weissenberg of a crystal belonging to any crystal system. In the case of crystals with 2-, 3-, 4- and 6-fold axis the zero and higher layer WEP's about the unique axis look alike. (b) The higher layer WEP of a monoclinic crystal about the non-unique axis a . The $Hk0$ spots fall on a straight line, while the $H0l$ reflections form a festoon. (c) The higher layer WEP of a triclinic crystal. The angles β^* and γ^* are computed from the lowest points of the $H0l$ and $Hk0$ festoons.

zero-layer Weissenberg and the higher layer WEP's will all be exactly alike, as in Fig. 2 (a), because the axial rows are always central.

However, if the axis of rotation is not the unique axis c , but either a or b , the zero-layer Weissenberg resembles the zero layer of an orthorhombic crystal (Fig. 1 (c)), but the higher layer WEP is as in Fig. 2 (b). The reciprocal rows $H0l$ and $H0\bar{l}$ being non-central, these reflections record on a festoon and not on a straight line, while the $Hk0$ reciprocal lattice row, being central, records as a straight line on the WEP.

As an illustration, the indexing in the case of a monoclinic crystal is now considered.

The zero layer enables b^* and c^* to be found, but not γ^* . It is customary to choose the angle γ^* to be acute. This may be done by considering the higher layer WEP, say of the first layer. The $lk0$ group of reflections record in a straight line and the $10l$ reflections on a festoon. The distance of the lowest point of this festoon from the central line of the WEP allows us to calculate γ^* (Buerger, 1942). It is rather easier in the case of the monoclinic than in a triclinic crystal to locate the minimum point of the axial festoon, for the point of intersection of the $lk0$ straight line and the $10l$ festoon is the lowest point of the festoon. If γ^* thus found is acute, then on the part of the $lk0$ straight line on which this point lies k is positive, otherwise it is negative. The proper sequence of the axial rows from right to left, mentioned earlier, determines a right-handed system of co-ordinates. This enables the axial rows to be properly identified so that this layer and all other layers can be correctly and uniquely indexed.

It does not matter if the convention for γ^* is ignored. One may then index the zero layer itself first, consistent only with the sequence of axial rows for a right-handed system. The angle γ^* then found from the higher layer may turn out to be either acute or obtuse, and the unit cell is taken as found. In the case of a triclinic crystal it follows that the conventional choice of the angular parameters of the unit cell may be ignored.

5. CORRELATION BETWEEN WEISSENBERG PHOTOGRAPHS FROM TWO DIFFERENT SETTINGS: UNIQUE INDEXING FOR A TRICLINIC CRYSTAL

If the positional parameters of all the atoms are determined from three-dimensional data collected from only *one setting* of the crystal, the absolute configuration of the crystal can be found by comparing the intensity of any Bijvoet pair. However, it is found that, for reason of computational facility, a structure is quite often solved using two-dimensional data obtained by rotating the crystal about each of two different crystallographic axes. It is usual to use two different crystals ground to the form of cylinders along the crystallographic axes which

are used as the axes of rotation. This is so, particularly for crystals of the triclinic system. In such cases, when two different crystals are used for collecting intensity data, great care must be exercised in identifying the axes used as the axes of rotation; and the triclinic system is here taken to illustrate the procedure to be followed. Rotated first, say about the a -axis, a normal beam Weissenberg of the zero layer is taken and indexed using a right-handed system of co-ordinates mentioned earlier. The b^* , c^* and α^* values can be determined. Next, about the same axis, a higher layer WEP is taken in which the axial festoons may be identified by comparison of the zero and the higher layer photographs using well-known procedures laid down by Buerger (1942, pp. 342-4). From the lowest points of the axial festoons, β^* and γ^* can be calculated. From the a -axis rotation photograph, a and hence a^* , can be evaluated. Thus all the unit-cell parameters can be found from one setting of the crystal. In the second crystal rotated about, say the b -axis, all the parameters can again be found in the same manner. It is easy to choose the unit cell so that the reciprocal parameters obtained in the second setting are identical with those chosen from the first setting. But it must be pointed out that, if the crystal were mounted along the $-b$ -axis instead of the b -axis as assumed, identical reciprocal parameters can be chosen only on a left-handed system and not on a right-handed system.

In actual practice, it is not necessary to take a higher layer WEP in the second setting. Since a^* , c^* and β^* values are already known from the first setting, they can easily be identified in the zero-layer photograph in the second setting also. The sequence of axial rows would show if the co-ordinate system is right-handed or left-handed, i.e. if the axis of rotation is b or $-b$. However, since the angle between c^* and a^* and $-c^*$ and $-a^*$ is the same, the doubt remains whether the axes chosen as c^* and a^* are not really $-c^*$ and $-a^*$ respectively. While this does not matter in centrosymmetric structures ($P\bar{1}$), it is of the utmost importance in non-centrosymmetric crystals for determining the absolute configuration. For the latter, since the $00l$ reflections are common to the zero-layer Weissenberg photographs about the a - and b -axes, the Bijvoet inequality that $I(00l) \neq I(00\bar{l})$ may be used to resolve the ambiguity. If in the first setting $I(00l) > I(00\bar{l})$, the same must be true in the other setting also. If this is not found to be so, then what had been assumed as $00l$ in indexing the photograph about the second setting must now be taken as $00\bar{l}$.

One must draw attention to the fact that all this is necessary only for correlating the data from the two settings and has as yet nothing to do with determining the absolute configuration. To be more explicit, it makes certain that one does not use, say, the a -axis in one projection and the $-a$ -axis in the other.

If the unit-cell angles differ sufficiently from 90° , any such mistake may become apparent from unusual interatomic distances, etc. If, however, the unit-cell angles are close to 90° , any differences from accepted interatomic distances will be small and may well be overlooked as being due to errors that are usual in X-ray crystallography.

Having thus fixed the co-ordinate system correctly, the determination of absolute configuration still remains to be done by comparison of intensity between reflections of any Bijvoet pair. It is obvious that if a mistake is made in correlating the photographs in the two settings, the structure and absolute configuration determined will be wrong.

6. DOUBLE-LAYER WEISSENBERG PHOTOGRAPHY

One may record on the same film by normal beam photography reflections belonging to two different layers. The necessity was suggested by the following consideration. Since the absorption factors are usually large when anomalous scattering is present, great care should be taken to see that for both reflections of the Bijvoet pair the absorption corrections are identical. This is essential as the differences in the intensity of the Bijvoet pairs is usually quite small. Many crystals belonging to the monoclinic, trigonal, tetragonal and hexagonal classes have a tendency to form needles along the unique axis. In all these systems, excepting the trigonal, there are no Bijvoet pairs in any layer about the unique axis. The reflections to be compared, hkl and $h\bar{k}l$, may, however, be obtained in the Weissenberg photograph of any one layer about a non-unique axis. To cut the crystal in the required direction is impossible where a liquid at normal temperatures has been crystallized in a capillary tube at low temperatures. Even when the substance is a crystal at room temperature it has quite often proved impossible to cut it along the required axis and grind it into a good cylindrical specimen. If the specimen is not perfectly cylindrical, absorption corrections for each of the two reflections of a Bijvoet pair will be different, and if not perfectly corrected may vitiate the comparison of intensity in the determination of the absolute configuration.

To obviate the difficulty, a simple double-layer screen has been devised so that by normal beam Weissenberg photography (Wooster and Wooster, 1933; Buerger, 1942, pp. 242-4) the reflections of the L and \bar{L} layers are recorded on the same film. The reflections hkL and $hk\bar{L}$ are recorded simultaneously on the same film separated by a distance $D (= 2R \tan \mu)$, where R is the radius of the film. If the rotation of the camera is less than the angle corresponding to a translation equal to D , there will be no overlapping of spots of the two layers.

After many trials the design of the double-layer screen which proved

most satisfactory is shown in Fig. 3.† The central tube B, between two layer slits A and C, can be varied in length by adding or removing the small stepped rings which fit snugly into one another. It is found that if the rings are made of non-ferrous magnetic alloy and magnetized in the direction of the axis of the tube they hold on to each other quite well, and no other mechanical support is necessary. The beam catcher is permanently fixed to one of the rings, which can always be brought to the centre.

A second method using two vertical variable apertures on either side of the crystal, together with the conventional screen tubes, is also being tried for separating the two layers hkL and $hk\bar{L}$. The double-layer method of recording the Bijvoet pairs has the following advantages. For crystals that have only a 2-, 4- or 6-axis this method may be used. The LP factor

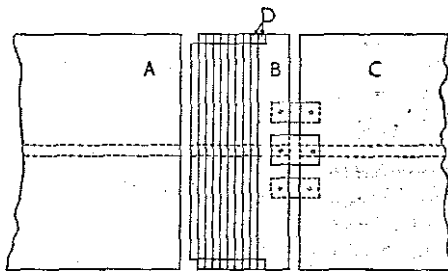


FIG. 3. The double-layer screen, in which A and C are conventional screen tubes and B is attached to C by metal strips. Stepped rings D (if necessary, magnetized) fit on to B to give a central screen tube of variable length.

is identical for the Bijvoet pair hkL and $hk\bar{L}$. If the crystal is cylindrical about the axis of rotation the absorption corrections are also the same. Further, both reflections will be elongated or contracted in the same manner. The reflections also occur simultaneously and so any fluctuations in the intensity of the incident beam will not matter at all. In other cases, where both reflections of a Bijvoet pair are not flashed simultaneously, a stabilized X-ray unit would be essential.

In the triclinic system the reflections to be compared are of the type hkl and $\bar{h}\bar{k}\bar{l}$. These will not be recorded on the same side of the film in any conventional Weissenberg camera. In the double-layer method they may be obtained on the same film and on the same side of the central line as follows. The slots of the double screen are adjusted to photograph the L and \bar{L} layers. One slit is closed and the hkl data is recorded through the other. The crystal is now rotated by exactly 180° . The first slit is now

† This design is due to Dr. G. Suryan.

opened while the other is closed, and $hk\bar{L}$ reflections are recorded in an adjacent part of the same film. The reflections hkl and $\bar{h}\bar{k}\bar{l}$ are now separated by a distance D , and these may be compared for the determination of the absolute configuration, provided the intensity of the incident beam has been constant throughout the experiment and the exposures for the two layers was the same.

Acknowledgements

The authors thank the Council of Scientific and Industrial Research, India, for supporting the project on low and high-temperature crystallography. Thanks are also due to Professor R. S. Krishnan for his interest in the problem, and to Dr. G. Suryan and Dr. S. Swaminathan for many invaluable discussions.

REFERENCES

- Abrahams, S. C., Collin, R. L., Lipscomb, W. N. and Reed, T. B. (1950). *Rev. sci. Instrum.* **21**, 396.
 Bijvoet, J. M. (1954). *Nature, Lond.* **173**, 888.
 Bijvoet, J. M. (1955). *Endeavour* **14**, 74.
 Buerger, M. J. (1942). *X-ray Crystallography*. Wiley, New York.
 Dauben, C. H. and Templeton, D. H. (1955). *Acta cryst.* **8**, 841.
 Kaufman, H. S. and Fankuchen, I. (1949). *Rev. sci. Instrum.* **20**, 733.
 Manohar, H. and Ramaseshan, S. (1961). *Tetrahedron Letters* **22**, 814.
 Peerdeman, A. F. and Bijvoet, J. M. (1956). *Acta cryst., Camb.* **9**, 1012.
 Peterson, S. W. (1955). *Nature, Lond.* **176**, 396.
 Singh, A. K. and Ramaseshan, S. (1963). This volume, p. 309.
 Singh, A. K., Swaminathan, S. and Ramaseshan, S. (1962). To be published.
 Wooster, W. A. and Wooster, N. (1933). *Z. Kristallogr.* **84**, 327.

DISCUSSION

S. RAMASESHAN: The concept of the double-layer line screen is not new. Prof. Bijvoet and his collaborators have used such an arrangement in their studies of the absolute configuration of NaClO_3 and NaBrO_3 (see this volume, p. 225. See also A. W. Hanson, *J. Sci. Instrum.* **35**, 188, 288 (1958) and the references given therein).

G. KARTHA: While using the double-slit method it seems advantageous to use half slits instead of full slits, so that one could record both hkl and $\bar{h}\bar{k}\bar{l}$ (say) in the same run on the top and bottom halves of the film respectively.

S. RAMASESHAN: Yes. In fact Hanson's double-layer screen has only half slits.

R. SRINIVASAN: I think it is possible to have the hkl and $\bar{h}\bar{k}\bar{l}$ reflections on the same side of the film by changing the ratio of the translation to the rotation, so that instead of the usual coverage of $0-180^\circ$, one can have $0-360^\circ$ on each side of the film.

S. RAMASESHAN: This is of course possible. Prof. Buerger has described an $8^\circ/\text{mm}$ camera in his book. But this involves a major modification of the Weissenberg

camera. In this work we devised attachments only for the traditional $2^\circ/\text{mm}$ camera.

D. HARKER: It is to be noted that the point group of the reciprocal lattice is that of the crystal when anomalous scattering is present. In order to observe the Bijvoet inequality, the two reflections must not be related by the true symmetry of the crystal but *must* be related by the Laue point group, that is the true point group plus a centre of inversion.