6. Conclusion

Our X-ray investigations on α-CuNSal have shown a reversible and continuous structural phase transition from a commensurate to an incommensurate orthorhombic phase at $T_i = 303$ K and a reversible first-order phase transition into a monoclinic commensurate phase at 241 K. There also exists an intense temperature-dependent diffuse scattering along **a*** and we assume that it is caused by dynamic atomic movements associated with the phase transition at T_i. Within the incommensurate phase we observe a pronounced diffuse scattering around the satellite reflections which is explained by phase fluctuations of the modulation wave. The results are discussed within the frame of a simple model assuming equal amplitudes of the modulation wave for all atoms of the chelate molecule.

At the moment refinements of the structures within the three phases are performed and we hope that these investigations will supply important information on the dynamic processes at the phase transition.

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The Polarization Factor for a Repeatedly Reflected X-ray Beam: Special Cases

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Abstract

A method for determining the polarization factor for a repeatedly reflected X-ray beam is described. It is shown that, provided the relative orientations of the pre-specimen reflectors are restricted to special geometries (the usual cases), the appropriate expression for an unpolarized beam reflected *m* times can be simply derived. The treatment is extended to a plane-polarized beam, resulting in an expression dependent on polarization effects from the specimen alone and hence independent of the state of perfection of crystal monochromators. The latter expression may have some relevance to experiments performed with synchrotron radiation.

Many of the techniques used today for measuring X-ray diffraction data have as an integral part of their instrumentation a system of pre-reflectors, reflecting the beam before diffraction by the specimen takes place. Such systems may include one or more crystal monochromators and/or focusing mirrors, usually serving either to select a particular wavelength of radiation or to produce a convergent beam of X-rays. The common feature of most – if not all – these arrangements is the relative orientations of the pre-specimen reflectors with respect to one another and, in some cases, to the specimen itself. These geometries are restricted to two types: those in which the diffraction plane (the plane containing the incident and reflected beams) of the *i*th reflector is parallel to the diffraction plane of the first reflector ($\rho = 0°$ geometry), and those in which the diffraction planes of the first and *i*th reflectors are perpendicular to each other ($\rho = 90°$ geometry).

A general formula for the polarization factor for a system of one monochromator plus specimen has been

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derived by Azároff (1955), but extension of this formula to a system containing more than one pre-specimen reflector becomes complex if the generality is maintained (Vincent, 1982). However, if the system consists of pre-specimen reflectors with the two special geometries mentioned above – the usual cases – then it is possible to derive the polarization factor for a beam reflected m times in a straightforward way. It is the purpose of this note to indicate the method of derivation of such a formula for an unpolarized beam of X-rays and also to show the form of the equation for a plane-polarized beam, the latter having possible applications in synchrotron radiation experiments.

Unpolarized beam

Let there be m reflectors of which the first $m-1$ are pre-specimen reflectors with geometries restricted to $\rho = 0$ or 90° and the mth is the specimen with unrestricted values of ρ. Assume initially that all reflectors are ideally mosaic. The incident beam of X-rays on the first reflector is unpolarized and hence may be resolved into two equal, mutually perpendicular components so that one component (σ) lies in the diffraction plane and the other (π) normal to it, these components describing the directions of polarization of the beam. This definition implies that for the $\rho = 0°$ geometry the σ component lies parallel to the normal to the scattering planes and the π component in the planes, and *vice versa* for the $\rho = 90°$ geometry. It follows therefore that the orientation of the first reflector is explicitly defined as in the $\rho = 0°$ geometry and hence the orientations of the remaining reflectors are all relative to this case. Thus for the other $m-2$ pre-specimen reflectors this is according to whether their diffraction planes lie parallel or perpendicular to the diffraction plane of the first reflector. For the specimen the angles of ρ are general, but still relative to the first reflector, being given by the Azároff (1955) definition.

On expressing the beam in terms of the amplitude of the electric vector $\mathbf{E}_0$, it may be shown that, with the above conditions, the contributions to the intensity from the σ and π components after the ith reflection in terms of the intensity just before it, are given by

$$\overline{{}_iE_\sigma^2} = k_i^2\,\overline{{}_{i-1}E_\sigma^2}(\cos^2 2\theta_i \cos^2\rho_i + \sin^2\rho_i) \qquad (1)$$

and

$$\overline{{}_iE_\pi^2} = k_i^2\,\overline{{}_{i-1}E_\pi^2}(\cos^2 2\theta_i \sin^2\rho_i + \cos^2\rho_i), \qquad (2)$$

where $1 \le i \le m$ and $\overline{{}_0E_\sigma^2} = \overline{{}_0E_\pi^2} = \overline{E_0^2}/2$. k_i is a constant for each reflector and $2\theta_i$ is the angle between the incident and reflected beams. The terms in brackets in (1) and (2) account for the component that is normal to the scattering planes being attenuated by cos 2θ on reflection. The resultant contribution to the intensity from both components after the ith reflection is given by their sum:

$$\overline{E_i^2} = \overline{{}_iE_\sigma^2} + \overline{{}_iE_\pi^2} \qquad (3)$$

and hence $\overline{E_m^2}$ may be determined in terms of $\overline{E_0^2}$ from these relationships.* It will be seen from (3) that the choice of $\rho = 0$ or $\rho = 90°$ to define the geometry of the first reflector becomes arbitrary. Moreover, adding 90° to ρ_i for *all* reflectors merely interchanges the directions of the σ and π components relative to the first reflector.

The last step is to express the final intensity in terms of the intensity just before the mth reflection. This is the ratio $\overline{E_m^2}/\overline{E_{m-1}^2}$, which is related to the beam intensities by

$$I_m/I_{m-1} = \overline{E_m^2}/\overline{E_{m-1}^2}. \qquad (4)$$

Equation (4) may be written as

$$I_m = K I_{m-1} p_m,$$

where p_m, the polarization factor for a beam reflected m times, is

$$p_m = \left[\prod_{i=1}^{m} (\cos^2 2\theta_i \cos^2\rho_i + \sin^2\rho_i) + \prod_{i=1}^{m} (\cos^2 2\theta_i \sin^2\rho_i + \cos^2\rho_i)\right] \times \left[\prod_{i=1}^{m-1} (\cos^2 2\theta_i \cos^2\rho_i + \sin^2\rho_i) + \prod_{i=1}^{m-1} (\cos^2 2\theta_i \sin^2\rho_i + \cos^2\rho_i)\right]^{-1} \qquad (5)$$

from an appropriate use of the above equations, and $K = k_m^2$.

Equation (5) is entirely a function of $\cos^2 2\theta_i$ (with $|\cos 2\theta_i|$ replacing $\cos^2 2\theta_i$ for those reflectors considered ideally perfect) if the reflections from the specimen are also measured in either of the two special geometries (the case with diffractometers). However, for data collected on films or with area detectors, ρ_m varies from reflection to reflection and therefore the mth term in (5) will be a function of ρ_m as well. Methods of calculating ρ_m for various film techniques

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* Only if the pre-specimen reflectors are of the $\rho = 0$ or 90° geometries and the specimen (with general values of ρ) is the last reflector, will equations (1) to (3) be applicable since the components σ and π remain orthogonal on reflection up to – but not necessarily including – the last reflection. It can be shown (Vincent, 1982) that if ${}_{i-1}E_\sigma$ and ${}_{i-1}E_\pi$ are orthogonal the angular deviation δ of ${}_iE_\sigma$ from ${}_{i-1}E_\sigma$ projected onto a plane normal to the diffraction plane is given by $\cos\delta = (\cos^2\rho_i \cos 2\theta_i + \sin^2\rho_i)(\cos^2\rho_i \cos^2 2\theta_i + \sin^2\rho_i)^{-1/2}$. A similar expression for γ, the deviation of ${}_iE_\pi$ from ${}_{i-1}E_\pi$, is obtained by interchanging $\cos^2\rho_i$ and $\sin^2\rho_i$. It is evident that both δ and γ are zero when $\rho_i = 0$ or 90°, but non-zero for general values of ρ_i.

have been discussed by, for example, Arndt & Sweet (1977), Buerger (1967) and Whittaker (1953).

In principle, X-rays reflected off focusing mirrors or mirror monochromators will also suffer from polarization effects. However, the critical angle θ_c for total reflection of X-rays is so small (Witz, 1969) that $\cos^2 2\theta_c \simeq 1$ and hence their contribution to p_m can be neglected.

Plane-polarized beam

It is worth considering the form of p_m for a plane-polarized beam under the same conditions as stated in the previous section, as it may have some relevance to synchrotron radiation experiments. With this type of source it is possible to achieve a working beam which is almost plane-polarized (to within ~1%, European Synchrotron Radiation Facility, 1979). For the present purposes it will be considered completely plane-polarized with $\mathbf{E}_0$ lying, as it does, in the electron orbital plane. In terms of E_σ and E_π, this means that the magnitude of one of these components is zero and the other is parallel and equal to E_0. Although some of the previous relationships for an unpolarized beam are no longer valid here, the form of (4) and hence (5) allows the elimination of the zero component directly.

Equation (5) may be rewritten as

$$p_m = \frac{{}_mP_\sigma + {}_mP_\pi}{{}_{m-1}P_\sigma + {}_{m-1}P_\pi}, \qquad (6)$$

where P_σ and P_π refer to the contributions to p_m from the components σ and π respectively. Taking the σ component as being zero, (6) reduces to

$$p_m = \frac{{}_mP_\pi}{{}_{m-1}P_\pi},$$

or, more explicitly,

$$p_m = \frac{\prod_{i=1}^{m} (\cos^2 2\theta_i \sin^2 \rho_i + \cos^2 \rho_i)}{\prod_{i=1}^{m-1} (\cos^2 2\theta_i \sin^2 \rho_i + \cos^2 \rho_i)}$$

$$= \cos^2 2\theta_m \sin^2 \rho_m + \cos^2 \rho_m. \qquad (7)$$

(Alternatively, for zero contribution from the π component, $p_m = \cos^2 2\theta_m \cos^2 \rho_m + \sin^2 \rho_m$. It is clear that a knowledge of the direction of E_0 relative to the first reflector is necessary.)

Hence, for a plane-polarized beam, the polarization factor is independent of the polarization effects of the pre-specimen reflectors with the important consequence that the state of perfection of crystal monochromators used in the experiment need no longer be of concern (Vincent & Flack, 1980). Moreover, when $\rho_m = 0°$ in (7) $p_m = 1$, implying no correction for polarization effects whatsoever (as realized by Templeton, Templeton, Philips & Hodgson, 1980; indeed it is the ideal case). Similarly, when $\rho_m = 90°$, $p_m = \cos^2 2\theta_m$, implying a correction equal to $1/\cos^2 2\theta_m$. Other aspects of these two cases have been discussed by Vincent & Flack (1980). General values of ρ_m are calculated according to the measuring technique adopted (see above).

In summary, the reciprocal of (5) is the expression to be used to correct data for polarization effects for an unpolarized beam reflected m times. It has been shown that the influence of focusing mirrors, for example, on p_m is small enough for them to be neglected from the calculation. Hence p_m is generally only dependent on polarization effects from crystal monochromators and the specimen, giving typical values for m of 2 or 3. It has also been shown that, for a plane-polarized beam, p_m is a function of the polarization effects of the specimen alone (7) and therefore a knowledge of the state of perfection of crystal monochromators – a problem in accurate work – is not required. The relevance of (7) to synchrotron radiation experiments has been pointed out, but a correct application depends on how near the working beam is to being completely plane-polarized.

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