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Space and Time Inversion in Physical Crystallography

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Abstract

Conventional (point) symmetry, antisymmetry, magnetic and complete symmetry are used for the description of specific features of space, time and some crystallographic phenomena. The Onsager principle is extended to phenomena described by second-rank axial tensors. As a result it is seen that the symmetric part of such a tensor changes the sign on time reversal. The actions of two operations - time reversal R and time inversion T ($\bar{T}=\bar{1}$, 'spatial inversion') - are compared. It is shown that the equations of crystal physics derived by Voigt are in agreement with the Onsager principle.

Introduction

A formal (analytical) apparatus of tensor crystallography based on the works by Curie, Neumann, Voigt and Shubnikov permits one to predict important symmetry characteristics for different physical phenomena occurring in crystals. The simplest example is the pyroeffect which may, although not necessarily, be revealed in a polar crystal with a special (unique) polar direction. On the other hand, symmetry characteristics allow one to state that if the symmetry conditions are violated the phenomenon under consideration cannot be revealed at all. For example, the pyroeffect (in the generally accepted sense) in centrosymmetric crystals cannot be detected, *i.e.* it is forbidden. The above statements are based on the concepts of conventional point symmetry using orthogonal transformations in three-dimensional space (proper and improper rotations, group O_3).

Works on thermodynamics of irreversible processes and, first and foremost, the Onsager (1931) work have established the additional symmetry requirements for some phenomena to be realized. They follow from invariance of relationships describing physical phenomena with respect to time reversal R ($t \rightarrow -t$). Some phenomena (*e.g.* magneto-electric effect) which are allowed from the standpoint of orthogonal spatial transformations cannot be physically realized in all crystals, the relationships describing these phenomena, generally speaking, do not meet the requirements imposed on them by operation R (Landau & Lifshitz, 1979).

Antisymmetry (Shubnikov & Belov, 1964) and magnetic symmetry (Sirotin & Shaskol'skaya, 1982) provide the allowance for requirements imposed by both operations R and the operations inherent in the O_3 group. At the same time, practice shows (see below) that the use of magnetic symmetry eliminates some difficulties, giving rise to others. This necessitates the introduction (in addition to symmetry) of physical characteristics of crystals under consideration, *i.e.* a concept concerning two types of crystals - those having a magnetic structure (Landau & Lifshitz, 1960) and those without it. The situation seems to be rather peculiar - to judge some, say, magnetic properties of a crystal, *e.g.* piezomagnetism or magnetoelectric effect, on the basis of magnetic symmetry of the crystal one should know *a priori* whether the crystal is magnetic or not.

Therefore, it is very important to establish purely symmetric characteristics of physical phenomena in crystals which are to be used (after due account of crystallophysical relationships in terms of time reversal R) in a way similar to that used at the beginning of this article. In the following this problem is solved within the framework of complete symmetry (Zheludev, 1983).

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1. Antisymmetry, complete and magnetic symmetry

The use of conventional symmetry in physical crystallography results in the fact that we treat unequally even such simple phenomena as electric and magnetic properties - there are ten classes for polar crystals and thirteen for axial ones. This is associated not with symmetry uniqueness of the phenomena themselves but rather with the fact that conventional symmetry treats differently 'quantitative' characteristics of phenomena (for example + and − signs, two 'opposite' colors, *etc.*) and those characteristics of the phenomena which take into account right and left forms (the signs of enantiomorphism). Indeed, conventional symmetry deals with figures of only one 'quantitative sign' (*e.g.* of one color), whereas figures or their parts can possess both signs of enantiomorphism. Even this fact already proves that, for example, an electric dipole and magnetic moment cannot be described similarly within the conventional symmetry.

The first steps towards equal treatment of the indicated characteristics of crystals *via* the extended concept of point symmetry were undertaken by Heesch (1930) on the basis of group theory and by Shubnikov (1951) who used the geometrical method.

In antisymmetry, according to Shubnikov & Belov (1964), two pairs of signs (*i.e.* two colors and two signs of enantiomorphism) are used so that, for example, a right white tetrahedron of the general form has a corresponding right tetrahedron but of black color. Transition from such a figure to the other (antifigure) is realized *via* an operation of anti-identity denoted in antisymmetry as $\underline{1}$. Since the present paper uses the same notation for another operation in complete symmetry, in what follows operation $\underline{1}$ in antisymmetry will be denoted as $\underline{1}^a$. It can easily be seen that using the above extension we encounter some difficulties in our attempts to describe physical phenomena - it would have been more natural for figures and 'antifigures' to differ by both pairs of signs.

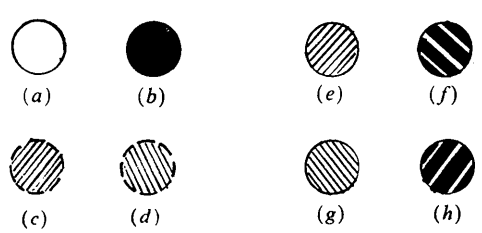

Fig. 1. The simplest elements used in complete symmetry. (*a*), (*b*) Positive (+) and negative (−) scalar spheres; (*c*), (*d*) left (+) and right (−) pseudoscalar spheres; (*e*), (*f*) left white and right black spheres; (*g*), (*h*) right white and left black spheres. Operation $\bar{1}$ transforms sphere (*c*) into sphere (*d*) and sphere (*e*) into sphere (*g*); operation $\bar{\underline{1}}$ transforms sphere (*a*) into sphere (*b*) and sphere (*f*) into sphere (*g*); operation $\underline{1}^c$ transforms sphere (*a*) into sphere (*b*), sphere (*c*) into sphere (*d*), sphere (*e*) into sphere (*f*) and sphere (*g*) into sphere (*h*).

This drawback of antisymmetry extension is associated with the fact that it is intended for the description of two-color figures. In conventional symmetry and antisymmetry a tetrahedron of the general form is chosen as a 'brick' of a figure, *i.e.* a figure with symmetry 1. For such a figure the sign of enantiomorphism is determined by its form. In physics no 'privileges' can be granted to any characteristic (any pair of signs). This may be attained, for example, by considering the above 'quantitative' characteristic as that of a scalar and a sign of enantiomorphism as a pseudoscalar. Such an interpretation of the conventional symmetry extension to two pairs of 'opposite' signs received the name of complete symmetry (Zheludev, 1983). Geometrical interpretation of complete symmetry should use scalar and pseudoscalar spheres as 'bricks', their symmetry groups being $\infty/\infty/mmm$ and $\infty/\infty/\underline{mmm}$, respectively.

Identical treatment of both pairs of signs in complete symmetry permits one to determine the transformation of a figure into an antifigure (the corresponding operation in complete symmetry is also denoted by $\underline{1}$, so in what follows we shall refer to it as $\underline{1}^c$) as a transformation with a corresponding change of both signs (right black sphere is transformed into left white). Equivalent transformation is also that of spheres characterized by only one sign - the operation of spatial inversion ($\bar{1} = c$) - which does not change the sign of a scalar sphere but alters that of a pseudoscalar one. In turn, a complex operation of 'inversion with an additional change in the sign',* $\bar{\underline{1}}$, alters the sign of a scalar sphere but preserves that of a pseudoscalar one. From the aforesaid it follows that in the general case $\underline{1}^c = \bar{1} . \bar{\underline{1}}$ (Fig. 1).

Equivalent interpretation of scalar and pseudoscalar quantities leads to equivalent interpretation of electric and magnetic phenomena - of the 90 groups in the complete symmetry of crystals, 31 groups describe spontaneously polarized crystals and 31 spontaneously magnetized ones. In that light, the generalization of magnetic symmetry based on two pairs of 'opposite' signs (Sirotin & Shaskol'skaya, 1982) seems to be at least inconsistent and formally illogical, which is associated with the fact that both pairs of signs in magnetic symmetry are pseudoscalars. One pair of signs is related to magnetic moments (their poles have opposite signs of enantiomorphism) while the other pair is to describe 'geometrically axial' directions not related to magnetism. It is also taken that on the action of the operation of time reversal R magnetic poles change their signs, whereas geometrically axial ones preserve it. Magnetic symmetry (similar to antisymmetry) is described by 122 groups (out of them 90 are analogous to those

* This additional change of sign (on inversion) relates to both scalar and pseudoscalar signs (to each one separately or to both simultaneously), $\bar{\underline{1}} = \bar{1} . \underline{1}^c$.

used in complete symmetry and 32 are non-magnetic ones, similar to grey noncolored groups in antisymmetry). The division of axial directions into two types mentioned earlier on the basis of symmetry consideration of a general (group-theoretical) approach is by no means justified. This also gives rise to certain difficulties in the interpretation of some physical phenomena using magnetic symmetry (see § 3). Within the framework of magnetic symmetry, electric and magnetic properties of crystals cannot be treated equally (in the indicated 32 groups, 'grey' with respect to magnetism, electric polarity is not forbidden).

2. The Onsager principle and tensor relationships used in conventional symmetry

Interaction of different forces described by polar- and axial-vector quantities results in some new phenomena, of which the only physically allowable ones are those meeting the requirements of time reversal - left- and right-hand-side parts of relationships describing such phenomena should have the same signs on the action of operation R. Thus, two polar-vector and two axial-vector quantities changing sign on the action of operation R may be related only through a quantity which does not linearly depend on time. If one of the vector quantities changes its sign on the action of operation R while the other preserves its sign, they should be related through a quantity linearly dependent on time.

A detailed analysis of symmetry characteristics in connection with the requirements following from time reversal was carried out by Onsager (1931) who established the well known kinetic-coefficient symmetry principle (Landau & Lifshitz, 1960). According to this principle the following condition is valid for second-rank polar tensors, *i.e.* for relationships between similar vector quantities (say two polar or two axial vectors), equally affected by operation R:

$$\mathbf{a}_{ij} = \mathbf{a}_{ji}. \qquad (1)$$

Examples of such relationships are

$$\begin{aligned} &\mathbf{P}_i = \mathbf{a}_{ij}\,\mathbf{Q}_j \\ &R(+ \quad ++) \\ &R(- \quad +-) \\ &\mathbf{M}_i = \mathbf{a}_{ij}\,\mathbf{S}_i \\ &R(- \quad +-) \\ &R(+ \quad ++), \end{aligned} \qquad (2)$$

where $\mathbf{P}$ and $\mathbf{Q}$ are polar vectors, $\mathbf{M}$ and $\mathbf{S}$ are axial vectors, and $\mathbf{a}_{ij}$ is the symmetric second-rank polar tensor.

If two polar or two axial vectors are affected differently by time reversal, the Onsager condition written in the form

$$\mathbf{a}_{ij} = -\mathbf{a}_{ji} \qquad (3)$$

means that the quantities under consideration are related through an axial vector (3). This case is described by the following 'vector products'

$$\begin{aligned} &\mathbf{P} = [\mathbf{HQ}] \\ &R(+ \quad --) \\ &\mathbf{M} = [\mathbf{H\,S}] \\ &R(- \quad -+), \end{aligned} \qquad (4)$$

where $\mathbf{H}$ is the axial vector linearly dependent on time.

It can be shown that for a second-rank axial tensor the condition

$$\mathbf{A}_{ij} = \mathbf{A}_{ji} \qquad (5)$$

will be analogous to condition (1) when both ifferent) end vectors are differently affected by operation R:

$$\begin{aligned} &\mathbf{P}_i = \mathbf{A}_{ij}\,\mathbf{H}_j \\ &R(+ \quad --). \end{aligned} \qquad (6)$$

In turn, the condition analogous to (3),

$$\mathbf{A}_{ij} = -\mathbf{A}_{ji}, \qquad (7)$$

is valid if both different end vectors of the axial tensor are affected equally by operation R. The restrictions imposed on the vectors by (5) and (7), on the one hand, and (1) and (3), on the other, have 'opposite meanings', otherwise we should arrive at a contradiction - the relationship $\mathbf{P} = [\mathbf{HQ}]$ would permit the change of the sign of two (polar, in this case) vectors under the effect of operation R:

$$\begin{aligned} &\mathbf{P}_i = [\mathbf{Q\,H}] \\ &\mathbf{R}(- \quad -+). \end{aligned} \qquad (8)$$

Yet this contradicts condition (1) since two equal vectors should be related *via* a symmetric polar tensor [see (2)] and not a vector [see (8)].

3. Crystallophysical phenomena within the framework of conventional symmetry

At present three phenomena give rise to some difficulties related to symmetry - piezomagnetism (Borovic-Romanov, 1954), magnetoelectric effect (Astrov, 1960) and magnetogyration (Zheludev, 1964; Zheludev & Vlokh, 1983). It is commonly accepted that in piezomagnetism

$$\mathbf{r}_{ij} = \mathbf{k}_{ijk}\mathbf{H}_k \qquad (9)$$

(where $\mathbf{r}$ is the strain tensor, $\mathbf{H}$ is the magnetic field and $\mathbf{k}$ is the third-rank axial tensor) and in the magnetoelectric effect (6)

$$\mathbf{P}_i = \boldsymbol{\alpha}_{ij}\mathbf{H}_k \qquad (10)$$

(where $\mathbf{P}$ is the electric polarization and $\mathbf{H}$ is the magnetic field), the 'time parity' principle is violated. The point is that, according to the accepted concepts, relationships (9) and (10) satisfy the conditions imposed by the Onsager principle only for crystals with a 'magnetic structure'. Such a possibility is provided by magnetic symmetry (for crystals with a 'magnetic structure' tensor $\mathbf{k}_{ijk}$ and $\boldsymbol{\alpha}_{ij}$ change the sign after application of operation R).

The interpretation of these phenomena from the standpoint of magnetic symmetry is not justified for the reasons considered in the *Introduction* and § 1. Relationship (9) satisfies the Onsager principle in terms of complete symmetry where the crystal is axial not only because of the presence of a magnetic structure. Of course, in crystals with a magnetic structure piezomagnetism can readily be detected although this does not prove that this phenomenon is *a priori* impossible if the crystal is axial not because of the presence of a magnetic structure.

The so-called 'time-parity violation' for the magnetoelectric effect can only be established in the case (as is commonly accepted) where it is taken that operation R does not change the sign of a symmetric second-rank axial tensor, $\boldsymbol{\alpha}_{ij}$ (as is accepted in electrodynamics, vector $\mathbf{P}$ does not change its sign, whereas vector $\mathbf{H}$ changes its sign). As was shown in § 2 [see (6)], it is just in the case under consideration that $\boldsymbol{\alpha}_{ij}$ changes the sign on the action of operation R, which lifts the 'prohibition' on the realization of the phenomenon in crystals possessing no magnetic structure.

Magnetogyration, a new phenomenon which has recently been predicted and then observed, consists in the appearance in crystals of optical activity linearly dependent on the magnetic field and described by the expression

$$\mathbf{g}_{ij} = \boldsymbol{\delta}_{ijk}\mathbf{H}_k \qquad (11)$$

where $\mathbf{g}$ is the symmetric second-rank axial vector, $\boldsymbol{\delta}$ is the third-rank polar tensor analogous to that describing the piezoeffect, and $\mathbf{H}$ is the magnetic field. From the commonly accepted symmetry standpoint (with no account of a possible change in the sign of $\mathbf{g}_{ij}$ on operation R) magnetogyration contradicts the Onsager principle and is possible only in crystals with magnetic structure. In fact, it has been discovered and studied in nonmagnetic crystals, *e.g.* cadmium sulfide and lead germanate (Zheludev & Vlokh, 1983) (Fig. 2). If we take into account the Onsager principle extended to second-rank axial tensors, (11) will describe phenomena allowable from the symmetry standpoint. Concluding this section, we should like to note that although the Onsager principle cannot be readily applied to all crystallophysical phenomena the requirements imposed by it, if properly used and accounting for its extension to second-rank axial tensors, permit one to draw the conclusion that all three above-mentioned phenomena show no 'violation of time parity'.

4. Crystallophysical phenomena in terms of complete symmetry

According to the generally accepted concepts time is homogeneous, whence the law of conservation of energy follows, whereas space is both homogeneous and isotropic, whence the laws of conservation of momentum and moment of momentum follow (Landau & Lifshitz, 1976). Then space cannot be characterized by polar-vector and axial-vector quantities. For time the situation is reversed – it cannot be described by scalar characteristics (energy being taken to be a scalar quantity).

Taking into consideration that space and time can be characterized by scalar, polar-vector or axial-vector quantities alone (it is just such quantities which describe the well known properties of space and time symmetry), we come to the conclusion that the change in the sign of time ($t \to -t$) (time reversal) may be accompanied by a change in direction of polar-vector and axial-vector quantities. In particular, such behavior should be observed for linear and angular velocities, quantities linearly dependent on time. Force (a polar vector) and force moment (an axial vector) do not change their signs on the action of operation R. Energy (a scalar quantity) does not change its sign upon time reversal. Since pseudoscalar quantities do not participate in the description of well known properties of space and time symmetry, the effect of operation R on their behavior is not determined. We should like to remind the reader that from the extended Onsager principle (§ 2) it follows that quantities described by a symmetric second-rank axial tensor (in particular by a pseudoscalar) should change their signs on the action of operation R.

Thus, within conventional symmetry the operation of time reversal R in crystal physics may change, in principle, the signs of polar and axial vectors and pseudoscalars. The theory of electromagnetism determines, in addition to energy which does not change its sign on the action of R, the behavior of the polar vectors of an electric dipole and the axial vector of magnetic moment, the former preserves its sign, whereas the second alters it. Quantum mechanics determines the behavior of energy, not changing the sign on the action of operation R, and the 'direction

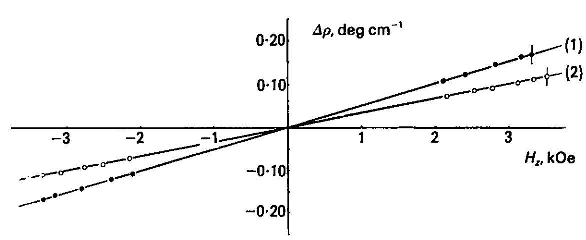

Fig. 2. Magnetogyration part (with subtracted Faraday effect) of a rotation of light polarization plane *versus* the strength of a magnetic field. (1) CdS crystals, (2) $Pb_5Ge_3O_{11}$: ε_u^+ (lead germanate) crystals. (1 oersted = 79.5775 Am^{-1}.)

of the motion', changing the sign on this operation (Elliot & Dawber, 1979).

Specific behavior of vector and scalar quantities under the action of operation R are summarized in Table 1, which also provides the data on the action of spatial inversion $\bar{1}$ (complete symmetry) and inversion plus recoloring, $\underline{\bar{1}}$. Comparison of the listed data shows that the first and the third lines of Table 1 are consistent with operation $\bar{1}$ (line four). Moreover, line two is consistent with line one.* It is very important to emphasize here that lines one and four (operations R and $\bar{1}$, the latter being denoted as T in complete symmetry) are also consistent (see Zheludev, 1983, Appendix III). The consistency of operation $\bar{1}(T)$ with the known operation of time reversal R is quite important and should be used in two aspects. Firstly, since this operation is unique and its action is well defined, it is possible to relate geometric images (*i.e.* a polar vector and a pseudoscalar) to time. These images change sign on the action of spatial inversion (but not on inversion of space) (see Table 1). Secondly, the use of the indicated images provides quite a simple verification of the validity of any relationship with respect to time reversal. For that it suffices to know such geometric images that describe the quantities under consideration - polar or axial vectors, scalars or pseudoscalars (higher-rank tensors can be represented as a set of these quantities).

Fig. 3 illustrates some relationships of crystal physics and also the fulfilment of requirements imposed

* Operation R compared with T is defined for polar and axial vectors in 'opposite' ways. Yet this does not contradict the requirements imposed by operation T on relationships describing actual electromagnetic phenomena [see (6) and (8)].

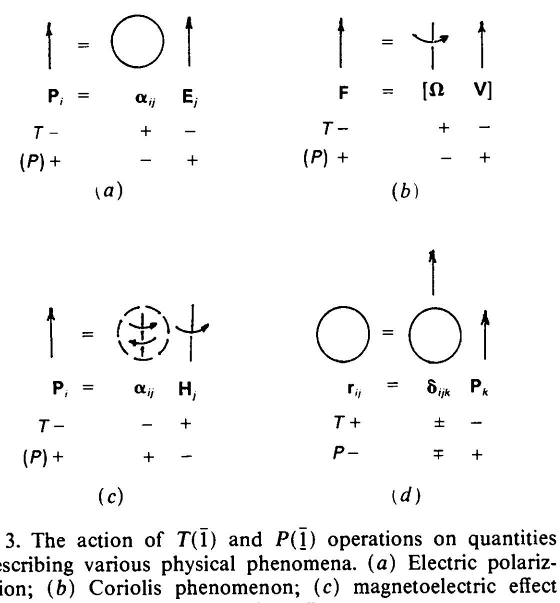

Fig. 3. The action of $T(\bar{1})$ and $P(\underline{\bar{1}})$ operations on quantities describing various physical phenomena. (*a*) Electric polarization; (*b*) Coriolis phenomenon; (*c*) magnetoelectric effect [equation (10)]; (*d*) inverse piezoeffect.

Table 1. *The action of space and time transformation operations on vector and scalar quantities*

Operation	Polar vector	Scalar	Axial vector	Pseudoscalar
Time reversal R in crystal physics (conventional symmetry)	∓	+	±	−
Time reversal in the theory of electromagnetism	+	+	−	
Time reversal in quantum mechanics	∓	+	±	
Spatial inversion $\bar{1}(T)$	−	+	+	−
Inversion with 'recoloring' $\underline{\bar{1}}(P)$, complete symmetry	+	−	−	+

by operation $\bar{1}(T)$ (called here time inversion to distinguish it from other operations) and $\underline{\bar{1}}(P)$ (space inversion). Note that simple tensor relationships (no higher than second-rank tensors), which describe the phenomena occurring in reality, meet the demands of operation T alone, while those of higher order meet the requirements of operations T and P.

All tensor relationships used in crystal physics are obtained from the well known formulae for transformations of axial and polar tensor components occurring during the transformations of the reference system (the change in the sign of enantiomorphism for the reference system results in the necessity of using sign − for axial tensors in these equations *etc.* (Nye, 1964). The above rules uniquely correspond to the requirements following from the transformations associated with operation $\bar{1}(T)$.

As is seen from Table 1, multiplication of operations $\bar{1}(T)$ with $\underline{\bar{1}}(P)$ in complete symmetry always transforms a phenomenon into an antiphenomenon ($\bar{1}\,.\,\underline{\bar{1}} = \underline{1}^c$). In its application to the problem of particles and antiparticles in high-energy physics, such multiplication is equivalent to a so-called CPT transformation (Zheludev, 1977): CPT = -1, $\underline{\bar{1}}(P)\,.\,\bar{1}(T) = -1$ (letters P and T have different meanings in these relationships).

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Experimental Determination of Triplet Phases and Enantiomorphs of Non-centrosymmetric Structures. I. Theoretical Considerations

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Abstract

Information on the triplet phase sum Φ_Σ of the structure factor product $F(-\mathbf{h})F(\mathbf{h}-\mathbf{g})F(\mathbf{g})$ can be deduced from the rocking curve of a ψ-scan experiment scanning through a three-beam position. For non-centrosymmetric structures, four typical profiles can be observed. For $\Phi_\Sigma = 0, 180°$, asymmetric profiles result, whereas a nearly symmetrical decrease or increase of the two-beam intensity appears for $\Phi_\Sigma = \pm 90°$. In a first approximation this behaviour can be explained by the interference between the directly diffracted wave of **h** and the 'Renninger *Umweg*' wave of **g** and **h** − **g**. Their phase relationship and the amplitudes are governed by a spatial resonance term, which causes a phase shift of 180° and a continuously turning on and off of the *Umweg* wave amplitude scanning through the three-beam position. This interference can be displayed by a phase-vector diagram which outlines the main features of the ψ-scan profiles. The semi-quantitative results are confirmed by calculation based on the dynamical theory. The distinction between $\Phi_\Sigma = \pm 90°$ allows the experimental determination of enantiomorphs.

1. Introduction

It has been suggested for a long time that multiple-beam X-ray diffraction can be applied to determine the phase relationship of the waves involved. In a three-beam diffraction case three reciprocal-lattice points (r.l.p.) *O*, *H*, *G* simultaneously lie on or close to the Ewald sphere. Then, three strong wave fields are propagated in the crystal owing to the reciprocal-lattice vectors (r.l.v.) **O**, **h**, **g** with the propagating vectors $\mathbf{K}(\mathbf{n}) = \mathbf{K}(\mathbf{O}) + \mathbf{n}$, $\mathbf{n} = \mathbf{O}, \mathbf{h}, \mathbf{g}$, according to Bragg's law. From a more or less kinematical point of view, the amplitude of the total wave field propagated in the direction **K**(**h**) results from the interference between the 'direct' wave diffracted at the lattice plane (**h**) and the detour excited wave ('Renninger *Umweg*' wave) diffracted at the lattice planes (**g**) and (**h** − **g**). This depends on the phase difference and on the amplitudes of both waves given by their structure factors $F(\mathbf{h})$, $F(\mathbf{g})$ and $F(\mathbf{h}-\mathbf{g})$, respectively. Therefore, the diffracted intensity in the three-beam case bears information on the phase difference (Lipscomb, 1949):

$$\Phi_\Sigma = [\varphi(\mathbf{g}) + \varphi(\mathbf{h}-\mathbf{g})] - \varphi(\mathbf{h})$$
$$= \varphi(-\mathbf{h}) + \varphi(\mathbf{g}) + \varphi(\mathbf{h}-\mathbf{g}),$$

which represents a structure-invariant triplet phase relationship. The influence of this interference on the two-beam intensity can be measured by a Ψ-scan experiment monitoring the integrated intensity $I(\mathbf{h})$ while the crystal is rotated about the direction **h** and scanned through a three-beam position. The resultant Ψ-scan profiles must depend on the triplet phase Φ_Σ. They can be explained by the continuously turning on and off of the amplitude of the *Umweg* wave and an additional phase shift $\Delta(\Psi)$ by 180° when the r.l.p. *G* passes through the Ewald sphere (Hümmer & Billy, 1982).* If it is borne in mind that Bragg diffraction is a spatial resonance phenomenon (Ewald, 1917), the behaviour of the *Umweg* wave is nothing but the behaviour of every resonance phenomenon passing through the resonance.

* In the cited paper there is an error. $\Psi < 0$ and $\Psi > 0$ correctly mean that the third r.l.p. *G* lies inside or outside the Ewald sphere respectively, *i.e.* all the Ψ-scan profiles drawn in the paper refer to an in-out rotation sense.

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