Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1975). A**31**, 153

Comments on *Multiple diffraction of X-rays and the phase problem* by R. Colella.

By Ben Post, *Polytechnic Institute of New York, Brooklyn, New York* 11201, *U.S.A.*

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Several serious errors which were included in a paper entitled *Multiple Diffraction of X-rays and the Phase Problem* by R. Colella [*Acta Cryst.* (1974). A**30**, 413–423] are noted and discussed.

(1) On p. 414 of Colella (1974) reference is made to the difference between the intensities of the 113 and $\bar{1}\bar{1}3$ multiple diffraction peaks in an Umweg pattern of a perfect gemanium crystal which had been recorded by Cole, Chamber & Dunn (1962). The crystal had been rotated about [222] while monitoring the very weak reflection from the (222) planes parallel to the surface. The reference includes a comment to the effect that '... a glance ... immediately shows the importance of the phase effect ... it is apparent that two crystallographically equivalent planes, (113) and ($\bar{1}\bar{1}3$), whose structure factors differ only by phase with respect to 222, produce peaks with different intensities. *This simple observation shows that a theory able to correlate structure factors and intensities in Umweganregung plots, if available, could be used for phase determination*, at least in principle' (author's italics).

Further on, on the same page, we are told that labeling in reciprocal space 'merely corresponds to a particular choice of origin'. That is true, of course. It applies to all reflections involved in dynamical diffraction. It is also seriously inconsistent with the observations made concerning the significance of the 113/$\bar{1}\bar{1}3$ intensities.

It is true that the phase of 113 differs from that of $\bar{1}\bar{1}3$. However, when reflections are involved in multiple dynamical diffraction, it is essential to take into account, not only all the reciprocal-lattice points in diffracting position, but also the relevant coupling terms. The situation is illustrated in Fig. 1.

It should be clear from Fig. 1 that, in the three-beam diffraction case under discussion, 113 and $\bar{1}\bar{1}3$ do not 'differ only by phase'. The coupling terms must be considered, but they are not even mentioned. Their significance is brought out more clearly by our Table 1, listing the 113, $\bar{1}\bar{1}3$ pair of reflections, the azimuthal angles at which they occur, together with three additional pairs related to the first by symmetry. The terms coupling the *hkl*'s to 222 are listed in the last column. The intensity relationship between $\bar{1}11$ and $\bar{1}33$ is identical with that between 113 and $\bar{1}\bar{1}3$. It is therefore difficult to accept the idea that an intensity difference between $\bar{1}11$ and $\bar{1}33$ requires a new theory for its explanation.

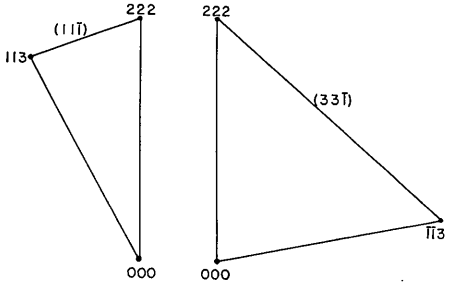

Fig. 1. Geometry of three-beam diffraction, (coupling terms in round brackets).

Table 1. *Multiple diffraction peaks*

Ge(222) Cu $K\alpha_1$

hkl	φ	Intensity	222–*hkl*
113	5·425	Strong	11$\bar{1}$
$\bar{1}\bar{1}3$	25·180	Weak	33$\bar{1}$
3$\bar{1}\bar{1}$	34·820	Weak	$\bar{1}$33
311	54·575	Strong	$\bar{1}$11
$\bar{1}$11	65·425	Strong	311
$\bar{1}$33	85·180	Weak	3$\bar{1}\bar{1}$
3$\bar{1}$3	94·820	Weak	$\bar{1}$3$\bar{1}$
1$\bar{1}$1	114·575	Strong	131

Incidentally, the phase problem in silicon and germanium, under conditions of multiple diffraction, has been treated elegantly by Ewald & Héno (1968). Their treatment is not discussed in the Colella paper presumably because they dealt only with 'Laue case diffraction'. Actually, the Ewald–Héno treatment is quite general and is not at all restricted to transmission cases. It holds for all cases where *n*-beam dynamical solutions exist. Such solutions do not exist in symmetrical two-beam Bragg diffraction, near the exact Bragg angle, but do exist when three or more beams are involved.

(2) In discussing Umweg reflections which may occur when strong reflections are monitored, the statement is made that 'in the experimental part of this work, no effect whatsoever (within 1%) was found in reflections such as 400 with Co $K\alpha$ radiation in germanium'.

We have recorded many such charts in our laboratory with perfect silicon, germanium and gallium arsenide specimens. In Fig. 2, we show partly indexed 400 Umweg charts for germanium, obtained using Cu $K\alpha_1$ and Co $K\alpha_1$.

The failure of the author to observe Umweg peaks for 400 was undoubtedly due to the use of an incident beam with 30′ of vertical divergence. A large bandpass, such as is made available when the vertical divergence is so large, has little effect on the visibility of Umweg peaks when *weak* reflections are monitored, though it does result in significant peak broadening. When *strong* reflections are monitored, considerable background is trans-

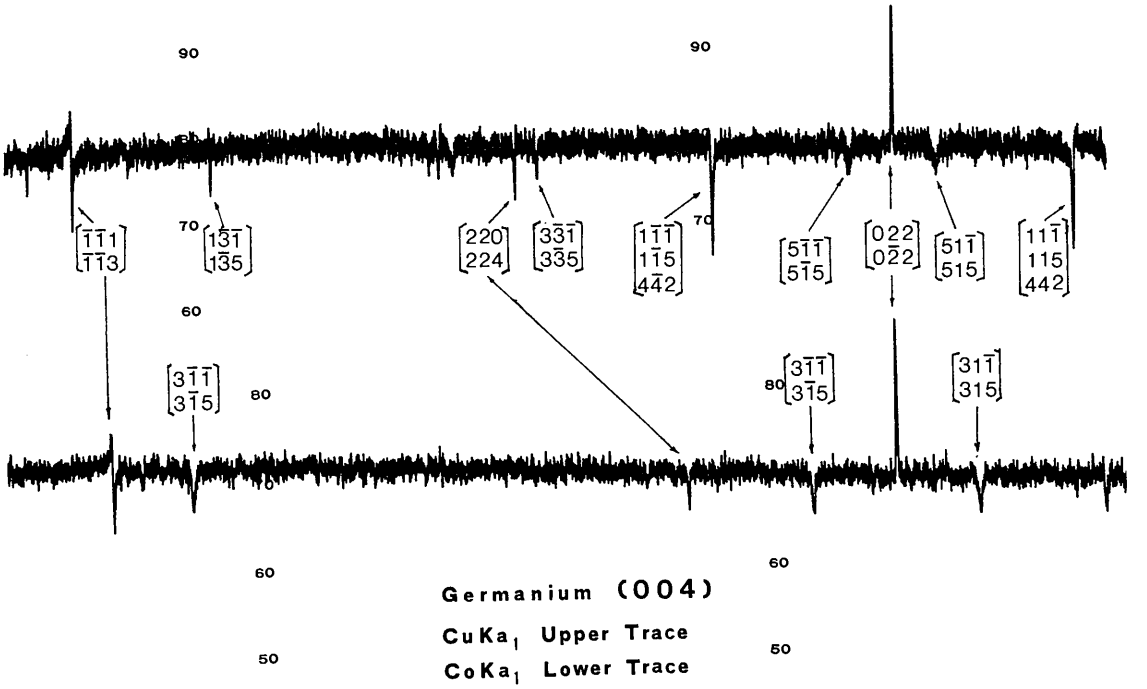

Fig. 2. Umweg patterns of germanium 004.

mitted through the large bandpass; this tends to overwhelm the effects of the very sharp Umweg peaks. To record the patterns in Fig. 2, we therefore used an incident beam with a divergence of less than 2′ of arc in any direction.

(3) On page 421 the 'effects of lattice imperfections' are discussed. The (222) surface of the germanium crystal was subjected to severe grinding by the author. This resulted in an eightfold increase in the 113/222 diffracted intensity, compared to a twofold increase for the ratio 113/$\bar{1}\bar{1}3$. We are then informed that 'this shows that the *ratio* between Umweganregung peaks is much less sensitive to lattice imperfections than the peaks themselves'.

It is surprising to find so sweeping a generalization, based on only one bit of evidence, published in a scientific journal. There may, of course, be additional evidence somewhere to support the generalization but it is neither cited nor alluded to in the published paper.

Also the author speaks of '*the ratio* between Umweg peaks' when he should in fact speak of the *ratios*. The two ratios (between two peak intensities) are, in general, different from one another, and they do not necessarily support the same conclusion.

At best the point made in the quoted statement and in the entire paragraph preceding the quote is either trivial or incorrect. Consider two peaks with initial intensities A_0 and B_0, which change on grinding to $A=\alpha A_0$ and $B=\beta B_0$. The ratio, $R=A/B=\alpha A_0/\beta B_0$. The case discussed by the author is one where $\alpha > R$. It is not, however, necessarily true that α will always exceed R; it may be equal to or less than R depending on the relative magnitudes of α, β, A_0 and B_0. For example, if β equals 1 (*i.e.*, B_0 remains constant) the change in A will equal, not exceed, the ratio A/B. Other physically reasonable cases can be readily generated. If we focus on $R'=B/A$, we find that, even when α is greater than R, β may be smaller than R', and the author's generalization again does not hold.

Incidentally, no mention is made in the paper of the fact that (113) is inclined by less than 30° to (222) compared to 80° for ($\bar{1}\bar{1}3$). That might have helped explain why the grinding of the (222) surface affected 113 more than $\bar{1}\bar{1}3$.

(4) Major emphasis is placed throughout on the definition of the integrated intensity of an *n*-beam reflection. We are repeatedly informed that such an intensity is determined by means of a double integration over the two relevant angles, θ and φ. That seems rather obvious; it is difficult to conceive of a definition of an integrated intensity which does not involve integration over an area. To achieve satisfactory integration of the diffracted intensity in multiple diffraction it is only necessary that the divergence of the incident beam exceed the acceptance angle of the reflection, a condition which it is usually almost impossible to avoid. To record such an intensity it is then only necessary that the receiving aperture of the detector be larger than the diameter of the diffracted beam. No time-consuming scan over either θ or φ is needed. The recorded intensity will be integrated even if both the crystal and the counter remain stationary.

The tedious integration procedure described in the paper appears to have been imposed on the author, not by the intrinsic requirements of the experiment, but by the unusually large divergence of the incident beam and the measurement technique used. The double integration which was used involved separate θ scans across the reflection at 3·33′ intervals in φ. As might be expected, the measured halfwidth is about 25 minutes of arc, approximately equal in magnitude to the vertical divergence of the incident beam. The calculated halfwidth is only 22·8 *seconds* of arc.

(5) One last point: it is difficult to understand how the referees could have expected the reader to assess the validity of the numerous calculated results presented in the paper, when virtually no information is included concerning details of the calculation techniques employed by the author. Throughout the paper, calculated halfwidths and intensities are discussed without even a mention of 'modes of propagation', degrees of excitation of the various modes,

effects of polarization, absorption, or the variation of each of those quantities with deviation from the exact n-beam angle. Without detailed discussions of such quantities, the results must be accepted on faith.

It is hard to allocate blame where so many are deserving. Luckily, in this case there is enough for all.

References

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Acta Cryst. (1975). A**31**, 155

Reply to Post's comments on my paper *Multiple Diffraction of X-rays and the phase problem. Computational procedures and comparison with experiment.*

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It is shown that the errors in the paper by R. Colella [*Acta Cryst.* (1974). A**30**, 413–423] pointed out by B. Post [*Acta Cryst.* (1975). A**31**, 153–155] do not in fact exist.

There is no doubt that the big difference observed between 222–113 and 222–$\bar{1}\bar{1}3$ is due in part to the fact that the dispersion equations in the two cases involve structure factors with different magnitudes, such as $F_{11\bar{1}}$ and $F_{33\bar{1}}$, for example.

It is also true, however, that a difference between the two cases would exist *even if the structure factors were all equal*, as it happens to a good approximation in neutron diffraction. One can easily verify this statement by examining the determinantal equation [equation (8) of my paper (Colella, 1974)] and observing that the diagonal terms are essentially different in the two cases.

It is obvious that two reflections with different phases correspond to different Miller indices and therefore to different nodes in reciprocal space. The 'coupling terms' [in Post's (1975) notation] are bound to be different in any case. The intensity differences are affected by the atomic positions, besides the coupling terms. In this respect multiple diffraction can in principle solve the phase problem. The key point is that in dynamical multiple diffraction more than two beams are coherently interacting and the phases do not get lost, as it happens in two-beam diffraction without anomalous dispersion.

Ewald & Héno's (1968) treatment, quoted in the references of my paper, is essentially concerned with the Laue case and considers $2n$ solutions. As explained in my paper, the transition to the Bragg case is not a trivial one, and $4n$ solutions must be considered when some of the diffracted beams are parallel to the surface of the crystal. Substantial changes are involved in the boundary conditions.

My failure to observe Umweganregung effects on the 400 with Co $K\alpha$ was in fact due to a large vertical divergence (of the order of 1°). Since these are the conditions in which most of the crystallographic work is done, I felt that it would be of some interest to develop a procedure for predicting whether not Umweganregung effects might be present in given experimental conditions.

As to my statement concerning the ratio (or ratios?) between Umweganregung peaks, it is neither trivial nor incorrect. It is only limited to one particular experiment and its main value is to stimulate further research in this area. That the Umweganregung peaks generally increase upon grinding is a rather obvious result and had been previously reported (Colella & Merlini, 1966).

I do not understand the statement about the different angles formed by the (113) and ($\bar{1}\bar{1}3$) planes with (222) in relation to the effects produced by grinding, and I believe that it is not justified.

The other points of Post's paper seem to me irrelevant or inconsequential.

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Schottky defects in KI and RbI.

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The temperature dependence of the thermal expansion of KI and RbI at high temperatures is shown to be related to the concentration of thermally generated Schottky defects. The experimental value of the energy of formation of these defects for RbI has been estimated for the first time. The two halides are found to obey the 'law of corresponding states' established by Pathak & Vasavada [*Acta Cryst.* (1970). A**26**, 655–658].

Introduction

The experimental value of the energy of Schottky-pair formation for KI has been determined by Ecklin, Nadler & Rossel (1964). A similar value for RbI is not available in the literature. Theoretical attempts to estimate these values have been made by Boswarva & Lidiard (1967), Rao & Rao (1968) and others.