Letter to the Editor

Towards Improved Alignment of Powder Diffractometers: A Comment

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Ideally, all X-ray diffractionists would wish that their goniometers be perfectly aligned. This requires calibration at low angles, which makes high demands upon the accuracy of the goniometer construction. The necessity of improving alignment is well discussed by Schreiner (1986), who stated that indications of ". . . substantial alignment errors are frequently found in even the most respected diffraction laboratories . . .". We fully endorse his view. Schreiner (1986) described a new method for the alignment of a Philips powder diffractometer equipped with a theta-compensating divergence slit. He claimed that this method provides excellent data down to 1°2θ or less. Schreiner's alignment method certainly is an improvement compared to previous methods. His data demonstrate, however, that the method is only of limited use, owing to imperfect construction of the slit.

The theta-compensating divergence slit is a horizontal cylinder with two openings, on the front side and the back. It controls the height of the incident X-ray beam by rotation. The slit should permit irradiation of a 12 mm long rectangle of the sample at all angles >0°2θ. At very low angles, however, because of the virtual height of the focus of the X-ray tube, the X-ray beam will not only strike the sample and the sample support, but some radiation will pass directly to the detector. The recording of this incident beam, up to 0.3°2θ, has different intensitites in Schreiner's Figures 4a and 4b, which indicates the occurrence of backlash. This backlash of the slit rotation can obstruct accurate alignment of the goniometer.

There are indeed indications of inaccurate alignment in the data. The interference of the incident beam stops at 0.3°2θ (Figure 4a) or is absent. In our own laboratory, we find that the interference always stops at 0.82°2θ when we apply the same conditions (12 mm irradiated sample length and a 0.2 mm receiving slit). Our goniometer is equipped with a self-developed theta-compensating divergence slit and a long fine focus Co X-ray tube. Apparently in Schreiner's set up the rotating slit was aligned on the upper side of the focus.

Another indication is the flexure at about 7.5°2θ in the path of the background intensity of Figure 4a. It is our experience that the background intensity gradually decreases from 0.82 to about 8°2θ, mainly due to the Lorentz polarization factor, and gradually increases to higher angles, mainly due to an increase of the irradiated sample volume. The peak positions of the Pb-myristate calibration sample deviate considerably (0.04–0.05°2θ) from the theoretical positions. Below about 10°2θ, the deviation increases to 0.08°2θ.

Schreiner introduced an extra source of errors by the application of different generator settings during the alignment procedure and measurements (25 kV and 0.1 mA to 45 kV and 40 mA). This causes displacements of the focus due to thermal expansion of the tube and the tube shield. Alignment and recording should be carried out at fixed ratings. If the diffracted beams are too strong for the detector, the latter can be protected by putting a filter at a suitable place, e.g. in front of the receiving slit.

An unusual peak, measured at 0.4°–0.5°2θ on the calibration sample (Figure 4b), was attributed by Schreiner to a combination of (1) backlash of the slit, (2) inaccurate centering of the X-ray beam on the 2θ axis, and (3) occultation of the beam by the edge of the sample support. These suggestions, however, cannot be true for the following reasons.

(1) According to our experience with the Philips theta-compensating slit, the backlash could not resist a goniometer movement of about 0.5°2θ, because the cog belt of the slit would certainly break or pull away the goniometer. The data in the Tables 1 and 2 show that this did not happen. (2) If inaccurate centering was responsable for the peak, then this peak should represent the incident beam and, consequently, the measured values would have been 0.4–0.5°2θ too high, instead of the reported 0.04–0.08°2θ (Table 1). Moreover, the incident beam is much too strong to have produced this peak. (3) A sample displacement of 700 μm is required to cause artificial peaks by occultation (van der Gaast and Jansen, 1985). We do not believe that Schreiner has misaligned his goniometer to such a degree.

Most probably, the peak was caused by total reflection of the incident beam from the smooth surface of the sample (James, 1948). Because the refractive index of Pb-myristate is close to that of glass (Philips Nederland, Almelo, 1981, personal communication), this is also true for the position of the total-reflection peaks of the two materials. Total reflection from a smooth glass surface occurs at 0.47–0.50–2θ (Lely and van Rijssel, 1949; van der Gaast and Vaars, unpublished results). There is no total reflection peak in the pattern of the quartz reference sample (Figure 4a) because it consists of novaculite, a polycrystalline quartz. Grinding of the novaculite will never yield a sufficient smooth surface.

The application of a theta-compensating divergence slit is a useful approach towards attaining substantial improvement of XRD measurements, particularly at low angles. Schreiner's slit, however, demonstrates imperfections, which obstruct accurate alignment of the gonimoeter, and, therefore, will yield irreproducible data. Consequently, one cannot presently assess the utility of Schreiner's alignment procedure in itself.

The construction of an accurately rotating divergence slit is an intricate technical problem. Moreover, rotating slits always have the disadvantage that the center of the irradiated area creeps away from the θ-axis. To avoid these problems, we developed a divergence slit equipped with a vertically moving upper and lower bar which are independently steered. The bars are motor-driven and computer-controlled, and permit irradiation of exactly the same portion of the sample at different angles. Thus, the goniometer is aligned very accurately; the peak positions of calibration samples are always within $0.01°2\theta$ of the theoretical values. A publication, offering a detailed description of the slit system and the attained results is in preparation.

Acknowledgement

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Author Response to the Comments of S. J. vd Gaast, A. J. Vaars and J. H. F. Jansen

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I am glad to see stimulating discussions arising from the publication of the diffractometer alignment methods we use in our laboratory, not only from v.d. Gaast *et al.,* who point out certain limitations and difficulties, but also by private communication from other workers who have employed our method in their laboratories. Surely these exchanges serve to increase general awareness of the alignment problem and to characterize the limits of performance one might reasonably expect from existing commercial equipment.

With respect to the comments of v.d. Gaast *et al.,* I make the following observations:

The commercial theta compensating slit we use does indeed have mechanical limitations which become apparent at low angles, and the minimization of these effects was one of the main reasons we developed the alignment procedures. It should be noted that the original slit design did not include as its primary objective routine work below 1–$2°2\theta$.

Backlash in our slit system does not arise in the cog or belt drive, but rather from the substantial clearance between the rotating slit cylinder and its housing. This clearance permits the cylinder to seat above or below its centerline depending on the direction of rotation of the drive. This is why the alignment procedure calls for "good tension" on the belt. Even with this tension, the cylinder can be moved by hand within its housing and cause a change in the slit aperture or its position and this appears equivalent to a 0.2–$0.3°2\theta$ backlash (or 0.1–0.15–θ). We find that a light coating of thin oil tends to minimize this tendency.

The earlier rise in intensity for the Pb myristate ($\approx 0.5°2\theta$, Figure 4b) compared to the quartz ($\approx 0.3°2\theta$, Figure 4a), is most probably due to total reflection as v.d. Gaast *et al.* suggest. However, total reflection alone should not result in a *peak,* as the reflection coefficient increases monotonically below the critical angle due to absorption. Because our slit backlash is not entirely reproducible, however, we have not attempted a detailed assessment of the diffractogram below about $0.5°2\theta$.

A new slit system of the v.d. Gaast *et al.* design could potentially avoid the difficulties we observe with our commercial slit system. Indeed, we have designed and built a digitally programmable slit system for another instrument in our laboratory in order to permit greater control than is possible with the commercial unit. However, the objective of the article was to allow users of existing equipment to derive maximum benefit from it without redesigning it. The ability to work below $1°2\theta$ is of limited value in routine powder work, but would be great value in the characterization of new large d-spacing multilayer structures where flatness and compaction of the study sample are not a problem. These structures are becoming of great interest with the development of such materials fabrication techniques as MBE, etc.

With respect to interpreting the peak positions obtained from the Pb myristate, one must proceed with caution. First, the "theoretical" peak locations given in Table 1 are for an arbitrary d-spacing of 40.20 Å. The true d-value is not known precisely, so the $\Delta 2\theta$ values should not necessarily be interpreted as misalignment. Second, the sample, for all practical purposes is a single crystal and not a powder. Hence, the entire illuminated arc does not contribute to diffraction. Rather only a narrow strip diffracts, the location of which depends on the exact setting of the θ-shaft. Third, the θ-shaft has a 0.02–$0.04°$ backlash in its coupling to the 2θ shaft. This is quite acceptable for powder work due to the focussing geometry, but can be a source of error when the sample is a single crystal. Fourth, as v.d. Gaast *et al.* point out, the thermal expansion of the tube and shield cause a shift in the 2θ zero angle. The shift on our system is known to be about $0.03°2\theta$ over a 2 hour warm-up period. The use of attenuators as v.d. Gaast *et al.* suggest would avoid this offset; however, the method is not entirely without its own set of complications, such as fluorescence, scatter, changes in the spectral distribution, etc.

For these and other reasons we do not reset the zero angle based on the absolute peak positions of the Pb myristate. Rather we consider the peak location of the (101) quartz line to be a more accurate indicator of 2θ zero angle offset. This peak should occur at $26.66°2\theta$ (α). In the article this peak was observed, to be at $26.63°2\theta$, approximately $0.03°$ low, as expected from thermal expansion. Another reason that we do not reset the zero angle, is because our software automatically applies an external calibration correction to remove this offset (as well as other linear and nonlinear angular dependencies). Furthermore, it would not make sense to reset the zero due to continually varying thermal conditions in our laboratory. When the most accurate d-values are desired and use of an internal standard is inappropriate, we will re-measure and re-establish the calibration curve immediately prior to the run in question. While the ideal situation would call for more precise thermal stabilization, I believe ours is not atypical of most laboratories, and therefore this procedure is of general interest.

v.d. Gaast *et al.* touched on one point which has long been of interest to us — the flexure of the background at about 7°2θ in the quartz (Figure 4a). We have observed this effect in many but not all prepared samples (for example, the effect is absent in Figure 4b for the Pb myristate). The origin of the decrease in the background between 7 and 2°2θ is not understood. The most likely cause we have identified to date is that surface roughness occults scattered background rays at angles below the average surface angle. This is at least consistent with SEM images of the surface of the quartz reference standard we use. However, many other factors surely play a role as well. For example, the Compton scatter contribution to the background decreases with angle, as does TDS below the largest d-spacing in the material. Some background also originates from air and slit scatter, detector noise, specimen fluorescence, anomalous scatter, and plasmon scatter. Some of these contributions are affected by the Lorentz polarization factor while others are not. In general the makeup of the background is a complex problem, and the nature of its angular dependence at small angles and in the presence of sample surface roughness is not clear.

Computer Comments

Powder Diffraction provides this column as a service to its readers and as such, cannot be held liable for the success or failure of program software or system hardware described here. The editors reserve the right to determine the suitability of any contribution for inclusion. While this column is part of the Departments Section, it is compiled and edited by:

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Compatible

Compatibility seems to be the pervasive topic of personal computer users. Not only are we concerned that the peripheral hardware variations must be accommodated, as discussed in previous Comments, but now O.D. Jefimenko in a letter to BYTE[1] provides another gem for thought. It seems that computer compatibility may be a one-way affair. The "compatibles" are designed to execute machine language programs created for the IBM-PC*, -XT*, and -AT* on the IBMs. But one often finds that neither the IBMs nor the compatibles can execute (or often even read) machine language programs created on a different machine. Thus Jefimenko admonishes the program developer creating software by using a compatible computer to verify that the intended compatible is in fact "two-way compatible".

With the increased availability of AT clones[2] providing a very favorable price/performance, one expects more program development will follow using non IBM systems. On the other hand, recent court rulings may elicit a moderating response if, as David Bunnell suggests[3], protectionism abounds in '87. It is mid-November (following a period of record setting cold temperatures) when I am writing these words. My crystal ball does not provide the foresight to know how things will be shaping up as you read this so I will not pursue the topic further.

1. Jefimenko, O.D., "Compatibility — A One-Way Street", *Byte,* 1986, 11(12) 24.
2. Knorr, Eric, "An AT by Any Other Name", *PC World,* 1986, 4(12) 232–45.
3. Bunnell, David, "Fighting PC Protectionism", *PC World,* 1986, 4(12) 17–26.

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For the past two years we have coordinated a Tutorial Workshop, DISK, DOS, COMPUTE stressing the first two steps to using the personal computer in addressing problems of interest to powder diffractionists. Now that you have progressed to COMPUTing, would you help me in the design of a Workshop which will meet your needs. Specifically I am asking YOU to send a postcard identifying a topic you, your colleagues and/or students would find sufficiently compelling to induce your attendance. But even though we may not be in a position to incorporate all topics in a workshop presentation, be assured that the suggested topics will be used to advance this column in directions concomitant with your interests.

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