New Optical Devices for Major Advances in X-ray Diffraction

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One of the most fascinating developments in the field of X-ray diffraction has been driven by the general availability of a broad range of optical devices for X-rays. It has become difficult to select a suitable device for a particular application even for experts in the field. There are mono- and polycapillaries which may be shaped in specific ways as one large group, and mirrors which mainly represent a large variety of artificial crystals as multilayered structures, i.e. multilayer optics. While these types of devices have become more generally available within the last decade, monochromators based on well-defined single crystals have already been in use for a long time. Nevertheless, there are still options for further improvements in order to enhance the quality or to open new experimental opportunities. In this contribution own efforts to apply multilayer-based mirrors or single-crystal monochromators with rather high-energetic X-rays will be described, and even a combination of both types of devices has been configured.

The main goal was to achieve 'better' diffraction data at high diffraction angles but with a generally available laboratory instrument. In order to reach high resolution (large $sin\theta/\lambda$) it is necessary to use short wavelength (high-energetic) X-rays. Commonly available are molybdenum or silver targets, where molybdenum is more generally used while a silver source better suits our particular needs, e.g. absorption and extinction problems with intermetallic compounds. Tab. 1 compiles selected parameters for the most intense of the characteristic X-ray emission lines for molybdenum and silver.

Table 1: Characteristic X-ray emission lines of molybdenum and silver.

		$K\alpha_2$	$K\alpha_1$	$K\beta_3$	$K\beta_1$	$K\beta_2$
Mo	E [keV]	17.374	17.479	19.590	19.608	19.965
	λ [Å]	0.7136	0.7093	0.6329	0.6323	0.6210
	$I_{rel.}$	52	100	8	15	3
Ag	E [keV]	21.990	22.163	24.912	24.942	25.456
	λ [Å]	0.5638	0.5594	0.4977	0.4971	0.4870
	$I_{rel.}$	53	100	9	16	4

Despite the relatively small difference in wavelength, silver radiation allows to collect data to much higher resolution and thus collect much more data as compared to molybdenum radiation (Tab. 2). For a number of reasons it was desirable to use a single wavelength beam. The elimination of overlapping problems are most important when the dispersion of $K\alpha_1$ and $K\alpha_2$ becomes significant, along with related problems with integration of intensities. The actual intensity ratio of $K\alpha_1$ to $K\alpha_2$ is easily changed in quite a wide range, however, this fact is very rarely taken into account. Based on the values compiled in Tab. 2 few options were evaluated. The most intense $K\alpha$ line consists of two quite narrow contributions, $K\alpha_1$ and $K\alpha_2$, at an intensity ratio of about 2 : 1. In addition the X-ray target provides $K\beta$ contributions at slightly higher energies. For silver as well as molybdenum the '$K\beta$ line' contains three distinct contributions, where $K\beta_1$ and $K\beta_3$ are very close in energy, while $K\beta_2$ is more separated from the former two. Intensity of $K\beta_1$ and $K\beta_3$ together is about 20% of $K\alpha_1$ while $K\beta_2$ is only 10% as compared to the main $K\beta$ contribution. This typical intensity distribution is the reason why $K\alpha$ radiation is almost exclusively used in diffraction experiments. When it comes to true monochromatization the situation is not so clear any more. Typical crystal monochromators using the Ge(111) reflection do not allow to completely separate $K\alpha_1$ from $K\alpha_2$ for molybdenum, not to mention silver radiation. In order to leave any usable intensity, about 10% of $K\alpha_2$ are retained. Obviously, monochromatization is only possible at the expense of loosing most of the

Table 2: Comparison of selected angular ranges and respective resolution limits for Mo Kα and Ag Kα radiation. 2θ = 150 – 160° is the technically achievable limit.

Mo $K\alpha$						
2θ [°]	55	100	153			
$sin\theta/\lambda$ [Å^{-1}]	0.65	1.08	1.37			
d [Å]	0.77	0.46	0.37			
Ag $K\alpha$						
2θ [°]	42.8	74.6	100	120	138	150
$sin\theta/\lambda$ [Å^{-1}]	0.65	1.08	1.37	1.54	1.67	1.72
d [Å]	0.77	0.46	0.37	0.32	0.30	0.29

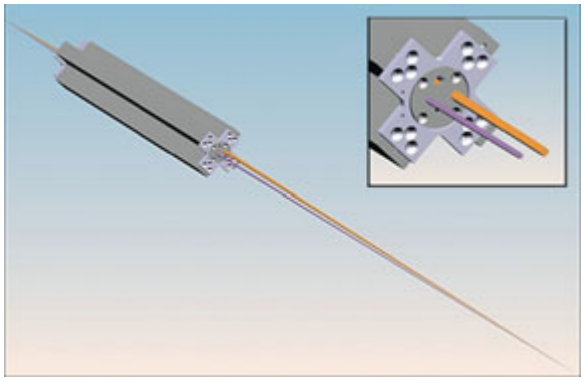

Fig. 1: Multilayer optics for Ag *Kα (orange) and* Ag *Kβ (violet) radiation. Four mirrors are arranged side by side, one pair is optimized for one particular wavelength each. Insert shows both beams leaving the optics; an additional aperture allows for particular selection.*

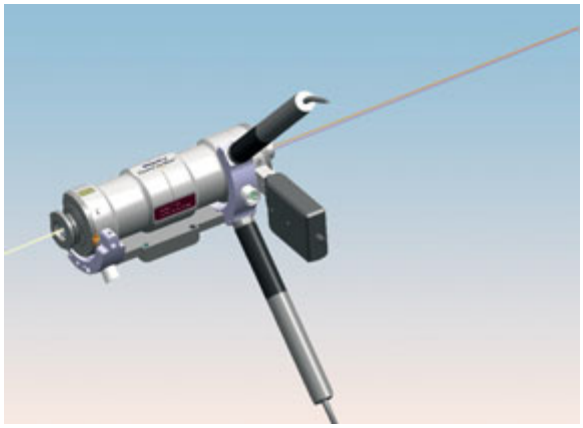

Fig. 2: Assembled mirrors in housing. The two rod-like motors allow for precise alignment, the motor in rectangular box drives aperture for wavelength selection.

available intensity. In case it would be possible to use a device which retains most of the available *Kβ* intensity, a setup such as this could provide a monochromatic beam with reasonable intensity. Based on these ideas various options were carefully evaluated, however, efforts quite soon focused on multilayer-based mirrors. Although such mirrors were already commonly in use with longer wavelength radiation, there was very little experience in particular with silver radiation. The short wavelength with the associated very small total reflection angle puts very high demand on the fabrication of the multilayer. In close cooperation with *Rigaku Innovative Technologies*, née *Osmic*, a mirror setup for Ag *Kα* radiation was designed and fabricated. In connection with the small focus (100 μm) of a rotating anode source the setup provided a very well defined beam which gave exceptionally good data with single-crystal diffraction. As expected there was still room for further improvements, a main one came from the fact that the alignment of the optics needs to be done at the level of one tens of a micron. This could not be reached with mechanical set screws which had to be replaced by specific motor-driven devices. After this modified setup had proven excellent long-term stability, a mirror setup for Ag *Kβ* radiation was designed. Here the close interplay of experimental experience with real devices and high-level modeling on the other side turned out to be most important. In the final device mirror setups for *Kα* and *Kβ* contributions are mounted in the same housing (Fig. 1). After careful alignment the particular wavelength is selected by moving the front aperture to the proper position (Fig. 2).

First experiments indicate further improvements of the *Kα* setup with respect to the prototype. Clearly, the *Kα* arrangement may be considered as high-intensity option while the *Kβ* part offers high resolution. As the development of this truly new optical device was purely experimental indeed, additional experiments were driven towards improvement of single crystal monochromators. Using the Ge(220) reflection in a *Johansson*-type setup allows clear separation of $K\alpha_1$ and $K\alpha_2$ for molybdenum but even for silver radiation. The basic setup is well established in X-ray powder diffraction, however, for single crystal experiments the line-shaped beam as obtained is not usable. Since cutting down the beam by a slit system largely reduces intensity, a dedicated single-bounce mirror was designed in cooperation with *AXO Dresden GmbH*. In this setup again all mechanical tools needed for alignment have to be upgraded in order to reach the necessary precision more easily.

Thus far, for both basic monochromating arrangements usable devices have been reached. A careful evaluation will display which design is best suited for any particular experiment.

Especially the rotating anode – multilayer setup has allowed to collect high-quality data sets for a decisive number of crystals and to tackle some very demanding problems. In general terms one major advantage comes from the fact that data with very high resolution (large diffraction angles) are obtained (Fig. 3). While in general ten observations per refined structural parameter are considered adequate (see requirements for IUCr journals), data sets providing around 100 observations per parameter have routinely been obtained (compare Tab. 3). An

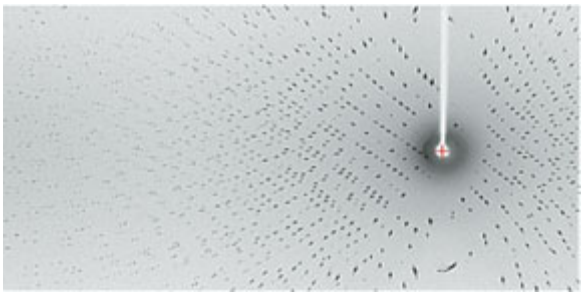

Fig. 3: Typical diffraction image obtained with a single crystal applying Ag *Kα radiation after multilayer optics. Clear Bragg peaks are still observable at 2θ ≈ 155° to the left.*

improvement by one order of magnitude may certainly be considered most significant. In course of particular structure refinements the increased number of observed structure factors has a number of advantages. Firstly, correlations are considerably reduced or even become negligible, which is always very important when partial or mixed occupancies, disorder or pseudo-symmetry are involved. For highly symmetric structures along with quite small unit cells the number of observable intensities is notoriously small. Most structures studied at the institute belong to this category. Finally, at high resolution diffraction intensities are originating from scattering at the core electrons of the atoms. Accordingly there is no influence from the particular bonding situation and these intensities are very characteristic for the particular atoms. On this basis high-resolution data allow to distinguish more clearly atom types, but also to provide the basis for detailed charge density studies. Following, a number of examples show the wide applicability and usefulness of the instrument.

Table 3: Skutterudite-type compounds.
Cubic, a ≈ 9.5 Å, no. refined parameters ≤ 27.

compound	$d_{min.}$[Å]	no. refl.	ind. refl.	$R_{int.}$[%]
$BaPd_4Sb_6Sn_6$	0.32	15078	2413	2.58
$BaPt_4Sb_6Sn_6$	0.30	12274	2869	4.28
$SrPt_4Sb_6Sn_6$	0.30	12139	2875	2.34
$CaPt_4Sb_{5.5}Sn_{6.5}$	0.30	11036	2862	3.11
$LaPt_4Sb_6Sn_6$	0.30	12477	2846	2.46
$CePt_4Sb_6Sn_6$	0.32	10904	2381	3.54
$PrPt_4Sb_6Sn_6$	0.32	9914	2383	2.11
$SmPt_4Sb_6Sn_6$	0.30	12462	2851	4.56
$EuPt_4Sb_6Sn_6$	0.32	21802	2383	3.26
$YbPt_4Sb_{5.5}Sn_{6.5}$	0.30	13160	2838	2.90
$YbCoPt_3Sb_6Sn_6$	0.31	10289	2560	2.60
$SnPt_4Sb_{5.5}Sn_{6.5}$ [1]	0.32	9685	2385	2.16

It was possible to prove that human otoconia are true single crystals (see "*Biomimetic Morphogenesis and Structure of Calcite Statoliths (Otoconia): An Approach towards Deeper Understanding of a Bio-Sensor and its Function*"). Due to the highly brilliant beam proper intensities are obtained for these very small crystals (5 – 10 μm). This is even more remarkable as the calcite material contains only light elements which are interacting only very weakly with the quite hard radiation. The successful structure refinement confirmed absence of twinning, which is quite common in rhombohedral structures.

For a series of digallides composition dependent changes of the structure could be studied in more detail. Partial occupancies at cationic sites along with the development of additional structural features were analyzed to high resolution and combined with solid-state NMR experiments (see "*Quadrupole Coupling – the Key to NMR Spectroscopy of Intermetallic Compounds*", [2]).

The complex intermetallic compound Co_4Al_{13} was reinvestigated. Vastly improved data quality facilitated a much more accurate structural model along with a detailed bonding analysis (see "*Shift of Paradigms in Understanding of Intermetallic Compounds by Analysis of Chemical Bonding within the Electron Localizability Approach*").

In a series of Skutterudite-type compounds high-resolution data have provided the basis for detailed analysis of mixed occupancies and disorder. Given suitable crystal quality high-quality data were obtained in all cases (Tab. 3). Short wavelength along with small crystal size made treatment of absorption effects quite easy, despite rather high absorption coefficients due to heavy elements forming the compounds [1, 3].

Various clathrate-type compounds have successfully been investigated. Mixed occupancies at distinct levels (Si/P or Si/B) have been resolved, but also partial occupancies sometimes including vacancies (see "*Intermetallic Clathrates Revisited*" and [4, 5]). However, it also became clear that crystal quality is still an issue, as expected. As quality of clathrate crystals is notoriously quite low, in few cases not all structural details could be analyzed due to data limitations.

Within a Special Priority Program of DFG (SPP 1178) charge density analyses of vanadium borides have been tackled. These experiments are most demanding as quite contrary criteria need to be satisfied. Since crystals of these hard materials are notoriously suffering from extinction effects, crystals should be very small. On the other hand data of the highest quality may not be obtained for exceedingly small crystals. Accordingly a lot of optimization needed and still needs to be done. Nevertheless, first results on both compounds VB and VB_2 are most promising. Clearly all enhancements reached in this most demanding field will be beneficial in most other experiments, too.

The highly brilliant and well defined beam allows for an exceptionally good signal-to-noise ratio and low background, too. This way the setup is very well suited to study phenomena where very strong and weak intensities need to be simultaneously observed. Along this line, superstructures, modulated structures and diffuse scattering have been studied (Fig. 4).

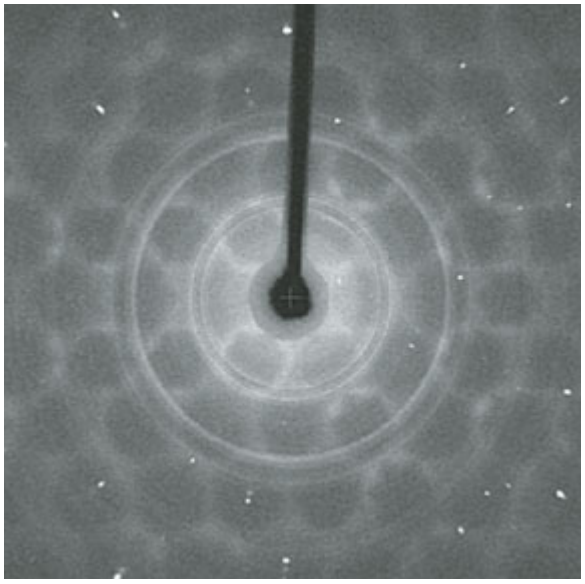

Fig. 4: Typical image obtained for a single crystal in the system Gd/B/Si. Very pronounced diffuse scattering is observed; special measures were taken to reduce intensity of sharp Bragg peaks.

The focus in this contribution until now has been solely on the conditioning of the primary beam. With respect to final data quality, of course, the detector system is also of particular importance. Details of the detector system, but also concerning goniometer and X-ray source are not within the scope of this article. Clearly all components of the experimental setup need to match in a perfect way, in order to achieve best possible results. The development of the beam conditioning system has already and will trigger further development of the entire setup. Beyond such improvements of the hardware, further improvements in software are equally important. However, it is already obvious that the current status allows to consider even new experiments. Much higher resolution due to a single wavelength will allow to study even very small powder samples. The possibility to detect also entire powder rings will provide a large advantage over one-dimensional detectors commonly used in powder diffraction. Silver radiation is well suited to investigate the pair-distribution-function (PDF) which is gaining importance with respect to nano-materials or quasi-crystalline compounds.

In conclusion, integration of a dedicated X-ray optics enabled vast improvements with diffraction experiments on a laboratory setup. Dramatic increase in collected diffraction data allows for striking improvements in derived structural information, but also allows for a more detailed analysis of disorder, very small crystals, etc. Hence technological advances of basically a commercial device have induced new opportunities for basic research.

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