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A PILOT STUDY OF THE USE OF UNFOCUSSED MONOCHROMATIC RADIATION FROM A STORAGE RING IN POWDER DIFFRACTION(x)

P. Thompson, A.M. Glazer,
Clarendon Laboratory, Parks Road, Oxford OX1 3PU, U.K.
A. Albinati,
Istituto di Chimica del Politecnico di Milano, P.zza Leonardo da Vinci 32, 26133 Milano, Italy
and
J.S. Worgan
Science Research Council, Daresbury Laboratory, Warrington WA4 4AD, U.K.

ABSTRACT.

The results of a trial powder diffraction experiment on the ADONE storage ring at the Frascati National Laboratories are described. A (220) channel-cut Si crystal was used to provide a monochromatic beam and it was demonstrated that Debye-Scherrer photographs could be obtained in several hours. It was also shown that very high resolution can be obtained simply by increasing the camera dimensions. Finally it is shown that with the higher fluxes of the SRS at the Daresbury Laboratory very fast exposures will be possible without the need for focussing.

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1. - INTRODUCTION.

A number of recent publications (Phillips, Templeton, Templeton and Hodgson, 1978 ; Templeton, Templeton, Phillips and Hodgson, 1980 ; Glazer, Hidaka and Bordas, 1978) show that it is possible to perform crystallographic studies with X-rays produced by accelerating electrons in synchrotrons and storage rings. The white spectrum is smooth without characteristic lines superposed, and a single wavelength can be chosen by the insertion of a suitable monochromator. As well as being tuneable over a wide wavelength range (0.3-2.5 Å), X-rays generated by synchrotrons have high intensity and an extremely small natural divergence (less than 0.4 mrads) which for many experiments removes the need for collimation ; indeed, for most practical purposes the beam can be treated as parallel. These unique properties provide several advantages for powder diffraction, and suggest a fresh appraisal of earlier ideas largely abandoned because they met with only limited success on conventional sources. It is well known, for example, that increasing the radius of a Debye-Scherrer camera produces a gain in resolution (see for example, Bradley, Lipson and Petch, 1941). However, with conventional X-rays the strong divergence of the beam means that high resolution can only be achieved by narrow collimation at the expense of intensity, resulting in time-consuming experiments.

In this paper we show that a synchrotron beam, even after monochromatisation, provides enough intensity for powder diffraction and its almost parallel nature allows one to obtain very high resolution. This will make powder diffraction on synchrotrons an important technique, not just for lattice parameter measurements, but particularly for structure refinement, either by the Rietveld (1969) method or by direct integrated intensity measurements.

There is, however, some confusion about the available fluxes from synchrotron sources because of the way in which the tables and graphs provided are drawn up and this can mislead those intending to carry out experiments on such sources, especially with regard to exposure time. What is needed is a realistic assessment of typical exposure times in a practical example, and it is for this reason that we have carried out a pilot experiment on the ADONE storage ring at the Frascati National Laboratories. From this and by comparing the flux incident on a typical specimen with that projected for the SRS at the Daresbury Laboratory we suggest in this paper ways of reducing the exposure times of the experiments.

2. - EXPERIMENT.

Two sets of experiments were performed, one with a normal Debye-Scherrer camera of radius 57.3 mm and one with a larger, purpose-built camera of radius 239 mm. In both cases a sample of Al_2O_3 was packed in a 0.2 mm Lindemann glass capillary which was used to record the diffraction pattern on double-sided Kodirex 35 mm X-ray film. The large camera was filled with He gas to reduce air scattering and absorption. ADONE was running at 1.5 GeV and started at a beam current of 80 mA which dropped during the experiment to 30 mA and the 220 reflection of a channel-cut Si crystal (Beaumont and Hart, 1974) was used to provide a monochromatic beam of wavelength 1.5 Å.

Approximately 0.5 mm length of sample was illuminated by the beam and the camera each time was mounted perpendicular to the electron orbit plane as shown in Fig. 1. This experimental configuration was used in order to make the best possible use of the nearly plane-polarised (in the XY plane) synchrotron radiation. The sample was rotated about, Y, to minimise the effect of preferred orientation.

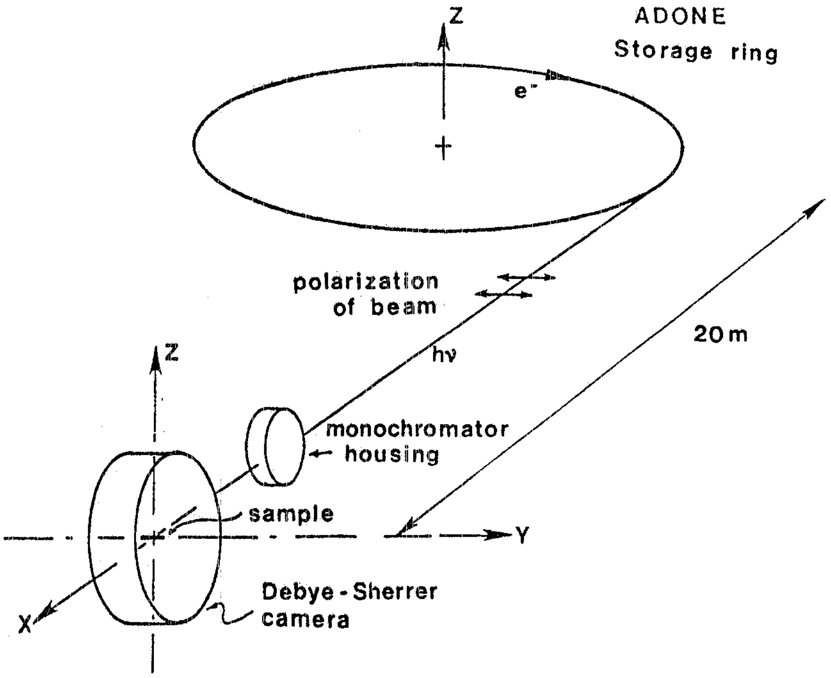

FIG. 1 - Diagram of experimental arrangement.

A reasonably intense diffraction pattern was obtained with the small camera in 9 hrs. The equivalent exposure in an ordinary X-ray laboratory on a 1 kW-rated Cu tube can be achieved in 1 hr, although this would contain both Kα_1 and Kα_2 radiation. With the larger camera, however, only three barely visible lines could be seen in 6 hrs. The lines were sharp, the same width, 0.2 mm (equivalent to the specimen width) as those seen on the small camera. This clearly demonstrates that the resolution ($\Delta d/d \sim 1.4 \times 10^{-3}$ at $2\theta = 100^o$) is increased by a factor corresponding to the increase in camera dimensions to a value of $\Delta d/d$ of 3.5×10^{-4} at $2\theta = 100^o$, comparable to the high-resolution time-of-flight powder spectrometer planned for neutron spallation sources.

3. - DISCUSSION.

To obtain an exposure with the above arrangement in which one could microdensitometer the profiles and interpret the integrated intensities would take much longer on ADONE, probably around 1 or 2 days. This may at first sight seem an inordinately long time to obtain a diffraction pattern. However, this seems a small penalty to pay for the increased resolution, when one bears in mind that a small side-port of a beam line providing a small portion (of roughly the sample dimensions) of normally unused beam, could be utilized. Indeed, a modified beam line is at the moment being planned for the ADONE source specifically for this purpose. It is then quite likely that long-exposure experiments of this type, where resolution is at a premium could become an important feature of future crystallographic investigations on synchrotrons.

Given the enormous fluxes produced by synchrotron sources it may be thought surprising that such long exposures are needed. The reason for this is first that after monochromatization, because the monochromator has such high resolution, only a narrow range of photon energies is passed and hence only a relatively small number of photons end up in the monochromatic beam. Using a mosaic monochromator, such as pyrolytic graphite, more energies are passed but with correspondingly less numbers of photons at each energy because of the almost parallel nature of the incident beam (with conventional sources it is the beam divergence, that allows graphite monochromators to be used with advantage). A gain in speed of about an order of magnitude can be obtained using a channel-cut Ge(111) crystal with the planes cut asymmetrically by 10° (Kohra, Ando, Matsushita and Hashizume, 1978). This increase in intensity arises from the increased wavelength bandpass ; however, the disadvantage of Ge over Si is in its absorption edge at 1.12 Å, below which the reflectivity drops drastically. The second problem is that because of the source size and small divergence at typical working distances from the source, say 20 m, the monochromatized beam measures a few square centimetres. Now, in X-ray diffraction, absorption depends exponentially on thickness and so with any cylindrical sample, as used in a Debye-Scherrer camera, one is confined to using a small specimen, typically 0.2×0.5 mm, thus intercepting only a fraction of the available beam. Such problems do not occur with other synchrotron experiments, such as EXAFS, where the whole beam and a large specimen is used. The most important factor is the actual flux incident on the sample and great care must be exercised when interpreting the flux graphs and tables normally supplied for synchrotron sources. In many cases these give photons/sec/mrads horizontal/mA in a 0.1 % bandwidth integrated over the vertical divergence.

As a result of the above experiment it is worthwhile to discuss and compare photon fluxes on other machines such as the SRS planned as a dedicated source for the Daresbury Laboratory.

Since in a typical synchrotron most of the intensity is contained within ±0.1-0.4 mrads (vertical) such a curve can be used for specimens whose vertical dimensions subtend an angle larger than this. When the dimensions are so small as to subtend angles of less than about 0.05 mrads (vertical) a better curve to use is one which plots peak photons/sec/mrads horizontal/mrads vertical/mA in a 0.1 % bandwidth in the electron orbital plane. A curve of this type is shown in Fig. 2 for the SRS at Daresbury, with and without a 4.5 T wiggler magnet.

However, for intermediate cases it is necessary to take into account also the angular distribution of flux in the vertical direction, since it falls off roughly as a Gaussian. Here the easiest method of estimating the flux is to use Fig. 2 together with a plot of full-width at half-height against wavelength (for example Fig. 3) and integrate the Gaussian function between the appropriate angular limits at the wavelength concerned.

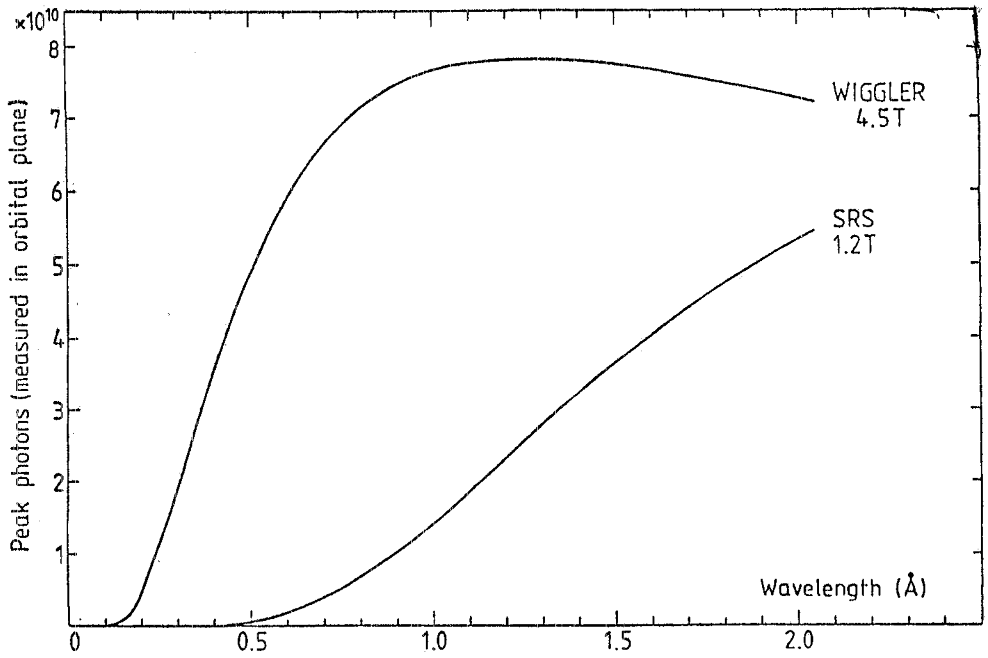

FIG. 2 - Plot of peak intensity (photons/sec/milli radian horizontal/milli radian vertical/mA beam in a 0.1% bandwidth) versus wavelength (Å) for 1.2 T, 2.0 GeV and 4.5 T, 2.0 GeV (wiggler).

It should be borne in mind that these graphs are calculated on the basis of the electron beam circulating on a single orbit and do not account for the finite extent of the source which will have some bearing on determinating photon fluxes incident on the specimen. It is not necessary to perform a detailed lengthy ray tracing analysis to establish this effect as simply qualitative arguments will suffice to give an idea of available fluxes. On the SRS the predicted source size is small in vertical dimensions, ~ 0.4 mm, and quite extended in the horizontal, ~ 14 mm. The vertical beam dimensions at 20 m and at a wavelength of 1.5 Å, will measure for a point source 5 mm on account of the natural opening angle $1/\gamma$, where $\gamma = E/m_0c^2$, the ratio of the electron energy to its rest mass energy, convolved with the electron divergence. For the extended source the

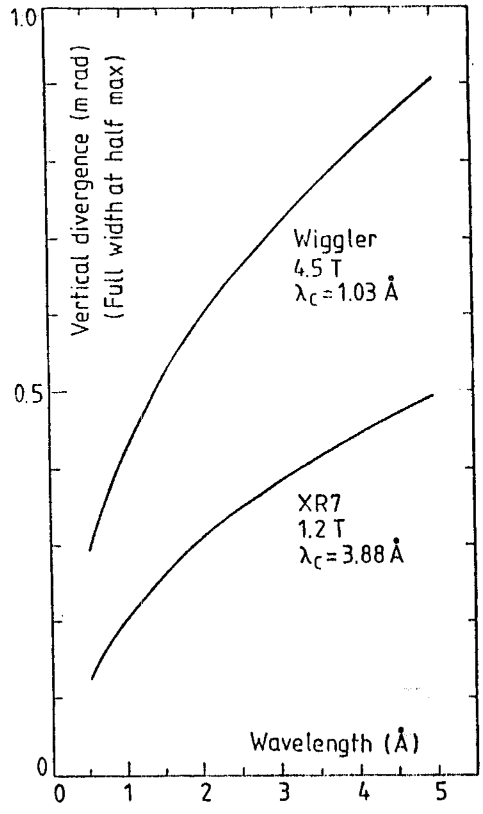

FIG. 3 - Plot of full-width at half-height of vertical distribution of radiation from the SRS (1.2 T, 2.0 GeV) and the wiggler (4.5 T, 2.0 GeV).

beam calculated to first order will measure 5.4 mm, and thus an approximate evaluation of the reduction in illumination on the monochromator due to this will be in the ratio of these lengths. In this case the reduction is 10 %. This varies, of course, with wavelength because the divergence of the radiation is smaller for shorter wavelengths (see Fig. 3), but it is never much worse than 20 % and can be regarded as negligible given the uncertainties in the as yet unestablished experimental performance of the SRS. In the horizontal the situation is quite different because the storage ring emits photons in a horizontal fan over the length of the bending magnets. The effect of the finite horizontal source is most easily visualised with reference to Fig. 4. In this digram we have exaggerated the source size in comparison with the specimen size, S, which subtends an angle ϕ radians given by S/D (D being the specimen-source distance), thus defining a length of arc PQ for a single electron orbit. This is commonly referred to as a point source and photons originating along the length of arc PQ will illuminate the specimen S with an intensity given by Figures 2 and 3 when the appropriate value of ϕ is used together with the vertical aperture. This intensity is smeared out over the horizontal source size (FWHM = σ_x) and would occupy an area abcd. The specimen, however, has a view of the source given by the area ABCD and since these two areas are equal there is no loss of illumination at S due to the finite extent of the horizontal source, providing any beam - defining slit is placed close to S.

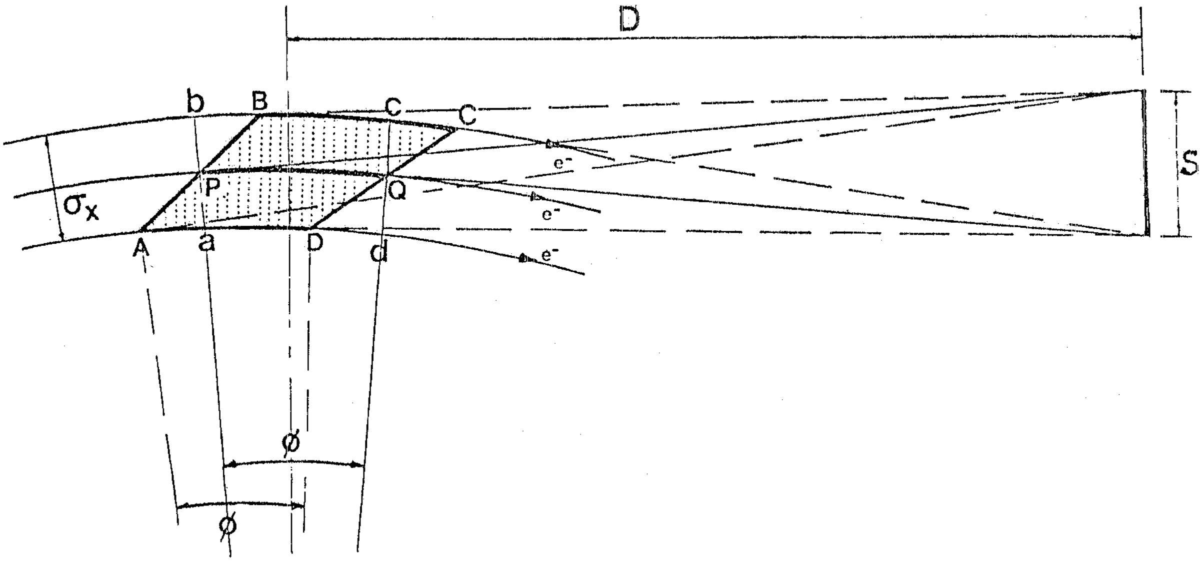

FIG. 4 - Diagram showing the finite extent of the horizontal source whose FWHM is σ_x. The sample S defines an arc PQ on a single electron orbit. The dashed lines are tangents drawn through S to represent extreme rays. The dotted area ABCD is the view of the source seen by S.

In the above analysis we have ignored the obliquity factors introduced by the rays coming to the specimen at different angles : because of the small angles involved these factors are close to unity.

The large horizontal source size becomes important when spatial resolution is required, as in X-ray topography and small-angle scattering experiments, where for the SRS collimation close to the source would results in a drastic reduction in intensity on the specimen. The effect of a vertically-dispersing monochromator is also irrelevant in the horizontal and only becomes important in the vertical if the source size subtends an angle (for the SRS 0.02 mrads at 20 m) on the monochromator which is greater than the glancing angles which the monochromator will pass. Even for Si (220) there is no reduction in intensity other than that due to the narrow wavelength band-pass. The photon fluxes calculated for a typical crystallographic specimen are given in Fig. 5 where the variation in intensity with wavelength is shown.

In Table I we compare estimated photon fluxes and corresponding exposure time, under a variety of experimental arrangements for the SRS, with our 9 hr test experiment with the standard camera on ADONE. As can be seen, very fast exposures will be possible especially by utilizing a long specimen. As shown in Table I we predict that our original 9 hr test experiment would be shortened to about 6 seconds by using a $0.2 \times 15\ \mathrm{mm}^2$ specimen on the SRS with wiggler.

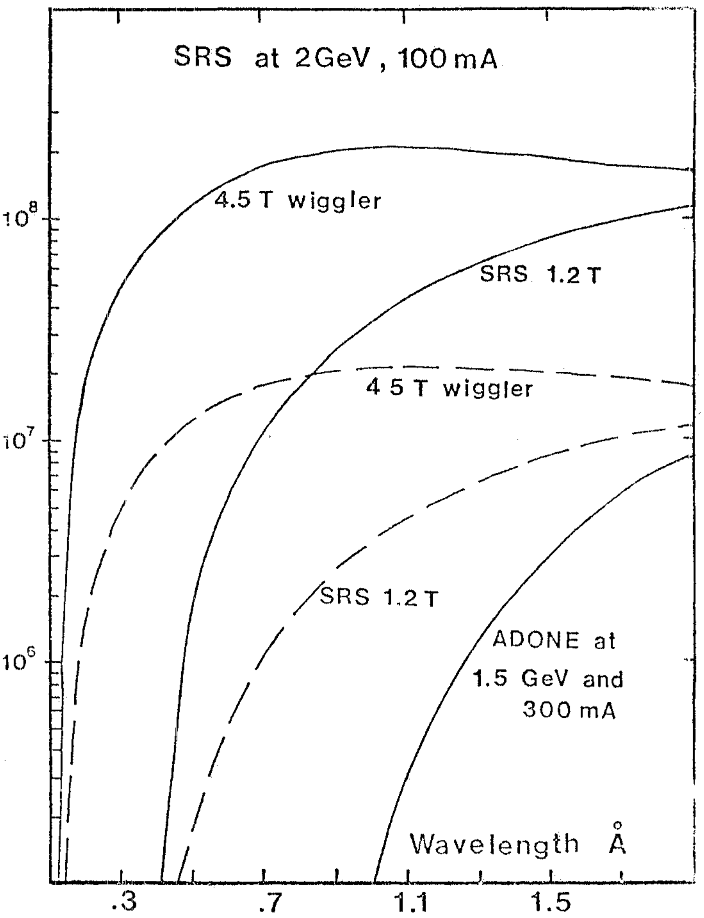

FIG. 5 - Plot of calculated photon flux incident on a sample 0.1 mm dia x 0.1 mm (dotted line) and 0.2 mm dia x 0.5 mm at 15 m from the source. The corresponding curve for ADONE is scaled up from measurement to the projected operating conditions of 1.5 GeV and 300 mA ; the sample is 0.2 mm x x 0.5 mm, at 15 m from the source, in order to have a direct comparison with the SRS.

It is worth noting that for a specimen of length, l, the angular spread is given by (Guinier, 1964),

$$\Delta\theta = \frac{d}{2R} + \frac{l^2}{16R^2} \cot 2\theta ,$$

where d is the specimen diamater and R the camera radius. Because of the loss in resolution caused by increasing the specimen length depends on $1/R^2$, whereas the effect of finite width depends on 1/R, the latter effect dominates so that a considerable increase in specimen length can be tolerated without loss of resolution in the equatorial region of the film, as demonstrated experimentally by Ievinš and Karlsons (1939).

Furthermore, the near parallel nature of the synchrotron beam means that one can use a camera of much larger radius than the standard size, because by using a long specimen it will then be possible to obtain acceptably short exposure times with little loss in resolution (ignoring line-broadening inherent in the sample itself). Hitherto this has not been possible because the large

TABLE I

a) ADONE (1.5 GeV, 100 mA)

Sample source distance (m)	20	20	20	15	20
Sample size dia (mm) x length (mm)	0.2 x 0.5	0.2 x 15	0.2 x 0.5	0.2 x 0.5	0.2 x 0.5
Monochromator	Si(220)	Si(220)	Ge(111)	Si(220)	Si(220)
Wavelength (Å)	1.5	1.5	1.5	1.5	2.0
Estimated photon flux (photons s^{-1})	$1.3 \times 10^{6(x)}$	3.9×10^{7}	1×10^{7}	2.3×10^{6}	7.8×10^{6}
Estimated exposure time (mins)	$540^{(x)}$	18	70	300	90

(x) Figures obtained experimentally

b) SRS (2 GeV, 100 mA)

Sample source distance (m)	20	15	15	15	
Sample size dia (mm) x length (mm)	0.2 x 0.5	0.2 x 0.5	0.2 x 15	0.2 x 0.5	
Monochromator	Si(220)	Si(220)	Si(220)	Si(220)	
Wavelength (Å)	1.5	1.5	1.5	1.0	
Estimated photon flux (photons s^{-1})	5×10^{7}	8.9×10^{7}	2.7×10^{9}	2.0×10^{6}	
Estimated exposure time (mins)	14	8	0.27	360	

c) SRS (2 GeV, 100 mA, 4.5 T wiggler magnet)

Sample source distance (m)	20	15	15	15	15
Sample size dia (mm) x length (mm)	0.2 x 0.5	0.2 x 0.5	0.2 x 15	0.2 x 0.5	0.2 x 15
Monochromator	Si(220)	Si(220)	Si(220)	Si(220)	Si(220)
Wavelength (Å)	1.5	1.5	1.5	1.0	1.0
Estimated photon flux (photons s^{-1})	1.1×10^{8}	2.0×10^{8}	6×10^{9}	2.2×10^{8}	6.6×10^{9}
Estimated exposure time (mins)	6	3.5	0.11	3	0.10

divergence of the beam from a conventional source causes broadening of the powder lines.

One of the main advantages of synchrotron radiation over conventional X-rays produced by a characteristic target is that of tuneability. Examination of Fig. 5 reveals that for a typical powder specimen and the SRS operating with the wiggler magnet, the range of wavelengths accessible with a usable photon flux is impressive ; the intensity varies by only a factor of 4 from 0.3 Å up to 2 Å, and from 0.7 Å to 2 Å it is approximately constant. On the other hand, for very tiny samples, as used in single-crystal studies, the incident photon flux is quite small, about the same as with a conventional X-ray tube.

Large gains in photon flux are possible by focussing the radiation, but this is difficult to achieve in practice, especially if short wavelengths below 0.7 Å are required. Double-focussing usually consists of two elements, a horizontal mirror collecting over the vertical aperture, focussing by total reflection, and a vertical, curved monochromator to focus horizontally. Mirrors present severe technological problems because the small angles of incidence mean that they must be long, of the order of a few meters and even segmented mirrors are difficult to support and align. Double-focussing has been achieved on the storage ring DORIS (Hamburg), where a photon flux of $5 \pm 2 \times 10^{11}$ photons s^{-1} in a focal spot of 1.1 mm dia was measured (Hendrix, Koch and Bordas, 1979), but the focal region was surrounded by a high background area of 2 cm^2, caused by stray radiation scattered from the various components placed in the optical path. A toroidal mirror and double germanium crystal monochromator have been used at SPEAR (Stanford) by Hastings, Kincaid and Eisenberger (1978) to produce double-focussing; however, economic considerations may prevent further use of toroidal mirrors because of the difficulties in manufacture.

4. - CONCLUSION.

As is usually the case certain "trade offs" must be made between intensity, resolution and cost. Focussed systems are expensive and have high intensity and low resolution, whereas unfocussed systems have low intensity and high resolution, and are much cheaper. Furthermore, channel-cut monochromators easily allow tuneability of the photon energies, a much more difficult problem for focussing optics. For single-crystal diffractometers it seems likely that tuneable radiation of slightly higher intensity than that available in the laboratory can be produced with relative ease by a single channel-cut Si monochromator, especially if the diffractometer is built close to the source. Such a system should allow easy tuneability down to 0.2 Å, but nevertheless to exploit the source fully one should take advantage of the high fluxes available with focussed optics.

Powder diffraction has distinct advantages with regards to intensity because larger specimens can be used. We have already shown in Table I that large gains in exposure time are possible without resolution loss. On the SRS plus wiggler this would mean that even with a beam current of 100 mA an intensity of 6×10^9 photons s^{-1} at 1 Å in an unfocussed beam of 0.2 mm x 15 mm at 15 m can easily be achieved, making diffractometer experiments an exciting possibility. In addition flat-plate geometry can be exploited, illuminating say 3 mm x 6 mm of sample with a photon flux of 10^{11} photons s^{-1}, with the SRS at 100 mA, and a distance of 15 m from the source. In this case the resolution will be determined by the slits and sample-detector distance, L. By making L long(x) a reasonable resolution can be obtained, about $\Delta d/d = 2.5 \times 10^{-3}$ at $2\theta = 100^{\circ}$. At the same time some loss of intensity results, but such a diffractometer system would allow easy adjustment of resolution and intensity to suit a particular experiment, without losing the advantage of easy tuneability with a channel-cut monochromator.

It is worth pointing out that with a Debye-Scherrer camera of very large radius the resulting exposure times would be offset by the considerable advantage of being able to resolve many, if not all, of the powder lines into singlets, thus permitting $|F(hkl)|^2$ to be measured directly.

Even the long exposure time demonstrated in our pilot experiment will be reduced by a factor of about 3000 using a long specimen on the SRS plus wiggler, making possible exposures in a few second, and so this type of experiment could be an exciting prospect for the future. For instance it will be then possible to use continuous-recording photographic methods (Glazer, 1972) to study phase transitions as they occur.

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(x) - We assume an evacuated pipe is placed along the sample-detector path to avoid air absorption and scattering.

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