Prospects for X-ray absorption with the super-bright light sources of the future

David Norman

CCLRC Daresbury Laboratory, Warrington WA4 4AD, England. E-mail: d.norman@dl.ac.uk

The immense growth in applications of X-ray absorption spectroscopy (XAS) has been enabled by the widespread availability of intense tunable X-rays from synchrotron radiation sources. Recently, new concepts have been proposed for fourth-generation light sources, such as the SASE (self-amplified stimulated emission) X-ray free-electron lasers (XFELs) being pursued at Hamburg (TESLA) and Stanford (LCLS), and the recirculator ring (MARS) at Novosibirsk. These sources offer expected gains of many orders of magnitude in instantaneous brilliance, which will unlock opportunities for qualitatively different science. Examples of new or greatly expanded techniques in XAS could include Raman X-ray absorption fine structure (XAFS), pump-probe experiments, time-resolved XAFS and small-spot X-ray spectromicroscopy, although the limited tunability of the sources might not allow conventional XAFS measurements. Multi-photon X-ray absorption could become a new field of study. There should not be a collective stampede to these new sources, however, and it is likely that storage rings will continue to be necessary for most XAFS applications. The extreme brightness of these future light sources will present difficult challenges in instrumentation, especially detectors and sample containment. Practitioners will also have to exercise caution, because the intensity of the beam will surely destroy many samples and in some cases there will be so many photons absorbed per atom that XAFS will be impossible.

Keywords: X-ray absorption spectroscopy; fine structure; accelerators.

1. Introduction

The advance of X-ray absorption spectroscopy has depended on developments in synchrotron radiation sources. The immense increases in X-ray brightness over the years (Fig. 1) have led to great leaps forward in sensitivity, time resolution and spatial resolution, which have opened up new areas of application of XAFS spectroscopy. It is no accident that the past three international XAFS conferences have been held near the world's biggest third-generation synchrotron light sources [XAFS-IX, ESRF, Grenoble (Goulon *et al.*, 1997); XAFS-X, APS, Chicago (Bunker *et al.*, 1999); XAFS-XI, Spring-8, Ako (these proceedings)].

Recently, ideas for so-called fourth-generation light sources have been proposed that would produce X-rays with many orders of magnitude increase in brightness compared with existing synchrotron radiation sources. This paper briefly describes what these super-bright light sources might be and what they might bring for XAS.

2. Fourth-generation light sources

The key to development of super-bright light sources is a particle accelerator with extremely low beam emittance, a small energy spread and long undulators with many periods. Ideally, figures of $\varepsilon \simeq 10^{-2}$ nm rad and $\Delta E/E < 10^{-4}$ are required, significantly lower than achieved at the present third-generation storage rings, with undulators of $\sim 10^4$ periods. Each of these characteristics is close to a physical limit. For emittance, this is the diffraction limit where the emittance (size × divergence) of the electron beam equals that of the X-rays given off, thus producing spatial coherence. For the energy spread and undulator periodicity, the limit is the quantum fluctuation of the emitted synchrotron radiation.

To achieve these beam properties, a low-emittance short-pulse source of electrons is needed, probably based on photocathode injection with a focused laser (Sheffield, 1992). Also, the low emittance must be preserved throughout the system. Emittance is degraded by emission of synchrotron radiation and intrabeam scattering, so storage rings based on conventional circulating beams are unable to sustain the low emittance needed for fourth-generation sources. This means that some sort of single-pass system is essential.

The main technique of promise for super-bright light sources employs the SASE principle for free-electron lasing (*e.g.* Hogan *et al.*, 1998). This yields intense X radiation that is coherent, diffraction-limited and can have linear or circular polarization as desired. The SASE theory is akin to that for operation of a travelling wave tube. A high-quality electron beam passing through a long undulator exponentially amplifies an existing radiation field at a resonance wavelength $\lambda_{\rm ph}$ given by

$$\lambda_{\rm ph} = (\lambda_u/2\gamma^2)(1 + K^2), \qquad (1)$$

where γ is the electron energy, λ_u is the undulator period and K is the undulator parameter. Coherent stimulated emission is produced because a bunch density modulation of the electron beam at the optical wavelength builds up as the beam passes through the undulator. This gives 'micro-bunching', with the electron beam sliced into many pieces separated by $\lambda_{\rm ph}$. The 'existing radiation field' can be provided by a conventional laser or can arise from the undulator radiation radiated spontaneously in the first part of the undulator. The beauty of SASE is that it does not need an optical cavity, unlike other types of laser, and hence can work at short wavelengths. To achieve X-ray wavelengths of ~ 1 Å with realistic undulator periods of a few centimetres, an XFEL needs electron beams in the range 10–50 GeV.

An SASE XFEL should produce X-rays with a peak brilliance of around 10^{34} [in the usual units of photons s^{-1} mrad^{-2} mm^{-2} (0.1% bandwidth)$^{-1}$], some eleven orders of magnitude higher than that from the brightest undulator sources on the most modern third-generation synchrotron radiation sources (Fig. 2). Much of that gain comes from higher intensity (peak currents in the kA range), some from a decreased source size (expected to be $\sim$25 µm diameter), about one order of magnitude from decreased divergence ($\sim$1 µrad), and a similar gain from the decreased energy spread (expected to be $\sim 10^{-4}$). The repetition rate is low and the average brilliance of SASE XFELs is predicted to be around 10^{26} photons s^{-1} mrad^{-2} mm^{-2} (0.1% bandwidth)$^{-1}$, some six or seven orders of magnitude higher than that of undulators at ESRF, APS and Spring-8 (Fig. 2). These figures are for the stimulated emission, but even the spontaneous emission from a multi-GeV XFEL peaks in the 10^{28} range, with an average brilliance of around 10^{20} or 10^{21} photons s^{-1} mrad^{-2} mm^{-2} (0.1% bandwidth)$^{-1}$, which represents a significant enhancement compared with the present third-generation sources.

Two SASE-based XFELs are currently being pursued. One at Hamburg is proposed as part of the TESLA high-energy physics project, a 250 GeV electron–250 GeV positron collider that is 32 km long and would employ superconducting RF (radio frequency) accelerating cavities (Brinkmann *et al.*, 1997). It is proposed to tap off 10–50 GeV beams part way along the linac and allow the beam to drift for 10–15 km before passing through the undulators for the

XFEL. The XFEL proposed at Stanford, the LCLS (linac coherent light source), would utilize the last one-third of the existing SLAC 3 km linac, with normal conducting RF, and a final beam energy of 14.3 GeV to produce X-rays as short as 1.5 Å (LCLS Design Study Group, 1998). The principle of SASE has been demonstrated at Hamburg, in the 250 MeV TESLA test facility (TTF) (Edwards, 1995). SASE lasing has recently been demonstrated at $\lambda < 100$ nm, with over three orders of magnitude gain over the spontaneous emission, but not yet achieving saturation (Rossbach, 2000).

A significant difference between a linac and a storage ring is the time structure. Storage-ring sources are quasi-continuous, depending on the machine-fill structure, with typical repetition rates of 500 MHz. The repetition rate for LCLS is proposed to be 120 Hz, while that for TESLA is likely to be as low as 5 Hz. On the other hand, the pulse length can be much shorter than that normally achieved in storage rings, potentially giving advantages for studying fast processes. LCLS is planned with pulses of 67 fs (r.m.s.) length, and TESLA XFEL is currently proposed to have 11315 bunches, each 80 fs (r.m.s.) long and 93 ns apart, making a charge of 1 nC in a bunch train 1.05 ms long, with 200 ms to the next bunch. In principle, a linac can be injected with a pulse structure tailored to the experimental needs. At TESLA, it is proposed that electron bunches for high-energy physics and for the XFEL be interspersed at *ca* 100 ms intervals and sent on different trajectories by kicker magnets. Some caution is probably necessary, however, because the needs of the high-energy physics programme might not be able to accommodate the ideal pulse composition for the XFEL, and compromise seems unlikely.

Another possible approach to a fourth-generation light source is the MARS (multi-turn accelerator recuperator source) concept developed at Novosibirsk (Kulipanov *et al.*, 1998). This uses the spontaneous undulator radiation in a single-pass recirculating system. MARS should attain a peak brilliance of around 10^{26} photons s^{-1} $mrad^{-2}$ mm^{-2} (0.1% bandwidth)$^{-1}$ for 1 Å X-rays, seven or eight orders of magnitude lower than the stimulated emission from an XFEL, but the higher repetition rate means that the average brilliance of MARS is predicted to be around 10^{23} photons s^{-1} $mrad^{-2}$ mm^{-2} (0.1% bandwidth)$^{-1}$, higher than for an XFEL.

3. Possible developments in X-ray absorption spectroscopy

This section draws heavily on the conclusions of discussions at a series of workshops at Hamburg (chaired by the author; Brinkmann *et al.*, 1997) and at Stanford (LCLS Design Study Group, 1998). For the spontaneous emission, experimental techniques that extrapolate from the present will probably suffice and allow advances to more dilute systems, such as semiconductor dopants, environmental pollutants or surfaces. To handle the great intensity of the stimulated emission, there are major instrumental challenges to be faced. The power density on optical components will be a problem. In many

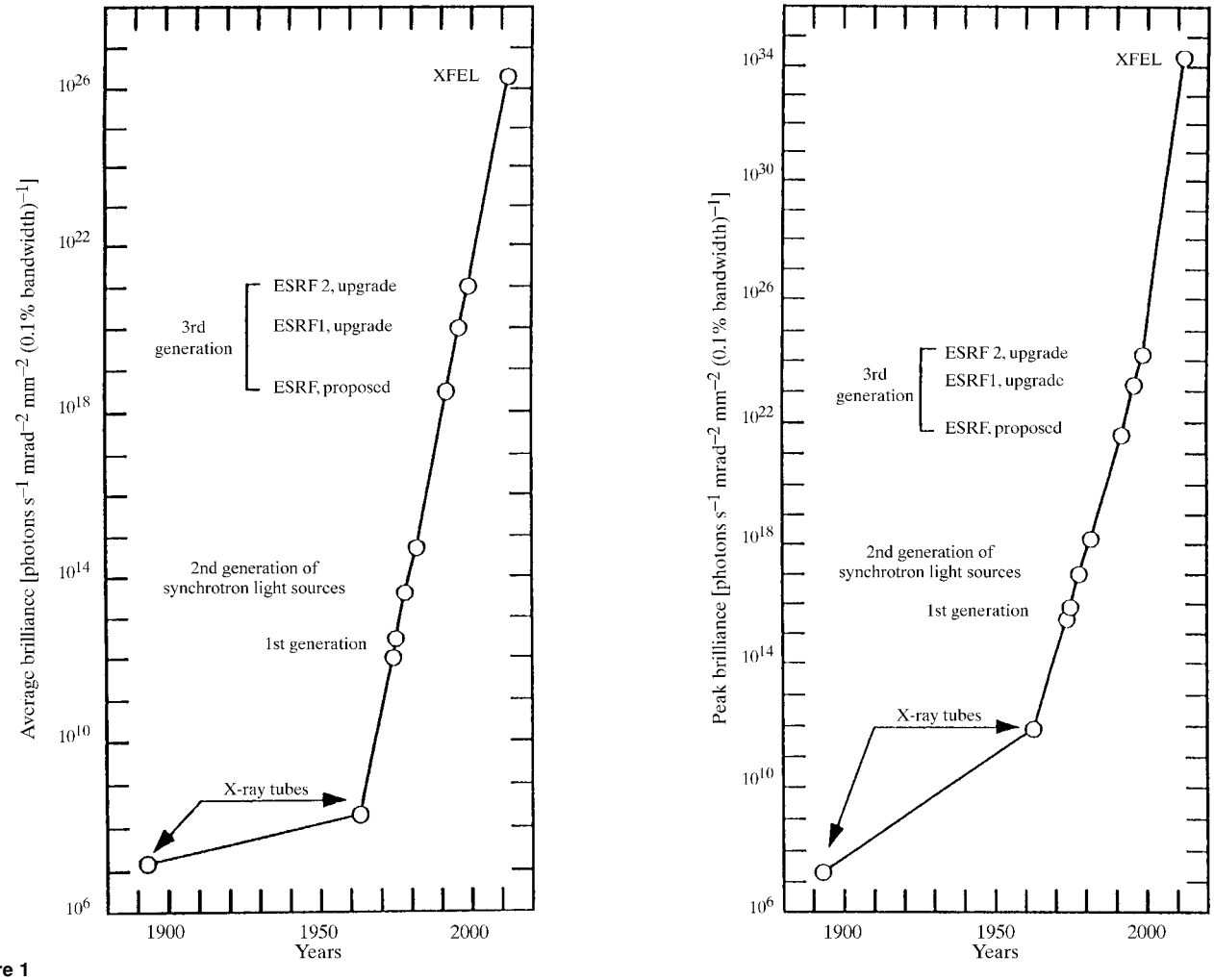

Figure 1
The increase in brightness from X-ray sources during the past 100 years. Average and peak (instantaneous) brilliance is shown. Taken from Brinkmann *et al.* (1997).

cases the X-ray flux will destroy samples, although it might be possible to collect data before damage sets in and to refresh the sample in some way, perhaps by having a continuous stream of samples presented in rapid succession before the beam. Detectors are often only just able to manage present-day fluxes; substantial advances will be needed to tackle orders-of-magnitude enhancements. Assuming that solutions to these challenges can be found, there are some exciting new possibilities for X-ray absorption spectroscopy.

Taking figures calculated for the Hamburg XFEL, at a photon energy of 2.0 keV, approximately 2.5×10^{13} photons bunch^{-1} are expected within an energy spread of 0.1% $\Delta E/E$. The corresponding value at 7.8 keV photon energy is $\sim 5 \times 10^{12}$ photons bunch^{-1}, at 12.4 keV, $\sim 3.5 \times 10^{12}$ photons bunch^{-1}, and at 20 keV, $\sim 8 \times 10^{11}$ photons bunch^{-1}. In other words, the stimulated emission from an XFEL should give intensities with the number of photons per bunch similar to the photon flux per second at existing insertion-device beamlines! The extremely small beam divergence of ~ 1 µrad places extreme demands on stability, but yields a beam diameter of ~ 100 µm at the sample position, even 100 m from the source. For systems that can cope with the flux without plasma formation (Doniach, 1996), it should be possible to reduce the beam size still further by focusing with capillaries (Thiel *et al.*, 1993), perhaps to as small as a diameter of ~400 Å (D. Bilderback, personal communication). The small bandwidth of the undulator could allow direct EXAFS (extended X-ray absorption fine structure) measurements without a monochromator, but only at moderate energy resolution. Otherwise, providing a monochromatic and tunable incoming beam could be tricky. As long as the heat-load can be handled, existing conventional techniques could be transferred to an XFEL source, and it will be possible to trade-off intensity for resolution, using for instance a four-bounce monochromator, and thus match core-hole lifetime widths and measure fine edge shifts.

3.1. *Multi-photon core-shell absorption*

Multi-photon absorption in outer shells is a thriving field of study, using low photon energies, especially with conventional laser sources, but multi-photon absorption of inner shells is completely unexplored. The dense photon beams available from the XFEL will open the possibility of examining hitherto inaccessible excited atomic states and allow sensitive tests of core-hole screening theories, important in wide-band materials such as oxide insulators and superconductors.

Two effects make core-shell multi-photon absorption more difficult to observe than for outer shells. First, cross sections are low, making absorption of the first photon less likely; and secondly, lifetimes of the excited states are shorter, reducing the probability of absorption of a second photon by the excited atom. By bunching its great intensity into ultra-short pulses, an XFEL can overcome both effects.

The theory is well established but impossible to solve exactly, even for the simplest atoms. Approximate cross sections can be estimated

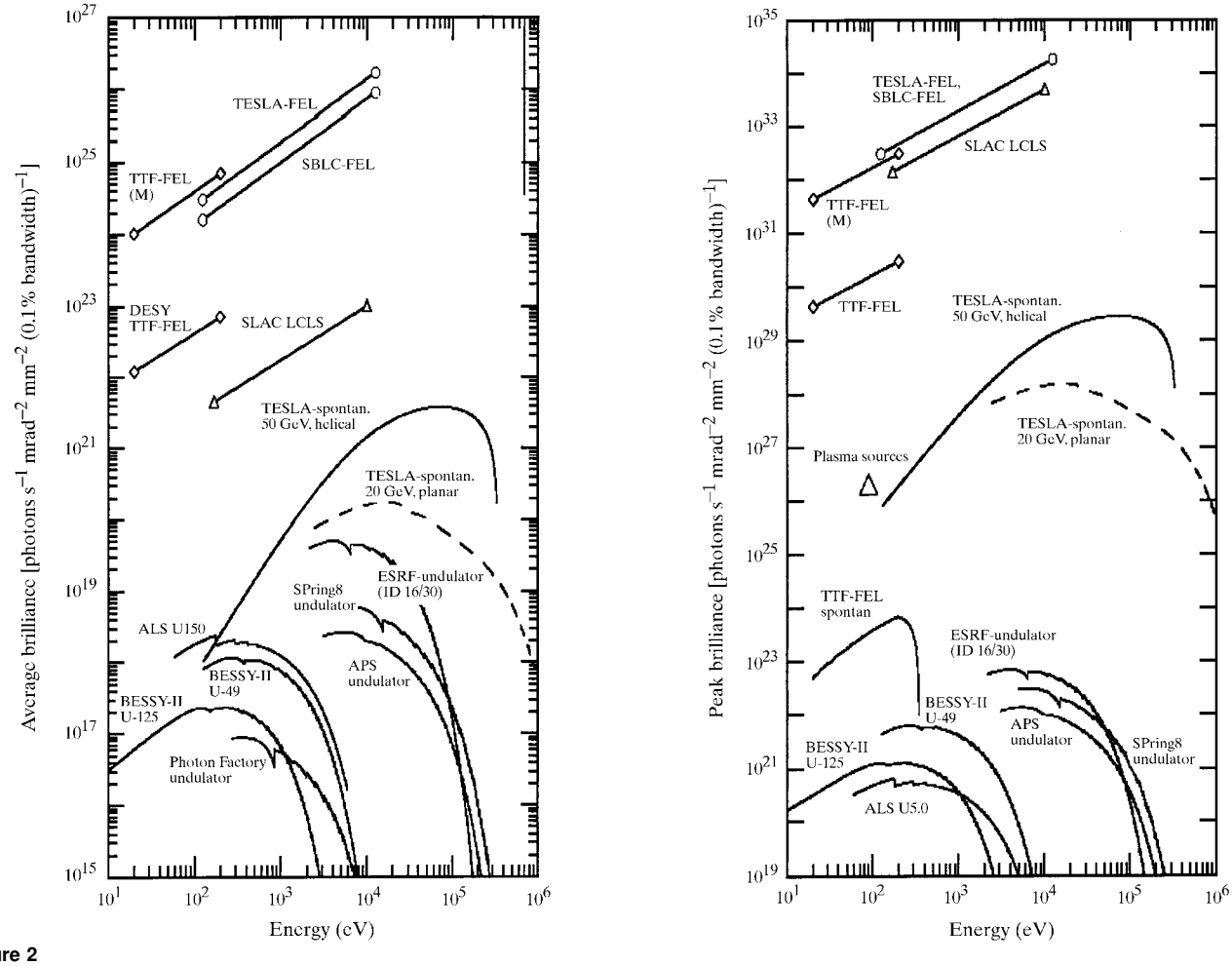

Figure 2
The average and peak brilliance expected from X-ray free-electron lasers compared with existing synchrotron radiation sources. Taken from Brinkmann *et al.* (1997).

by considering sequential absorption of photons in a 'golden rule' formalism (A. Kodre, personal communication). For example, consider double excitation of the *K* shell of copper. If all of the $\sim 5 \times 10^{12}$ photons bunch^{-1} of the TESLA XFEL were focused into a spot of 1 μm diameter, then *ca* 15 photons atom^{-1} will be absorbed. The short *K*-shell lifetime (~0.2 fs) thus leads to 0.04 photons absorbed per atom per lifetime, a weak effect. The expected non-uniformity of SASE radiation within a bunch (Brinkmann *et al.*, 1997) should, however, increase the multi-photon absorption rate, and other atoms have higher cross sections or longer lifetimes. Also, crucially, if capillary focusing can be used to put all of the photon beam onto a spot of *ca* 400 Å in diameter, as many as 100 photons will be absorbed per atom per lifetime! Multi-photon X-ray absorption is clearly thus feasible with the XFEL. However, it is not XAFS, and any attempts to measure XAFS with highly focused beams must beware the confusion of multi-photon absorption.

3.2. *Raman XAFS*

In the Raman process, an inelastically scattered photon loses energy to promote an electron into an unoccupied level, with the cross section for this event proportional to that for absorption. Fine structure (Raman XAFS) can be seen as a function of energy loss. This technique could potentially revolutionize structural work on systems containing light atoms, as they could be studied without samples having to be in vacuum, opening up new horizons in chemistry and materials sciences.

The state of the art with third-generation synchrotron radiation sources is that bulk measurements are feasible although time-consuming (Bergmann *et al.*, 2000) and polarization-dependent experiments have been demonstrated (Watanabe *et al.*, 1996). An XFEL will reduce the time scale for such experiments to a few seconds per spectrum for dilute samples, making Raman XAFS almost as routine as conventional XAFS is today.

3.3. *Time-resolved XAFS*

For fast measurements, the narrow energy spread of X-rays from undulators precludes energy-dispersive methods, making the fast sequential 'quick' XAFS (QEXAFS) method probably the technique of choice. An elegant possibility is the direct tuning of the electron beam energy by the XFEL. An energy change of approximately 10% within 100 bunches seems feasible, so that, for instance at the Fe *K* edge an energy range of ~700 eV can be covered within 10 μs. The intensity of stimulated emission from an XFEL should allow QEXAFS of dilute (sub-monolayer equivalent) systems in microseconds. This would allow investigations of the atomic structure during chemical reactions and phase transformations, such as on surfaces during heterogeneous catalysis. By observing the near-edge region, the valence of selected elements can be readily observed and, using circularly polarized X-rays, changes in magnetic short-range order can be followed. XFEL pulses are much shorter than the time scale for radiation damage (of the order of milliseconds) in biological samples, so single-pulse measurements, or measurements with a few consecutive pulses, should be possible before damage sets in. Similarly, XFEL pulses are shorter than the time scale for reaction of radicals or motion of molecular fragments (pico- to nanoseconds). Thus, fast XAFS experiments will be able to probe short-lived states.

3.4. *X-ray spectromicroscopy*

Small-spot spectromicroscopes theoretically should be able to achieve a spatial resolution limit of around 5 Å (Wichtendahl *et al.*, 1998), but in practice the resolution is limited not by the intrinsic parameters of the electron spectrometer but by the incident photon flux needed to obtain a tolerable signal-to-noise ratio. The limit is likely to be around 500 Å with third-generation synchrotron radiation sources, but an XFEL can push this down towards the nanometre region, especially if focusing can further reduce the beam size. This will then allow X-ray spectromicroscopy studies of samples and especially their surfaces, with a variety of spectroscopic techniques, including photoelectron spectroscopy, XAS and X-ray excited Auger electron spectroscopy.

4. Summary and words of caution

It is clear that the proposed fourth-generation light sources will offer unprecedented gains in brilliance and will open up new fields of study. It is less clear how to take advantage of these gains for X-ray absorption spectroscopy. There are some problems that, at the present, seem insurmountable: in many cases the intensity of the beam will destroy samples and sometimes there will be so many photons absorbed per atom that XAFS will be impossible. Even in those areas where these sources appear to be useful, there are major instrumental challenges to be solved, especially with detectors and sample containment.

It is likely that storage rings will continue to be necessary for most XAFS applications. There is, however, a danger that outsiders to the field will automatically assume that fourth-generation sources must be better than the third generation, and that funding will be diverted from storage rings into the more specialized, and possibly less useful, super-bright sources described here.

I am greatly indebted to Ronald Frahm, Larc Troeger, Alojz Kodre and Uwe Bergmann for interesting discussions, and to all who contributed to the scientific case for the Hamburg TESLA XFEL.

References

Bergmann, U., Mullins, O. C. & Cramer, S. P. (2000). *Anal. Chem.* **72**, 2609–2612.
Brinkmann, R., Materlik, G., Rossbach, J. & Wagner, A. (1997). *Conceptual Design of a 500 GeV e^+ e^- Linear Collider with Integrated X-ray Laser Facility.* DESY Report 1997–048, Hamburg.
Bunker, B. A., Morrison, T. I. & Heald, S. M. (1999). *J. Synchrotron Rad.* **6**, 121–807.
Doniach, S. (1996). *J. Synchrotron Rad.* **3**, 260–267.
Edwards, D. A. (1995). Editor. *TESLA Test Facility Linac Design Report.* DESY, Hamburg.
Goulon, J., Goulon-Ginet, C. & Brookes, N. B. (1997). *J. Phys. IV Colloq. C2.*
Hogan, M., Pellegrini, C., Rosenzweig, J., Travish, G., Varfolomeev, A., Anderson, S., Bishofberger, K., Frigola, P., Murokh, A., Osmanov, N., Reiche, S. & Tremaine, A. (1998). *Phys. Rev. Lett.* **80**, 289–292.
Kulipanov, G. N., Skrinsky, A. N. & Vinokurov, N. A. (1998). *J. Synchrotron Rad.* **5**, 176–178.
LCLS Design Study Group (1998). *Linac Coherent Light Source (LCLS) Design Study Report.* SLAC Report R-521, Stanford.
Rossbach, J. (2000). *European Particle Accelerator Conference*, Abstract FRXE06. To be published.
Sheffield, R. L. (1992). *Photocathode r.f. guns*, in *Physics of Particle Accelerators*, Vol. 184, edited by M. Month & M. Dienes, pp. 1500–1531. AIP.
Thiel, D. J., Bilderback, D. H. & Lewis, A. (1993). *Rev. Sci. Instrum.* **64**, 2872–2878.
Watanabe, N., Hayashi, H., Udagawa, Y., Takeshita, K. & Kawata, H. (1996). *Appl. Phys. Lett.* **69**, 1370–1372.
Wichtendahl, R., Fink, R., Kuhlenbeck, H., Preikszas, D., Rose, H., Spehr, R., Hartel, P., Engel, W., Schlogl, R., Freund, H.-J., Bradshaw, A. M., Lilienkamp, G., Schmidt, T., Bauer, E., Benner, G. & Umbach, E. (1998). *Surf. Rev. Lett.* **5**, 1249–1256.

 Received 16 August 2000 • Accepted 17 November 2000