Connecting Visible Wavelength Standards With X Rays and γ Rays

The 1996 centenary of W. K. Röntgen's discovery of x rays celebrated the penetrating visions offered by these "strange rays." Aside from their ubiquitous application to imaging the interior structure of visually opaque systems, x rays continue to have important applications in elucidating the geometrical and electronic structure of matter. In addition to the synchrotron radiation facilities, conventional x-ray sources available in modest laboratory environments have wavelengths well suited to reveal the arrangements of atoms in crystalline solids and biological molecules. In addition, spectroscopy of absorbed and emitted x rays reveals the electronic structure of atoms, molecules and materials. In a similar way, nuclear γ-rays reflect the energy level structure of nuclei in a wavelength range that extends as far beneath the scale of x-ray wavelengths as x-ray wavelengths lie below visible wavelengths.

X-ray diffraction, first reported in 1912, connects x-ray wavelengths with the dimensions of crystal lattices, but fails to connect either of these scales with the dimensions of macroscopic objects. From the early 1930's to the early 1970s, x-ray spectroscopy was an important contributor to the determination of fundamental constants such as N_A, *h/e,* and *hc/e.* These measurements were, however, limited by uncertainty in the connection between the x-ray scale and visible reference wavelengths. Up to the mid-seventies, the only well established direct connection was by means of ruled grating diffraction of long wavelength x-ray lines, a procedure that even in its late development was not sufficiently accurate. The paper *X-ray to Visible Wavelength Ratios* [1] represents the first results of a more direct and robust connection between these disparate spectral domains.

Because relative measurements of x-ray wavelengths were more accurate than those linking x-ray wavelengths to macroscopic standards, early workers in the x-ray region introduced local reference standards that approximated sub-multiples of optical units, but were more sharply defined. The local unit in the x-ray region was called the xu, a unit that was intended to approximate 0.001 Å (0.1 pm). Although originally defined by assigning a conventional value to the lattice spacing of rock salt, and later that of calcite, the x-unit was more often specified by assigning particular values (in xu) to the wavelength of one of the widely used reference lines in the x-ray region.

It was not until around 1930 that the 1926 demonstration of x-ray diffraction by a ruled optical grating achieved a refinement capable of providing a useful conversion factor between x-ray and optical units. Results from this work were at variance with the local x-ray unit calculated by making use of the electron's charge determined by Millikan's oil drop experiment. The disagreement (>0.2 %) remained controversial for over a decade. In the end, it was shown that the oil drop measurement of e contained an error arising from the viscosity of air.

Realization of the first x-ray interferometer by Bonse and Hart in 1965[2] opened another route to x-ray wavelengths, and subsequently to the γ-ray region. The path to a significant measurement began with Hart's "Ångström ruler" [3], an articulated silicon monolith able to scan over an extended, though limited, range. Subsequently, Bonse and TeKaat demonstrated the quasi-static re-assembly of separated components while retaining favorable intensity contrast [4]. The first combined x-ray and optical interferometer was realized at the NBS [5].

The subject paper [1] reported combined X-Ray and Optical Interferometry (XROI) of the lattice period of a silicon crystal, followed by accurate spectrometry to determine the two most commonly used x-ray reference wavelengths, Cu $K\alpha_1$ and Mo $K\alpha_1$. This measurement plan connected manifestly invariant quantities. The crystal spacing was determined with respect to the optical reference in the XROI measurement and then used, through absolute angle measurement, to link the optical "standard" to x-ray transition wavelengths. Although it has been proposed that the lattice period of silicon (at specific temperature, pressure and purity) should be treated as a "constant of nature" [6], we restrict such usage to transitions between atomic energy levels (x rays), or between nuclear energy levels (γ rays).

The subject paper describes both parts of the measurement (for x rays) with an emphasis on the XROI component owing to its perceived difficulty and novelty. The original cartoon illustration shown in Fig. 1 has been widely reproduced in textbooks and elsewhere, possibly on account of its deceptive simplicity. The stationary and moving platforms were supported by a flexure stage. In actual data taking, the mechanical stage was "locked" to an optical interference maximum by means of a piezoelectric actuator situated in the drive.

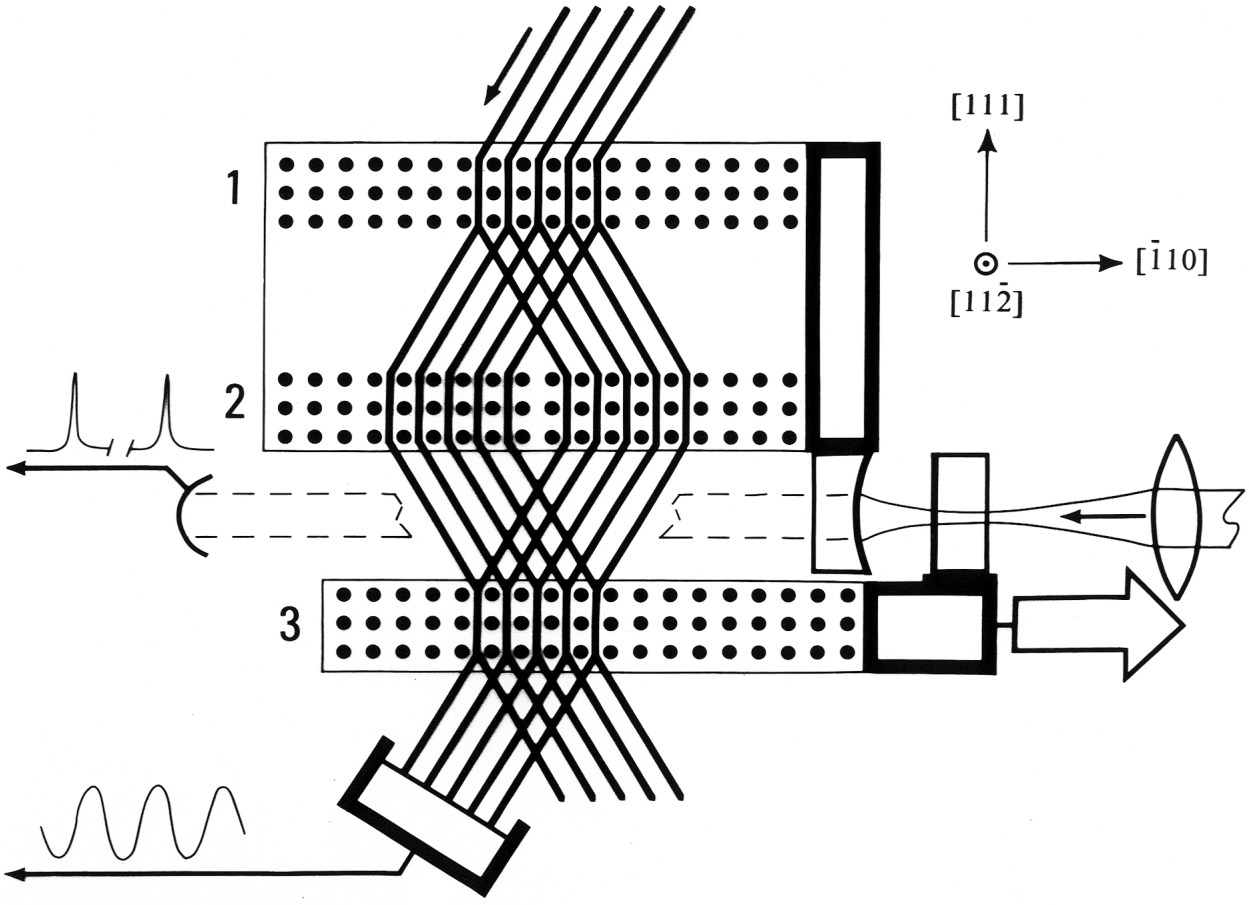

Fig. 1. Schematic of early x-ray and optical interferometry apparatus.

The possibility of a significant (1.8×10^{-6}) problem in this early measurement was suggested by a series of excellent measurements carried out at the Physikalisch-Technische Bundesanstalt (PTB) under the guidance of the late Peter Seyfried [7]. The discrepancy remained a puzzle until the NBS apparatus was retrofitted with additional interferometers designed to track the "pitch" and "yaw" errors. It became clear that the constancy in x-ray interference contrast over scans of hundreds of optical periods, from which rectilinear motion had been inferred, arose instead from mechanical noise that limited the maximum interference contrast [8].

The principal short term impact of this paper was its provision of enabling technology for three other efforts. The most familiar of these is the first "modern" determination of the Avogadro constant, N_A, connecting the ^{12}C-based scale of atomic masses with the artifact-based scale for macroscopic mass [9, 10]. This was followed by the first applications of the same measurement paradigm to the determination of the energy scale for nuclear γ-rays [11], and extension of the methods of the initial paper to the principal K-series x-ray lines of tungsten[12], several rare earth elements, plus thorium and uranium [13]. These short-term efforts led to a longer term multinational effort addressing the Avogadro constant, and a joint program of NBS/NIST and Institut Laue-Langevin that has extended optically based wavelength measurement in the γ-ray region up to 7 MeV.

NBS work on the Avogadro constant *via* the X-Ray Crystal Density (XRCD) approach began around 1970. The basic idea dates from 1913-14 when W. H. Bragg and W. L. Bragg used the inverse of N_A to infer the lattice constant of rock salt (NaCl). Subsequently, the XRCD procedure has appeared in several forms, not only addressing the problem of N_A determination, but also establishing the most modern (and likely the last) local wavelength unit for x rays, the A* unit [14]. All work in this area, prior to that at NBS in the early 70s, had two principal limitations.

The first limitation was use of liquid water as a density standard. Although much effort had gone into establishing the density of Standard Mean Ocean Water (SMOW), application of this value to a particular local water sample is problematical. In addition, water in its fully cleaned and degassed form is unstable with respect to re-dissolution of atmospheric gases, and it is relatively corrosive. To get around this problem, the NBS Mass Group introduced a density scale based on solid objects and used a fluorocarbon immersion fluid that was non-corrosive and had a significant capacity to dissolve gases [15]. Solid objects used in this initial work were readily available highly regular steel spheres.

A second limitation arose from the use of "tabulated" atomic weights. Such tabulated values approximate the world average of the geochemically variable isotopic abundances. Such variability in the case of silicon is large enough to prevent a significant determination of N_A. The NBS work was the first to employ the (now standard) practice of direct isotopic abundance measurement of the actual material used in the density measurement [16]. The importance of this is illustrated in Fig. 2 where we have shown a plot of crystal density as a function of the mean molar mass (atomic weight). Lattice changes over the normal range of abundance variability are small enough that the ratio of mean molar mass to density should be constant, determined by the slope of the line shown in Fig. 2.

Just as the x-ray region had a local unit, so too did the γ-ray domain. In this case, the *de facto* standard was based on a rather complex determination of the transition energy of the ^{198}Hg daughter of ^{198}Au*. The numerical value for this approximately 411 keV transition was used as a reference value for most other γ-ray transitions. In this role, it was (properly) used without

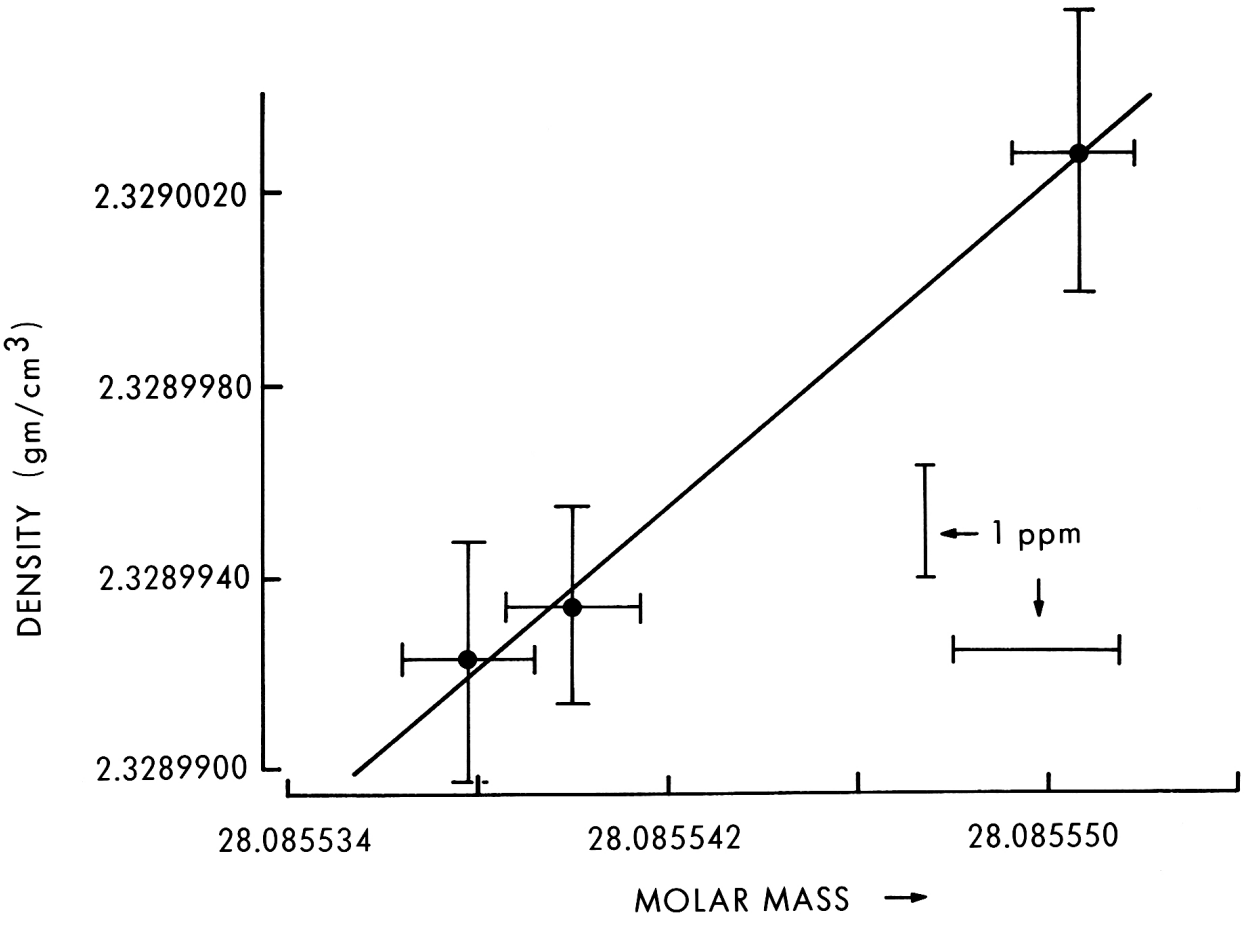

Fig. 2. Density response of silicon to molar mass changes.

uncertainty. However, in the case of fundamental constants or tests of physical theory, the uncertainty naturally entered directly.

Responding to a generally accepted need to improve this reference transition, NBS mounted an effort to extend the optically based measurement chain into the γ-ray region. Results for both the 411 keV and the 675 keV transitions in a strong ^{198}Au source activated in the NBS reactor were reported in 1978 along with new measurements of nine transitions in ^{192}Ir covering the range from 205 keV to 612 keV. In the case of the 411 keV line from ^{198}Au the result was 25×10^{-6} higher than the previous value and claimed a forty-fold improvement in accuracy [11].

The combined effects of this initial work and subsequent efforts toward improved linkages among the several wavelength regions have effectively unified the entire electromagnetic scale. The efforts arising from the subject paper may be thought of as beginning the process of extending the reach of frequency synthesis from the visible wavelength region into the domain of x rays and γ rays. The improved visible-to-x-ray and visible-to-γ-ray connections yielded new values for certain elementary particle masses, more critical tests of quantum electrodynamics (QED) (in the spectroscopy of one-electron heavy ions), a new, SI-based, all-*Z* tabulation of x-ray transitions, and improved estimates of nuclear binding energies with sufficient accuracy to impact nuclear mass values. Aside from these developments, which were anticipated, the NIST γ-ray instrumentation has had significant unanticipated usefulness in the determination of lifetimes of nuclear excited states in the sub-picosecond range and determination of interatomic potentials in the 10 eV to 100 eV range.

Several of the national metrology institutes (NMIs) have formed an international Avogadro group focusing on a possible atomic replacement for the artifact kilogram. Major programs are currently underway in Germany, Japan, Italy, and Australia. The needed isotopic abundance ratios are being determined at the Institute for Reference Materials and Measurements (IRMM) in Belgium, sponsored by the European Union. Most of the procedures in this worldwide effort are direct descendants of the initial NBS effort of the 1970's. NIST no longer has significant activity in this area with the exception of relative lattice parameter measurements and ad hoc contributions to the understanding of the troublesome molar volume anomaly in the period from 1994 to 2000. Overall, the initial Avogadro work at NBS led to improved methods of measurement in the areas of density, displacement, and molar mass as well as to the viable possibility of an atomically based replacement for the artifact kilogram.

The first generation of γ-ray measurements at NBS used radioactive sources activated in the NBS reactor. Extension of this work to higher energies required access to short-lived excited nuclei only accessible through targets internal to a high flux reactor. Only the research reactor at the Institut Laue-Langevin (ILL) in Grenoble is configured to allow access to such sources. A new γ-ray instrument specifically matched to this application was installed at the ILL in the mid-eighties and is now included in the ILL facilities inventory as GAMS4.

GAMS4 extends the optically based γ-ray wavelength scale to energies far higher than were accessible with activated sources from the NBS reactor. It has allowed determination of specific γ-ray transition energies leading to new values for the neutron mass [17] and to the possibility of a γ-ray/atomic mass determination of the molar Planck constant [18]. The neutron mass was addressed at an early stage and recently revisited with further improved results [19]. Because of the evolution in other parts of the fundamental physical constants, the molar Planck constant is now accurately established indirectly. The associated γ-ray measurements now are verifiers of high accuracy trap-based mass spectrometry results.

In addition to its use in high accuracy measurements, GAMS4 delivers higher spectroscopic resolving power than had been available previously. This exceptional resolution revealed (initially unexpected) broadening and fine-scale structural detail within individual γ-ray profiles. The basic understanding of these line shapes as recoil-induced Doppler profiles, modulated by collisional deceleration, emerged from a brief but very fruitful period in 1987 [20]. Our principal ILL collaborators, Hans Börner and his associates, have further developed the understanding of this complex process [21]. GAMS4 is now seen as an effective means for determination of nuclear excited state lifetimes in the sub-picosecond domain [22] and a fertile test bed for models of interatomic potentials in the 10 eV to 100 eV range [23]. This work has been widely recognized in Europe. It was identified as one of the two most significant nuclear physics results for 1992 [24]. Börner received the 1990 Roentgen prize of the German Physical Society, and a student who used GAMS4 for his thesis research received the F. Schlafli Prize of the Swiss Academy of Natural Sciences [25].

Two international workshops on applications of high precision γ-ray spectroscopy have now taken place. The first was in Grenoble in 1992, and the second, in South Bend, Indiana, in 1998, is summarized in a special issue of the NIST *Journal of Research,* January-February 2000. Most contributions to these meetings were based

on experimental work carried out using GAMS4 or on theoretical developments in molecular dynamic simulations attuned to past or future experimental results from GAMS4. As an ILL user facility, GAMS4 applications are part of the normal proposal stream. Up to 2000, when this commentary is being prepared, requests for access to GAMS4 have exceeded available time by a factor of two. In response to this proposal pressure, and to increase the very low efficiency of GAMS4, the ILL has undertaken new instrument development. This new facility, GAMS5, is operational but still under development.

Publication of the first comprehensive (all-Z) theoretical study of x-ray transition energies [26] came just after the first few of the new NBS experimental measurements. The extraordinary clarity of the initial comparisons and the unexpected linear Z-dependence of the discrepancy invited extension and refinement on the part of both theory and experiment. This first comprehensive calculation was in the Dirac-Hartree-Slater framework, and the puzzling Z-dependence shown in Fig. 3 was found to be due to use of incorrect values for nuclear radii. Subsequent refinements included some relativistic corrections and inclusion of a properly diffuse nuclear boundary [27].

Following this early period, a collaboration with Paul Indelicato (Paris) was initiated, aimed at progressively more refined, more rigorous and more detailed calculations. These initial efforts involved theoretical work at the level of multi-configuration Dirac-Fock with approximate allowance for QED effects. As this work progressed through stages of increasing refinement and understanding, it became clear that hole-state dynamics would have to be considered. NIST was fortunate in this respect to engage the collaboration of Eva Lindroth, who brought the techniques of many-body perturbation theory to bear on estimation of level shifts due to coupling of inner vacancy states to their associated decay continua [28].

All of these theoretical developments have now been linked with an expanded and improved experimental framework to produce a new and unprecedented view of principal x-ray transitions for all elements from neon to fermium. Previous attempts at such a synoptic overview have been for the most part entirely empirical, while there have been a few attempts to produce a comprehensive theoretical database. The NIST effort has combined these two approaches with certain important changes. First, the experimental database is skeletal rather than comprehensive. Items included in the experimental

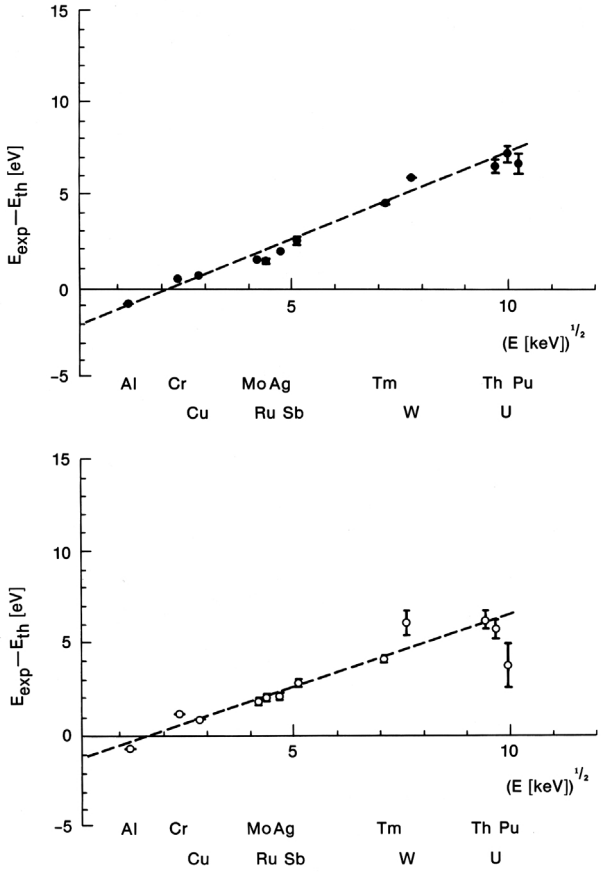

Fig. 3. Atomic transition response to errors in nuclear radii.

database were either measured directly in accordance with the best of modern practice, or were referenced to other transitions that had been directly measured according to best practice. Second, the theoretical component was constructed with a high level of rigor that included not only a multi-configuration basis set with relativistic and QED corrections, but also the modification of these levels due to their coupling to associated decay continua.

Richard Deslattes began work in the Crystal Chemistry Section of the Analytical Chemistry Division in 1962. He subsequently headed a newly named Quantum Metrology Section in the Physics Division of the Center for Absolute Physical Quantities. This Section became for a brief time the Quantum Metrology Division in the Physics Laboratory. Its remnants remain as the Quantum Metrology Group of the Atomic Physics Division of the NIST Physics Laboratory. In 1981-2 he served as Director of the Physics Division of the

National Science Foundation. In 1983 he was designated as a Senior NBS Fellow. In 1984-5 he was a U.S. Senior Awardee of the Alexander von Humboldt Stiftung, visiting the University of Heidelberg and working at the Max Planck Institute for Nuclear Physics, the Gesellschaft für Schwerionenforschung and the Institut Laue-Langevin. His awards include the Gold and Silver Medals of the Commerce Department.

Albert Henins came to NBS in 1970 as a Physicist. He continued to serve in that capacity until his retirement in 1998.

Prepared by Richard D. Deslattes.

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