

### *NIST Centennial Celebration Crystallographic Highlights*

The Centennial Celebration of the National Institute of Standards and Technology (NIST), formerly known as the National Bureau of Standards (NBS), takes place in the year 2001. NIST has a long history (> 50 years) of crystallographic research, and has made significant contributions to the advancement of the fields of crystallography, biology, and materials science. Many scientists from various divisions in diverse disciplines have contributed to this history. The research has been carried out as a fundamental part of the overall mission of NBS/NIST and has become an integral part of many aspects of its research programs. The following articles are designed to give a brief overview of the role of crystallography at NIST — past, present, and future. The articles cover a broad spectrum of topics including structural databases, high-pressure crystallography, neutron crystallography, structure determination via neutron and x-ray diffraction, quasicrystals, reduced cells, magnetic structure determinations, polymer crystallography, electron diffraction, materials properties databases, protein crystallography, novel biomaterials, biological minerals, crystallography of construction materials, and synchrotron radiation. An article on the protein databank is not included as this topic is discussed elsewhere in this newsletter. Finally, more detailed coverage of a few of the articles will be given in a one-day symposium, dedicated to the celebration of this special occasion, at the ACA meeting in Los Angeles.

*Winnie Wong-Ng and Alan D. Mighell*

### *High Pressure Crystallography*

Crystallographic studies began two years after the invention of the diamond anvil cell (DAC) at NBS in 1958. The instrument, developed initially for infrared spectroscopy, was modified in 1960 by Charles E. Weir and Gasper J. Piermarini for x-ray powder diffraction studies. Powder patterns were obtained on materials such as AgI, Bi, Tl, and several alkali halides and rare-earth elements. Compression data were obtained and many materials were shown, for the first time, to exhibit pressure-induced polymorphism.

In 1962, Alvin Van Valkenburg developed a gasket method to confine liquids in the DAC by placing a thin metal sheet containing a small hole with the liquid between the anvil faces. As a result, single crystals could be compressed in a hydrostatic environment in a gasketed DAC. This was very important to crystallography because it led Block, Piermarini and Weir in 1964 to develop a high pressure single crystal x-ray diffraction precession camera technique which utilized a DAC fabricated from Be metal to minimize x-ray absorption effects. For the first time, x-ray intensity data were obtained at high pressures from single crystals of ice VI and ice VII in equilibrium with water at room temperature. An analytical procedure was developed to calculate absorption corrections for the Be cell and it became possible to determine unknown structures at high pressure. The crystal structure of a high pressure polymorph of benzene (C<sub>6</sub>H<sub>6</sub> II) at 2.5 GPa was the first determined by this method. This work was of great importance because it proved that single crystal structure analysis was possible at high pressures utilizing a DAC. The method served as the foundation for later more advanced work with the introduction of automatic diffractometers and miniaturized DACs. In 1971 the group working with the

DAC at NBS invented the ruby fluorescence method of pressure measurement. These achievements, combined with many others at NBS, were, indeed, milestones, for together they ignited and fueled an explosion of activity, not only in crystallography, but in high pressure research in general, by laboratories throughout the world, an activity that continues unabated today.

*Gasper Piermarini and Stanley Block, Materials Science and Engineering Laboratory*

### *Neutron Crystallography at NBS / NIST*

Neutron diffraction at NBS / NIST started soon after the NBS Reactor went critical in the summer of 1969. The first instruments designed for crystallographic work were a low-resolution, single-counter powder diffractometer using radiation from a 220 Cu monochromator with variable take-off angle, mounted on the BT-1 beam port, and a single-crystal four-circle diffractometer at the BT-8 beam port. The development of the Rietveld method of profile analysis increased the range of complexity of the structures soluble with high-resolution powder diffractometers, and decreased the need for single crystals. This trend was felt at NBS / NIST, and the original powder machine was replaced, in rapid succession, first by a five-counter diffractometer of intermediate resolution, and then by the present day 32-counter diffractometer, whose resolution can be varied from low to high.

In parallel with these technical developments, significant improvements were made in the techniques of profile refinement. Revised versions of the original program were written that for the first time included background in the refinable parameters in the model, and that applied general constraints directly (E. Prince, *internal communication*, 1980). In addition, the entire procedure initially proposed by Rietveld (*J. Appl. Cryst.* 2, 65 (1969)) was placed on solid statistical grounds when it was proved that estimates of the parameters and their standard deviations are not significantly different whether the method of refinement uses peak profiles or integrated intensities (E. Prince, *J. Appl. Cryst.* 14, 157 (1981)). The complexity of the crystallographic problems studied at NBS / NIST has increased with time, from early work on simple structures in which light atoms, such as Li, coexist with heavy ones, such as Ta (A. Santoro, R. S. Roth and D. Minor, *Acta Cryst.* B33, 3945 (1977)), to more complicated, multi-phase cases in which the nuclear and magnetic configurations of each phase have to be determined with high precision (Q. Huang *et al.*, *Phys. Rev. B* 61, 8895 (2000)).

Present research focuses on relating crystal structure and physical properties of complex systems analyzed with multiple techniques, ranging from small angle scattering to spin-echo spectroscopy which are available at the NIST Center for Neutron Research. An example which illustrates the advance made possible by the use of modern methods is the determination of the complete crystal structure (including Li in an asymmetric unit of 46 atoms) of RUB-29, a microporous lithosilicate of formula Cs<sub>14</sub>Li<sub>29</sub>(Li<sub>18</sub>Si<sub>72</sub>O<sub>172</sub>)14H<sub>2</sub>O (So-Hyun Park *et al.*, *in preparation*). This material has been analyzed by the combined use of NMR, synchrotron x-ray techniques, and neutron powder diffraction.

*A. Santoro, NIST Center for Neutron Research*

### Magnetic Structure Determinations at NBS/NIST

Magnetic neutron scattering plays an essential role in understanding the microscopic properties of a vast variety of magnetic systems, from the studies of fundamental nature, symmetry, and dynamics of magnetically ordered materials to elucidation of the magnetic characteristics essential in technological applications. From the early days of neutron measurements at NBS/NIST, magnetic diffraction studies have been a central theme involving many universities, industrial and government labs from around the US and worldwide. Such measurements have been used to determine the spatial arrangement and directions of the atomic magnetic moments, the atomic magnetization density of the individual atoms in the material, and the value of the ordered moments as a function of thermodynamic parameters such as temperature, pressure, and applied magnetic field, on single crystals, powders, thin films, and artificially grown multilayers.

There have been hundreds of studies of magnetic structures and ordering at NIST, on wide classes of materials. Early work addressed materials such as spinels and ferrites, followed by rare-earth intermetallics (J. J. Rhyne, *IEEE Magn.* 8, 105 (1972)) and rare earth hydrides. One topic that has sustained interest over the years is the magnetic ordering that occurs in superconductors. The Chevrel-phase superconductors (e.g.  $\text{RMo}_6\text{S}_8$ ) and related compounds typically order antiferromagnetically at low temperatures ( $\sim 1\text{K}$ ), which happily coexists with superconductivity. In the rare and more interesting situation where the magnetic interactions are ferromagnetic, there is strong competition with superconductivity that gives rise to long wavelength oscillatory magnetic states and/or reentrant superconductivity (*Phys. Rev. Lett.* 52, 133 (1984)). The cuprate superconductors (e.g.  $\text{RBa}_2\text{Cu}_3\text{O}_{6+x}$ ) offer new and interesting perspectives into our understanding of “magnetic superconductors” (*High Temperature Superconductors*, Springer-Verlag, 1990)). The rare earth ions order at low temperature similar to “conventional” magnetic superconductors, while in the de-oxygenated, insulating state the Cu spins order above room temperature. In the superconducting regime the rare earth spins still order magnetically, while the Cu spins typically don’t order but rather exhibit quantum spin fluctuations which are thought to play an essential role in the formation of the (*d*-wave) superconducting pairs. Nevertheless, there always seems to be an exception to the rule, and indeed (weak) long range spin density wave order of the Cu spins has recently been observed to develop, at the same temperature as the onset of superconductivity (Y. S. Lee, et al., *Phys. Rev.* B60, 3643 (1999)). Other recent work includes the magnetic structures of the rare earth borocarbides (*Phys. Rev.* B55, 6584 (1997)), and the ordering at 136 K of the Ru moment in the superconductor  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  (*Phys. Rev.* B61, R14964 (2000)).

There has been a natural evolution in the complexity of materials that have been investigated; early work tended to be on relatively simple systems, but as the instrumentation has improved and calculational capabilities expanded, ever more complex structures have been successfully tackled. Magnetic neutron scattering will no doubt continue to play a dominant role for many years to come.

J. W. Lynn, NIST Center for Neutron Research

### Synchrotron X-ray Characterization of Materials

Synchrotron radiation sources provide intense beams of x-rays for leading-edge research in a broad range of scientific disciplines. The NIST Materials Science and Engineering (MSEL) program to characterize materials by means of this powerful probe began in the early 1980s, with the design, construction and commissioning of a monochromatic x-ray topography station (X23A3) at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. This x-ray facility also supported hard x-ray microscopy and parallel-beam x-ray radiography measurements. This early x-ray topography facility was the only dedicated monochromatic instrument of its type in this country. In 1989, an ultra-small-angle x-ray scattering (USAXS) capability was added to X23A3, specifically for the purpose of enabling anomalous ultra-small-angle scattering measurements.

Today, the NIST/MSEL synchrotron radiation program includes the utilization and operation of three additional beam stations at the NSLS. X23-A2 serves a large x-ray absorption fine structure (XAFS), diffraction anomalous fine structure (DAFS), and spectroscopy community; it provides stable scanning of monochromatic x-rays in the energy range from 4.9 keV to over 30 keV. X24A, which is a shared beam station, provides radiation in the 1.2 keV to 6 keV energy range, and is used for standing-wave x-ray measurements. Finally, the U7A station, which is also a joint effort, utilizes XPS and XAS to study the structure and chemical nature of diverse materials from a surface and bulk perspective in vacuum and under atmospheric reaction conditions.

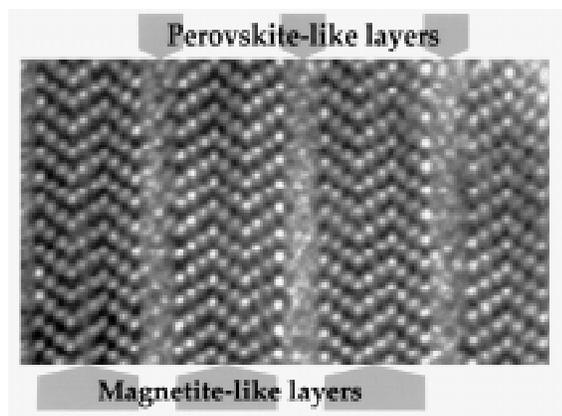
Looking to the future, NIST/MSEL became a partner in 1995 with the University of Illinois at Urbana/Champaign, Oak Ridge National Lab, and UOP, in a collaboration called UNICAT to instrument sector 33 at the Advanced Photon Source (APS) at Argonne National Laboratory. Thus, in 1998, a new NIST USAXS facility was installed and commissioned on the UNICAT undulator beam line, and in 2000 the next-generation x-ray topography experiment was installed on the bending magnet beam line. The emphasis throughout this program is on state-of-the-art measurements on advanced materials. Today, the combined portfolio of NIST facilities at the NSLS and the APS offer measurement capabilities in x-ray microtomography, ultra-small-angle x-ray scattering, high-resolution x-ray topography and XAFS. It also offers opportunities for cutting-edge experiments in structural crystallography and time-resolved structural scattering, surface/interface scattering, diffuse scattering, and magnetic scattering.

G. G. Long, A. J. Allen, D. R. Black, H. E. Burdette, D. A. Fischer, E. Nelson, R. D. Spal and J. C. Woicik

### Electron Diffraction via Transmission Electron Microscopy (TEM)

There are three major advantages in using TEM electron scattering for crystallographic studies: (1) an electromagnetic lens can focus electrons to a fine probe ( $< 10\text{ nm}$ ); thus single-crystal diffraction data can be obtained from a very small volume; (2) the scattering cross section for electrons is  $10^3$ -

$10^4$  as great as for x-rays and neutrons; thus it is possible effectively to detect subtle changes in a structure (e.g., ordering, distortions, short-range ordering); (3) TEM operates in a complementary image mode which enables direct imaging of structures and defects.



An example of structural imaging of the  $Ba_{26}Fe_{20}Ti_{21}O_{98}$  compound. The compound was shown to be an ordered intergrowth between a perovskite-like structure (in its hexagonal form) and a structure related to the magnetite-type block of  $Ba_{12}Fe_{28}Ti_{15}O_{84}$  phase.

Robert S. Roth was first at NIST to realize the possibilities of using TEM structural imaging to study structures of complex oxides. This effort was essential in establishing the important structural principles of crystallographic shear and intergrowth. In the second half of the 1980s, TEM studies of rapidly solidified Al-based alloys by Dan Shechtman resulted in one of the most important discoveries of modern crystallography – quasiperiodic structures (see a separate article in this issue). In 1986 the existence of a quasiperiodic decagonal structure, periodic in one dimension and quasiperiodic (10-fold symmetry) in two dimensions, was established by electron diffraction. Other NIST contributions to the new field of “quasi-crystallography” were (1) determining the m35 point group of the icosahedral phase using convergent beam diffraction and (2) finding the existence of “hypertwins”. Systematic use of TEM in studying complex phase transformations by analyzing domain interfaces allowed one to establish transformation sequences in the form of maximal group-subgroup relationships for numerous systems, including aerospace Ti-Al-Nb alloys and microwave dielectrics oxides  $Ca(Ca_{1/3}Nb_{2/3})O_3$ . With the help of high-resolution structural imaging, initial structural models were established for numerous newly discovered compounds.

L. A. Bendersky, *Materials Science and Engineering Laboratory*

### Crystal Structure Determination Studies

Discovery and development of new technologies has created a continuous demand for new and improved materials. Over the past fifty years, the crystal structure of a large number of phases in diverse areas of materials science have been characterized at NIST using single crystal x-ray and neutron powder diffraction methods. These materials include dielectrics, ferroelectrics, superconductors, microwave materials, magnetic materials, and

materials for optical applications.

The transition metal complexes involving five-member heterocyclic ligand compounds such as pyrazole, imidazole, and 1,2,4 triazole were of interest because of their optical and magnetic spectroscopic properties. These compounds contain more than one active site for coordination, hydrogen bonding, or both, potentially yielding novel structures and interesting spectroscopic properties. Another series of compounds containing boron was solved by Block and coworkers. These compounds included  $NaB(OH)_4 \cdot 2H_2O$ ,  $BaO \cdot B_2O_3$ , and  $PbO \cdot 2B_2O_3$ . In collaboration with the FDA, another branch of studies included a series of biologically important compounds, including a toxic compound in Agent Orange.

Since 1951, Roth and collaborators have maintained a continuous effort in the study of the structures of a variety of niobate, tantalate and titanate dielectric materials, which have potential industrial applications. Other areas of interest included the ionic conductors and PZT compounds. Examples of such materials included  $LiReO_3$ ,  $Li_2ReO_3$  and  $(Ti_{0.75}Pb_{0.25})_4Cl_5$ . In recent years, another important area of research emphasizes the search for new microwave dielectrics for component miniaturization in wireless communications. Various crystals studied so far belong to the systems Ba-Ti-Fe-O, Sr-Nb-Ti-O, Ca-Nb-Al-O, and Sr-Ta-O. Attempts to correlate these structures with physical properties are also being pursued.

The 1986 discovery of high  $T_c$  superconductors placed a demand on the crystallographic studies of new phases. Compounds of interest mainly are in the Ba-R-Cu-O (R=lanthanides and Y) and Bi-Pb-Sr-Ca-Cu-O systems. Examples included detwinned  $Ba_2YCu_3O_{6+x}$ ,  $Ca_2BiO_4$ ,  $Bi_{14}(Sr,Ca)_{12}O_x$ , and  $BaR_2CuO_5$ . Combined x-ray single crystal and powder neutron studies were carried out to understand the detailed structures, particularly the oxygen content.

W. Wong-Ng, R.S. Roth, S. Block, C. Reimann, A. Santoro, V. L. Karen, C.R. Hubbard, A.D. Mighell and, T.A. Vanderah

### Structural Studies of Biological Minerals in Dental Research

The crystallography program at the American Dental Association Health Foundation, Paffenbarger Research Center, National Institute of Standards and Technology was initiated in the early 1970s to provide a broad structural basis for understanding the various chemical phenomena associated with the tooth and bone minerals. Although x-ray powder diffraction was used extensively for the identification of materials and for the study of gross phase/structural changes, the major emphasis was on single crystal structural studies of biological minerals and related compounds associated with or with a potential bearing in mineralization processes. The primary importance was on calcium phosphates, but extended to calcium pyrophosphates, calcium carbonates and calcium bisphosphonates. A large number of highly hydrated magnesium and alkaline earth phosphates and arsenates were also investigated for comparative insights into nucleation phenomena.

Hydroxyapatite,  $Ca_{10}(PO_4)_6(OH)_2$  (OHAp), has been

considered as the prototype for the tooth mineral. However, apatites as they occur in biological tissues, mineral formations and laboratory products can incorporate wide variety of impurities and are seldom found in pure stoichiometric form. We have determined the structures of a number of substituted apatites to evaluate the structural changes associated with the substitution. For example, in a lead apatite, an apparent covalent Pb-O bond may account for the incorporation of Pb into bone mineral. Octacalcium phosphate,  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$  (OCP), is one of the most important calcium phosphates in biological mineralization. The most important role of OCP in biological mineralization is probably that of a precursor to other phases found in biological settings, especially defect OHAp. OCP has a layer type structure, with one layer quite similar to that of apatite and the other, a hydrated layer consisting of more widely spaced Ca, and  $\text{PO}_4$  ions and all the water molecules. The closeness of fit in the apatitic layer accounts for the epitaxial, interlayered mixtures formed by these two compounds which may account for the variation in Ca/P ratios in biological apatites. The crystal chemistry of OCP has been extensively investigated to illustrate how OCP affects the growth mechanisms, impurity-defect content, morphology, stoichiometry and other properties of OHAp. Dicarboxylate ions incorporated in the hydrated layer of OCP offers another mode of OCP involvement in biomineralization.

Our structural studies have shown that a number of calcium phosphates fall into class of glaserite compounds. Both  $\alpha$  and  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  belong to this class and can accommodate Mg ions in their structures affecting their relative stabilities. The mineral whitlockite, found in dental calculus, has a structure very similar to that of Mg-substituted  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ . The work was supported by NIDR grant DE05030 to ADAHF, and NIST.

*Mathai Mathew and Shozo Takagi, ADAHF- PRC, Polymers Div.*

### **Protein Crystallography at NIST**

Protein crystallography came to NIST during the mid 1980s, just before the old Bureau of Standards got its new name and broader mission in 1988, and before the Biotechnology Division was established in 1991. NIST's neutron source provided a key initial impetus for protein crystallography, during an era when X-ray sources and detectors were still rare and unreliable. The opportunity for neutron studies of ribonuclease and insulin crystals helped to attract some of the first protein crystallographers to NIST, including Alex Wlodawer (now at NCI), David Davies (NIH), and Gary Gilliland, who was hired in 1986 and now heads the Biotech Division.

Another key development for protein crystallography at NIST was the creation of CARB, the Center for Advanced Research in Biotechnology. With a central concept of industry-driven protein structural research, CARB was born at NIST in 1985. By 1989 CARB had grown into an alliance between NIST and the U of Maryland Biotechnology Institute, with a new laboratory building built on land contributed by the county, 5 km south of NIST. Although an x-ray diffractometer for protein work operated at NIST for a few years during the late 1980s, ever since 1989 the CARB laboratory has housed the equipment for NIST

protein crystallography. This creates a minor inconvenience for researchers driving between the two campuses, but a rich cross-fertilization of ideas among the various NIST, university, and industrial elements.

Macromolecular crystallography is now an essential discipline of biology, and is increasingly important at NIST as groups outside of structural biology see growing industry involvement in biomolecular structure and seek structural knowledge regarding their own projects. NIST's recent involvement in the Protein Data Bank and expansion of its Biomolecular Crystallization Database functions underscores the increasing importance of this field to NIST. It is likely that future developments will include expanded research in areas such as the measurement of quality and accuracy of structures, measurements of basic physical processes underlying crystal growth, crystal freezing, and protein diffraction, and methods of structure determination.

*Travis Gallagher, Biotechnology Division*

### **Structural Studies in the NBS/NIST Polymers Division up to the Year 2000**

Most scientists, let alone the general public, are unaware that the synthetic polymers (commonly called "plastics") that are ubiquitous in our everyday lives are nanocomposites made up of tiny crystallites embedded in a matrix of amorphous material. The industry that tailors materials properties by using sophisticated processing to define crystallinity and microstructure is a huge one. For this reason the characterization of microstructure has been an important ongoing activity within the NBS/NIST Polymers Division since its earliest times. The level of effort devoted to structural studies has waxed and waned with changing fashions in polymer research.

There have been only a couple of instances in polymeric materials where "conventional" crystallographic methods have been applied to define atomic arrangements within unit cells. Crystal structure has been an important input to studies in spectroscopy and physical properties of a variety of polymeric.

Following upon the heels of the discovery of chain folding in solution-grown polymer single crystals, the 1960s and 70s saw considerable NBS activity aimed at defining the kinetic behavior of the crystallization process and the resulting morphology. In the 1980s x-ray facilities were commissioned to examine structure-property relationships using wide-angle orientation texture and small-angle scattering. At about the same time small-angle neutron scattering emerged as a tool of choice for characterizing phase behavior in block copolymers, semicrystalline polymers, and molecular structure in interpenetrating polymer networks and hyperbranched polymers. More recent times have seen the beginnings of work using synchrotron SAXS. The challenges that will face the polymer materials science community in the second century of NIST's history cannot yet be foreseen, but one can be certain that scattering and diffraction methods will be as vital as ever.

*John D. Barnes, Polymers Division*

### *Databases and Computation in Modern Structural Science*

Dreams are important in driving new technology, and materials design is no exception. Today advanced computational technology is advancing our dream of designing new materials from first principles. Or is it? I would argue that the dream is not to assemble  $10^{22}$  to  $10^{23}$  atoms of various quantities, and let the computers determine optimal structure and derive properties from that structure. Instead, I believe the dream for the coming decades is to couple computer power with comprehensive structural databases and data exploitation (data mining) methods to develop new leads for materials to be optimized according to the requirements of specific applications

Materials design and development rarely starts with a blank computer screen. The projected application guides us to certain materials classes through experience, broad knowledge of material potentiality and creative thinking. The process almost always involves a general or specific application. Modern material science has opened the range of possibilities considerably over the last thirty years. Composites, advanced processing and finishing, and new manufacturing techniques are examples. At the same time, new approaches, such as materials selector software, open new avenues of interest. The ability to screen materials classes on the basis of a few desired properties is proving to be quite popular. Yet the process of materials design does not stop with the selection of a traditional or new material. Almost always, there is a need to optimize some aspect of a selected material. The considerations can take place at many different levels – atomic, cluster, microstructure, surface, etc. Where do modern structural databases fit in with this scheme? Where does computation support it?

Modern structural databases (e.g., the Inorganic Crystal Structure Database (ICSD)) provide a comprehensive and quality-controlled depository of data on the full structure of crystalline compounds. The ICSD now contains structural data on over 50,000 inorganic compounds that usually fall into a few structure types. Searching for new materials leads is facilitated by investigations of compounds in the same structure type. However, we can go further. Using new data mining techniques, the ICSD may yield additional structure-property correlations beyond the current structure type classifications. The real purpose of both database exploitation and computation is not to create data for every possible structure, but to generate ideas for structures in general, and specific structures as needed. The design and development of new engineering materials is a process of getting new ideas and gradually transforming those ideas into a real material, suitable for an application. Structural databases and structure computation will soon replace experimentation as the major source for the new ideas. Indeed, the real materials of tomorrow will come from the virtual materials of today.

*John Rumble, Jr., Standard Reference Data Program*

### *Crystallographic Data in the NIST Standard Reference Data Program*

All fields of experimental science generate numerical data in some form. Since the useful lifetime of these data is very long, and the volume of production continues to accelerate, data management is a significant issue. It is wasteful to repeat

measurements out of ignorance of what has already been measured and reported in the literature. Intelligent planning of new research often depends on a foundation of existing data. Thus every field of science should be concerned with the collection and organization of the data it produces.

Crystallographers have been at the forefront of science in this regard. Over the years, many outstanding crystallographers have dedicated portions of their careers to the exacting and unglamorous task of systematizing the data on crystal structures. In particular, the crystallographic community has led the way in applying modern computers to scientific data management. Today, a vast amount of crystallographic data can be accessed quickly and reliably by electronic means.

The National Bureau of Standards (now the National Institute of Standards and Technology) has played a key role in this process. The NBS Crystal Data Center was one of the charter data centers when NBS established the Standard Reference Data program in the mid 1960s. Under the SRD program, a productive collaboration between NBS and the Cambridge Crystallographic Data Centre has continued for more than 30 years. A close collaboration between NBS and the Joint Committee on Powder Diffraction Standards/International Centre for Diffraction Data also continues. NBS/NIST crystallographers have made important contributions to the development of software for evaluation and retrieval of crystal data. The Single Crystal (nonstructural) Database that they maintain is a comprehensive scientific numerical database with crystallographic data on all classes of materials. Most recently, the NIST Standard Reference Data program has joined in collaborative efforts with respect to the Inorganic Crystal Structure Database and the Protein Data Bank. Crystallography has been a key element of the SRD program and will undoubtedly continue to be in the future.

*David R. Lide*

### *The Inorganic Crystal Structure Database*

Crystallography has a long and successful history of self-organization and was one of the first areas to create numerical scientific databases. Virtually all structure determinations have been archived in databases that allow ready access and complete coverage. Crystallographic databases and computational archives support research on a daily basis for thousands of scientists worldwide. The crystalline structure of inorganic materials is of interest to analysts in areas such as materials design, properties prediction, and compound identification.

The Inorganic Crystal Structure Database (ICSD) contains full structural and bibliographic information for all structures from 1915 through the present. There are more than 50,000 entries in the current version and approximately 2500 new entries are added per year. Data items include bibliographic information, such as the article title, authors' names and literature citation; compound designation, such as chemical name, chemical formula, mineral name; and crystallographic parameters, such as unit cell, space group, element symbol with numbering, oxidation state, multiplicity for Wyckoff position,  $x,y,z$  coordinates, site occupation, thermal parameters and reliability index  $R$ , among others. The data are evaluated by experts in specific disciplines and by specialized computer programs.

Several types of evaluation are performed, including examination of an individual data item, looking for consistency within a complete entry, and checking the relationship of an individual entry to the entire database.

Over recent years, FIZ and NIST have been building a modern infrastructure for the Inorganic Crystal Structure Database. This has included a complete re-design of the ICSD database structure, conversion and loading of the data into a relational database management system, designing graphical user interfaces to access the data, and creating scientific application modules to analyze the results of a database search. The ICSD is marketed through a variety of computerized media which include both PC and Web-accessible versions of the database. The new Windows-based graphical user interface for the ICSD is tabular in design, allows for searching in five general categories of Chemistry, Crystal Data, Reduced Cell, and Reference Data, and will include enhanced features for the characterization of materials based on lattice and chemistry search modules, and 3-dimensional visualization and powder pattern simulation of inorganic structures.

Anticipating the needs of the materials community in both science and industry, the ICSD is helping scientists use crystallographic data models to visualize, explain and predict behavior of chemicals and materials. With increasing use comes an increasing range of computational techniques to analyze and correlate data, and to help researchers concentrate experimental work in directions that optimize the discovery process. Interoperability with other data sources and software tools appears to be one of the emerging driving forces for innovation today.

The Inorganic Crystal Structure Database is produced cooperatively by the Fachinformationszentrum (FIZ) (Karlsruhe <http://www.fiz-karlsruhe.de/>) and NIST (<http://www.nist.gov/srd/>)

Vicky Lynn Karen, Materials Science and Engineering Laboratory

### *NIST Materials Properties Databases for Advanced Ceramics*

The anisotropy of any physical property of a single crystal must be consistent with the observed symmetry in the physical structure of the crystal. By extension, anisotropy in the properties of polycrystalline materials should be correlated with the degree of texturing in the sintered body. Both crystal structure and texturing have important consequences for the behavior of materials subjected to external stimuli (temperature, pressure, and electromagnetic fields). Furthermore, structural data from crystallographic studies can be used to determine the coefficients of thermal expansion which, in turn, can be used in the evaluations of axial and volumetric derivatives of physical properties. Consequently, crystallography plays a central role in classifying and understanding the physical behavior of solid materials, and the associated data form a useful basis from which to study and pursue the development of new materials.

As a result, the NIST Standard Reference Databases (SRD) for high temperature superconductors (HTS, SRD Number 62) and structural ceramics (SCD, SRD Number 30) include a full complement of crystallographic data (crystal system, space group,

the unit cell parameters, the relative atomic coordinates  $x$ ,  $y$ , and  $z$ , and site occupancy numbers), along with the principal thermal (expansion, conductivity, diffusivity, and specific heat) and mechanical (elasticity, strength, hardness, toughness, and creep) properties. The HTS database also includes electromagnetic (resistivity, surface resistance, magnetic susceptibility, penetration depth, Hall coefficient, and thermoelectric power) and critical superconductor ( $T_C$ ,  $J_C$ ,  $H_{CP}$ ,  $H_{C2}$ , and  $H_{C3}$ ) properties.

The crystallographic data serve several functions in these databases. The data sets themselves are, of course, part of the reference information characterizing the materials and may be used for purposes of identification. Conversely, crystallographic data may be specified as part of the criteria when searching the database for properties of particular materials. These data also are used both in data evaluation efforts, to help ensure that only data from comparable materials are being analyzed together, and in developing or applying models of material behavior. Many physical properties depend significantly on the phase compositions of the constituent particles, the interface or grain boundary regions, and the possible surface layers. Similarly, the size, shape, and distribution of pores, which may be treated formally as a secondary phase, can have a dramatic influence on property values. Crystallographic data often provide the key to understanding the effects of phase composition and porosity in terms of structural features in the material.

R. G. Munro, Ceramics Division

### *Phase Equilibria Research*

Since the 1930s, NIST has collaborated with various industries on phase equilibria research. One of the first phase equilibria studies at NIST was by McMurdie et al. on the relation of MgO to Portland cement compositions. This was followed by the study of the PbO-SiO<sub>2</sub> system for its relation to glazes for whiteware.

Roth and his coworkers started phase equilibria studies of dielectric materials in the 1950s, with focus on the tantalate, niobate, titanate and tungstate systems, and their chemistry with rare-earth oxides. Phase relations have also been determined in the technologically important PZT-containing (PbZrO<sub>3</sub>-PbTiO<sub>3</sub>) system. A number of phases in the Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> systems later became sought-after piezoelectric materials. Since the mid-nineties, the emphasis has been shifted to microwave dielectric materials (Vanderah and Roth). Systems being investigated included BaO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>, SrO-TiO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub>, SrO-Al<sub>2</sub>O<sub>3</sub>-Nb<sub>2</sub>O<sub>5</sub>, and CaO-Al<sub>2</sub>O<sub>3</sub>-Nb<sub>2</sub>O<sub>5</sub>. Among the new phases discovered, a significant finding pertains to the dielectric properties of compositions prepared between Ca<sub>3</sub>Nb<sub>2</sub>O<sub>8</sub> and Ca<sub>2</sub>AlNbO<sub>6</sub>, which have relatively high dielectric constants and quality factors, and can be tuned to having near-zero temperature coefficients.

Since 1986, NIST has been involved with the EPRI and later the DOE programs in phase equilibria research of high T<sub>c</sub> superconductor systems. Following Roth's studies of the Ba-Y-Cu-O system, Wong-Ng and Cook investigated the phase transformation of BaR<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> (R = lanthanides and Y), and also the phase diagrams in the AO-R<sub>2</sub>O<sub>3</sub>-CuO (A = Ba, Sr) systems which are related to the development of coated

conductors. To provide basic information for the wire and tape development using Ag powder-in-tube techniques, multi-component phase diagrams of the Bi-Pb-Sr-Ca-Cu-Ag-O system have been successfully studied.

The compilation of published phase diagrams was started in 1933 and it was published by the American Ceramic Society (ACerS). This started a continuing relation between NBS and ACerS and has resulted in the publication (Roth, Cook, Ondik, and Vanderah) of 12 volumes of compilations and several volumes in special areas.

*R.S. Roth, H.F. McMurdie, T.A. Vanderah, H. Ondik, L.P. Cook, and W. Wong-Ng*

### **The NIST/CARB Biological Macromolecule Crystallization Database**

The Biological Macromolecule Crystallization Database (BMCD) was developed at NIST to assist crystallographers in developing strategies for crystallizing biological macromolecules. The database summarizes the information concerning crystallization that is available in the literature. The BMCD was established in 1989 with assistance from the National Institute of Standards and Technology (NIST) Standard Reference Data Program [Gilliland, G. L. (1988). *J. Crystal Growth* 90, 51-59]. At this time, the BMCD software was developed as an independent program for personal computers (PCs). Access to the data was provided through menu-driven software that allowed browsing and searching of the crystallization conditions of 1025 crystal forms of 616 biological macromolecules. The information, which included most of the crystallization protocols of biological macromolecules in the literature through the end of 1982, had been previously deposited in a formatted ASCII file in the Protein Data Bank.

In 1991 the second version of the BMCD software and data was released. The data included 1465 crystal forms of 924 biological macromolecules. In 1994 the BMCD became the NASA Protein Crystal Growth (PCG) Archive and incorporated data from crystal growth studies supported by NASA. The new software and data were released as Version 3.0 of the BMCD. The number of crystal entries was increased to 2218 for 1465 biological macromolecules.

Version 3.0 of the BMCD was subsequently ported to a UNIX platform to take advantage of the development of network capabilities that employ client-server tools. The first web implementation of the BMCD provided many of the features of the earlier PC versions of the BMCD. The searching capabilities and the data were increased in release 2.0 of the BMCD web software that now includes 3546 crystal forms for 2526 macromolecules. The current web implementation is available at <http://wwwbmcd.nist.gov:8080/bmcd/bmcd.html>. To facilitate the updating process, the current implementation provides a beta-test version of software that users can employ to submit their crystallization data directly to the BMCD. The BMCD's primary goal will continue to be an error-free and up-to-date crystallization database. The availability of the NIST BMCD on the Internet will facilitate the distribution and error correction of the data. Alternative ways for users to search, use and display the

data will continue to be added making it a useful resource for the macromolecular crystallographer.

*Gary L. Gilliland, Michael Tung, and Jane E. Ladner*

### **The NBS-JCPDS/ICDD Research Associateship Program**

The NBS-JCPDS/ICDD Research Associateship program at NBS/NIST was a long standing (1949-1986) successful industry-government cooperation to produce high quality x-ray powder diffraction reference patterns to be included in the Powder Diffraction File (PDF). Today the JCPDS/ICDD is known as the International Centre for Diffraction Data (ICDD). The PDF is a continuing compilation and the only comprehensive source of reference patterns gathered from many sources, and is widely used for phase identification and materials characterization.

The Associateship was established at NBS/NIST in July 18, 1949 to prepare high quality powder x-ray diffraction reference standards. In the early years, the Associateship was directed by H.F. McMurdie, and in the 70s and 80s by C.R. Hubbard. Their leadership ensured the quality of the patterns, as well development of state-of-the-art computer technology and x-ray diffraction instrumentation. The standard patterns were produced –by M.Morris, E. Evans, J. DeGroot, H. Swanson and others– using reproducible, controlled conditions of specimen preparation and the best recording instrumentation available. The consistent high quality of the patterns produced has been an integral foundation of the Powder Diffraction File (PDF). These patterns were also published in the NBS Monographs (21 volumes), products derived from the PDF, as well as the early issues of the *Powder Diffraction*. The Associateship was also involved in the implementation and testing of the computer software (led by Hubbard, A.D. Mighell, J.K. Stalick and N. Pyrrros) necessary for data collection and reduction, least-squares refinements and editorial processes. Concurrent with the Associateship efforts NBS also certified a number of Standard Reference Materials for use as internal standards and for improving powder diffraction analysis (SRM640, 640a, 640b, 660, 676, and 1874).

With the expanding capability for others to accurately measure and report XRD reference patterns, the mission of the JCPDS/ICDD Research Associate program was accomplished in 1986. A three-year program at NBS to produce high quality x-ray patterns of important ceramic phases followed. Further collaborations continue through the ICDD Grant-in-Aid program (W. Wong-Ng, and J. Kaduk of BP-Amoco), with emphasis on materials for electronic applications.

*H.F. McMurdie, C.R. Hubbard (ORNL), W. Wong-Ng*

### **Standard Reference Material™ for Single Crystal Diffractometer Alignment**

The importance of the investigation of the accuracy and precision of lattice parameters measured in the industrial, academic and government x-ray laboratories were recognized by the IUCr, ACA, Hauptman-Woodward Medical Research Institute (HWI), and NIST. As a result, two related projects have been developed: an international round robin study of a potential

alignment standard, and the certification of this material as a standard Reference Material™ (SRM).

The international round robin project was launched by distributing to various laboratories 50 sets of a ruby sphere along with a zeolite reference crystal through the Hauptman-Woodward Medical Research Institute. The results of this project confirmed that well-aligned diffractometers are important for obtaining accurate lattice parameters, and that the ruby spheres satisfy the



*W. Wong-Ng, T. Siegrist (Lucent), G. DeTitta (HWI), L. Finger (Geophysical Lab), H. Evans (US Geological Survey), E. Gabe, G. Enright (NRC, Ottawa), J. Armstrong, M. Levenson, L.P. Cook, and C.R. Hubbard (ORNL)*

criteria required of a SRM. Through extensive international collaborations, the ruby sphere SRM1990 has been certified. The primary technical objective of this SRM was to provide world-wide laboratories with an alignment standard to improve the accuracy of lattice parameter determination. These rubies are rhombohedral, with space group R3c. The certified room-temperature unit cell parameters ( $a/\text{Å} = 4.76080 \pm 0.00029$ , and  $c/\text{Å} = 12.99568 \pm 0.00087$ ) agree with the round robin data and are also supported by the Guinier-Hägg transmission data. The results of this work are expected to have a significant impact on accurate scientific investigations using single crystal diffractometers. These standards will be available in the near future at the SRM Office of NIST. The Web site for information is <http://www.nist/srm>

### ***A Natural Bone Cement – A Laboratory Novelty Led to the Development of Revolutionary New Biomaterials***

In the early 1980s, Brown and Chow of the American Dental Association Health Foundation Paffenbarger Research Center (PRC) at the National Institute of Standards and Technology (NIST) conducted studies on calcium phosphates aimed at developing remineralizing pastes for repairing early dental carious lesions. Based on the solubility properties of calcium phosphates, they formulated mixtures containing tetracalcium phosphate (TTCP) and dicalcium phosphate anhydrous (DCPA) or TTCP and dicalcium phosphate

dihydrate. Upon addition of water, these mixtures would rapidly form hydroxyapatite (HA), the major component of tooth mineral, at body temperatures. It was observed that some of the pastes became a hardened mass when left in test tubes for a few hours. Thus, the PRC scientists inadvertently discovered a new type of self-hardening cements that consisted of only calcium phosphates and formed HA as the only product.

By optimizing the particle size distributions of the cement ingredients, the scientists were able to develop cements with setting times of about 30 min and compressive strengths of 34 MPa (WE Brown and LC Chow, *Cements Research Progress* 1986, pp352 (1987)). From animal studies conducted at Northwestern University, Costantino and coworkers (PD Costantino et al., *Arch Otolaryngol Head Neck Surg* 117, 385(1991)) found that when implanted in bone defects, CPC was gradually resorbed and replaced by new bone. Dense and porous ceramic HA materials, which have good biocompatibility, have been used clinically for repairing bone defects. However, because these materials do not resorb, they must be used in granular forms to allow a blend of soft and bone tissues to form interstitially with the HA granules to achieve stable implant-tissue integration. This has limited the use of ceramic HA to repairing small defects in bone. In contrast, because of its self-hardening and *in vivo* resorption properties, CPC has the potential to be useful in a much wider range of clinical applications.

Continued research conducted by PRC scientists at NIST has resulted in many significant improvements in CPC. In July 1996, a CPC consisting of TTCP + DCPA was approved by the Food and Drug Administration for repair of cranial defects in humans, thus becoming the first material of its kind available for clinical use. CPC has become a subject of great interest to many scientists and clinicians worldwide, and several additional CPC products are now commercially available. With continuing improvements in cement properties and understanding of material-tissue interactions under various clinical situations, different CPC formulations with properties optimized for specific clinical applications are being developed.

*Laurence C. Chow and Shozo Takagi, ADAHF-PRC, Polymers Div.*

### ***Quasicrystals***

When, in 1982, Dan Shechtman produced an electron diffraction pattern from a rapidly solidified alloy with sharp spots that apparently had icosahedral point group symmetry,  $m-35$ , other members of the NBS staff were skeptical. After all, sharp diffraction is the consequence of periodicity. Conversely, it was thought impossible to have sharp diffraction from any aperiodic structure, and no structure with icosahedral symmetry could be periodic. Shechtman's pattern had to be produced by some peculiar kind of twin. But Shechtman had conducted several other careful experiments that ruled out any possibility that the observations could be explained by twinning. (Unless you believe that, for example, hexagonal close packed structures exist only as a periodic twinning of a face centered cubic structure.)

The level of skepticism was much reduced, within the NBS staff at least, if not in the broader crystallographic community, when it was demonstrated mathematically that there could be an underlying quasiperiodicity in the so-called Fibonacci sequence,

a discrete Fourier transform where the “orders” were not integers, but rather powers of the “golden mean,”  $\tau = (1 + \sqrt{5})/2 = 2 \cos 36^\circ$ . Further, it was demonstrated theoretically and confirmed experimentally that the aperiodic Penrose tilings would produce optical diffraction patterns with sharp spots having fivefold rotation symmetry. The mathematics of pentagonal or icosahedral quasiperiodicity predicts that the diffraction spots go out in reciprocal space by successive factors of  $\tau$  (in contrast to what would be expected from twinning) and get stronger, exactly what is observed experimentally. One of the important characteristics of quasiperiodicity is that it can always be described as periodic in a higher dimension, and diffract discretely in that and lower dimensions. The skeptics notwithstanding, thousands of papers, studying more than a hundred different metallic systems, have established not only that quasicrystals exist, but that they occur with other “noncrystallographic” symmetries, including five-, eight-, ten-, and twelve-fold axial systems, and that large stable quasicrystals can be grown with a high degree of perfection.

Many metallic systems exhibit sequences of periodic approximants with ever larger unit cells that converge to the observed true quasicrystals. The Patterson functions of all these structures are quite similar to one another and to those of the true quasicrystals. A number of “quasicrystal structure determinations” have been made, using methods of hyperspace crystallography. A few years ago the IUCr changed the definition of crystal based on discrete diffraction, so that these “quasiperiodic crystals,” or quasicrystals for short, are now included among crystals. There continue to be extensive studies of this fascinating extension of crystallography.

*J. W. Cahn and E. Prince, Materials Science and Engineering Laboratory*

### **The Fundamental Role of Reduced Cells in Crystallography**

In theory, physical crystals can be represented by idealized mathematical lattices. Under appropriate conditions, these representations can be used for a variety of purposes such as identifying, classifying, and understanding the physical properties of materials. Critical to these applications is the ability to construct a unique representation of the lattice. The vital link that enabled this theory to be realized in practice was provided by the 1970 paper on the determination of reduced cells by A. Santoro and A. Mighell (*Acta Cryst.* A26, 124 (1970)). This seminal paper led to a mathematical approach to lattice analysis initially based on a systematic reduction procedure and the use of standard cells. Subsequently, the process evolved to a matrix approach based on group theory and linear algebra that offered a more abstract and powerful way to look at lattices and their properties.

Application of the reduced cell to both our database work and our laboratory research at NIST was immediately successful. Currently, this cell is widely used: (i) as a standard cell for the reporting of triclinic crystals, (ii) in crystallographic database work (iii) in symmetry determination because of the close link between metric and crystal symmetry (A. Mighell, A. Santoro, and J. D. H. Donnay, *International Tables for X-ray Crystallography*, Vol. 1, 530 (1969)) and *Acta Cryst.* A36, 321(1980)), and (iv) for identifying crystalline materials (A.

Mighell, *J. Appl. Cryst.* 9, 491 (1976)). Today the scientific community routinely uses this identification strategy, as it has been integrated into commercial X-ray diffractometers.

Due somewhat to serendipity, the most significant and lasting value of this work is probably not reduction itself. Rather, reduction has played a key transition role in helping to move the discipline of crystallography in new directions with new insights. The research on reduction proved that there are excellent reasons for looking at the crystal lattice from an entirely different point of view. Consequently, with time, many other lattice-related papers followed, including papers on sublattices and superlattices, composite lattices, coincidence site lattices, and lattice-metric singularities in the indexing of powder patterns. At NIST, the mathematical analysis of lattices was pursued further and evolved to a matrix approach that offered a more abstract and powerful way to look at lattices and their properties. The matrix approach, in particular, has many applications, including for example, symmetry determination (V. L. Karen (Himes) and A. D. Mighell, *Acta Cryst.* A43, 375 (1987)).

*Alan D. Mighell, Materials Science and Engineering Laboratory  
Ceramics Texture Research at NIST*

The impetus for texture research in the Ceramics Division came from American Superconductor Corporation, Westborough, MA, (ASC) in 1994. During product development, ASC needed to do rapid, accurate crystallographic texture measurements on the high temperature superconducting wires (or “tapes”) they were manufacturing. Their goal was to correlate the observed texture with measured electrical and mechanical properties, which are known to be strongly influenced by texture. A major requirement was that the texture measurement technique could be performed using the conventional x-ray powder diffractometer available at ASC. A technique was developed at NIST for quantitative measurement of texture using scans performed on a conventional diffractometer; the scans can be obtained in about one hour. The data analysis method uses the technique of calculating the hkl omega scan from an untextured sample of the material being tested using a  $\theta$ - $2\theta$  scan of the sample over the hkl peak. The experimental omega scan from the textured sample is divided by the calculated omega scan to give the texture profile of the sample. The technique is best suited to the analysis of fiber texture. The software to perform the calculations of the analysis, TexturePlus, was developed at NIST. The technology was validated at NIST using SRM676 (untextured alumina) and successfully transferred to ASC in 1995.

It became clear that there were many potential users of this method in industry, particularly small businesses, and academia. As part of the thin film program, the technique was extended to analysis of diffraction data from thin films, where the thickness and linear x-ray absorption coefficient of the film were necessary input data. Validation of the thin film correction was achieved in 1998 with data obtained from electrodeposited films of copper, which are being introduced into chip interconnection technology as a replacement for aluminum. The software package TexturePlus was made available on the World Wide Web in 1999 on <http://www.ceramics.nist.gov/webbook/TexturePlus/texture.htm>. A workshop on Texture in Electronic Applications was held at NIST Gaithersburg in October 2000, attended by

about 40 researchers from industry, academia and national laboratories. At this meeting, the need for NIST to facilitate interlaboratory comparisons became apparent and will be the focus of future efforts.

*Mark D. Vaudin, Ceramics Division*

### ***Crystallographic Support for the Free Radical Research Program***

In 1956, the imaginative Herbert Broida, backed by the steady experimenter, Arnold Bass, proposed a basic research program to investigate atoms or very small molecules, with an unpaired electron in their outer shells, trapped in a solid matrix at low temperatures. The result of this proposal was the NBS Free Radical Program. Its concepts were supported not only by the NBS management, but also by the Department of the Army, as funding agency, as well as by several private-sector companies. Within the three-year duration of the Program, more than a hundred publications were produced.

Howard McMurdie, leading the NBS Crystallographic Section, responded by making equipment and personnel available. A liquid-helium cooled sample holder was built and fitted with beryllium windows to permit soft X-rays powder data to be recorded by a diffractometer. The detailed description of this apparatus by F.A. Mauer (in A.M. Bass and H.P. Broida, *Formation and Trapping of Free Radicals*, chapter 5, 117 - 167, Academic Press, New York and London (1960)) remains a good "beginners" introduction to low-temperature crystallography with sections on thermometry, calibration, vacuum technique, and gas handling features.

The X-ray diffraction studies and their crystal-chemical implications are described by H.S. Peiser (in A.M. Bass and H.P. Broida, *Formation and Trapping of Free Radicals*, chapter 9, 301 - 326, Academic Press, New York and London (1960)). At the outset he stressed the fundamental limitations: small concentrations of free radicals, the small diffracting power of hydrogen and the use of powder diffraction with limited texture-determining features. Nevertheless, the crystal structures of the matrices could thus be recorded and any influence of the free radicals was likely to be observable during deposition of the radicals and on warm-up of the conglomerate, when strongly exothermic reactions occurred. Pure argon and nitrogen deposited at 4.2 K showed considerable line broadening, indicating disordering which disappeared exothermically on annealing with formation of good crystals. Their structures were retained on re-cooling, enabling good cell-edge and coefficient-of-expansion measurements to be recorded. Evidence for a reported lack of a center of symmetry in cubic  $\alpha$ -nitrogen was absent. The evidence supported the space group  $Pa\bar{3}$  with  $a/\text{\AA} = 5.644 \pm 0.005$ .

*H. Steffen Peiser*

### ***Crystallography of Construction Materials***

Portland cement concrete over the past 100 years has become a ubiquitous construction material, with an annual consumption

at about 5 Pg (5.5 billion tons), second only to water in per-capita demand. The flexibility in application and speed of construction afforded by concrete has resulted in it largely supplanting other materials in construction of pavements, homes, and high-rise buildings. Improved understanding of the materials science of portland cement and concrete has come through increased knowledge of the chemistry and crystallography of the constituent materials; the clinker phases, cements, and cement hydration products.

NIST/NBS researchers have played an integral part in developing this understanding of portland cements. Work on the chemistry of portland cement clinker phases at NBS in the early 20<sup>th</sup> century (by P.H. Bates and A.A. Klein, Bureau of Standards Technol. Papers No. 78, 1917) demonstrated that  $3\text{CaO}\cdot\text{SiO}_2$ , or alite, was one of the primary constituents, as postulated by Henri LeChatelier. They also investigated the hydraulic properties of cement compounds in one of the first studies that addressed the relationships between cement performance and composition. Around 1925, the Portland Cement Association (PCA) sponsored a Fellowship at NBS that lasted until the mid-1960s. Researchers at NBS, including those who held the PCA Fellowship, were instrumental in forming the foundation of today's knowledge of portland cement chemistry.

Examination of the relationships between clinker phase constitution, individual phase solid solution, and reactivity of cements were a continuing theme of the work at NBS. At the same time, the chemistry and structure of hydration products were the subject of many studies. Work today at NIST is directed toward understanding the relationships between clinker composition and cement performance, and to better understand the newer blended cement systems. These studies build on the long history of cement science at NBS/NIST over the last century, combining them with recent computer modeling technology to deliver a virtual cement and concrete laboratory to the desktop that will aid in evaluating and optimizing cement-based materials.

*Paul Stutzman, Building Materials Division*