Final Technical Report-Grant # DE-FG02-97ER45628 "Structural Diorder in Materials"

1.0 Introduction

Since the grant was renewed in 2000 and 2003 final technical reports of the grant have been previously submitted for those years. For that reason this final technical report covers the last four years of the grant. We had an exceptionally successful and productive last four years under the support of the grant. Our progress takes three different aspects, described in more detail below: **1.1** instrumentation, infrastructure, and other research support at Sector 20 of the Advanced Photon Source (APS); **1.2** research on which Profs. Stern or Seidler were PI's; and **1.3** research on which Profs. Stern or Seidler were co-PI's or where Drs. Dale Brewe or Julie Cross were authors or co-authors. Drs. Brewe and Cross are the two research scientists (permanently stationed at sector 20) who are supported by the grant. They provide support to the scientific goals of the grant and more broadly provide research support for many general users at Sector 20. Finally, in section **1.4** we provide a complete list of publications resulting from funding in the grant on which at least one of Stern, Seidler, Cross, or Brewe were co-authors. Given the inclusion of operations funding in the grant, this is of course a subset of the full scientific impact of the grant.

1.1 Instrumentation, Infrastructure and Research Support at Sector 20, Advanced Photon Source

During the grant term, the funding has been split between the support of the research of the PI's and the more general support of research and operations at Sector 20 of the Advanced Photon Source (APS). Because of the DOE's recent decision to centralize to the APS future funding of present-BES-supported CATs' operations and general user support, we will only briefly summarize the present general state of operations at Sector 20, and then proceed to discuss in more detail only the specific issues most relevant for this (non-operations) renewal proposal.

After over a decade of concerted effort by Prof. Stern and his collaborators at UW, SFU and PNNL who have helped to form the Pacific Northwest Consortium Collaborative Access Team (PNC-CAT), sector 20 of the APS is now fully instrumented and operational, and has been accepting general users at both the ID and BM beamline for several years. In the last four years, funding from the grant has supported the research of Profs. Stern and Seidler, including their research students and post-docs who are listed in **1.1.3**, general and specific instrumentation at sector 20, and also two beamline scientists, Drs. Dale Brewe and Julie Cross, who have played a significant role in the research of the PI's, the research of many other members of PNC-CAT and general users, and the fabrication and operations of the beamline facilities.

While it is technically appropriate to expound on the broadly–successful development of Sector 20 by Prof. Stern (as director of PNC-CAT) and his collaborators (including Prof. Seidler, a member of the executive board of the PNC), we will instead focus on the aspects of the recent progress which are most relevant for the proposed research of (only) the PI's for the next funding cycle.

In the sections **1.1.1** and **1.1.2**, we provide detailed descriptions of two new (and novel) pieces of instrumentation recently developed at Sector 20 by the PI's – it is the special capabilities of these instruments which will be aggressively mined in future Sector research: high-throughput endstations for time-resolved XAFS and for q-dependent measurements of non-resonant x-ray Raman scattering.

1.1.1 High-throughput Endstation for Time-resolved XAFS

We have developed a unique time-resolved x-ray absorption fine structure (XAFS) capability on the picosecond (ps) time-scale that can extend over microsecond time periods. The apparatus performs pump-probe experiments with a laser pump and an x-ray probe. The laser is a Ti-sapphire laser producing 4μJ pulses of 250 femtosecond duration and 800 nm wavelength. A special and critical feature of the apparatus is that the laser fires pulses at the APS P0 clock rate (~272kHz), collecting data from a given x-ray pulse each time around the ring, resulting in more than two orders of magnitude faster data collection than other laser systems used in similar time-resolution XAFS experiments. Thus, measurements can be made, e.g., in hours instead of a week. This allows the collection of data at a rate similar to that of typical non-time-resolved experiments. Diffraction measurements can also be made concurrently with the same time resolution.

It is useful to discuss an example of the new types of experiments enabled by this apparatus. Our facility allows the scanning of the XAFS signal as a function of time delay between pump and probe pulses because a complete high quality XAFS spectrum (both *extended* (EXAFS) and *near-edge* XAFS (XANES)) can be obtained in less than 30 minutes. The only such XAFS measurement published with 100 ps time resolution [1] did not scan time delay because to obtain one spectrum with enough statistics required 40 hours at the Advance Photon Source (APS). By comparison, in 40 hours beamtime our facility at the APS would be able to scan about 100 – 200 time-delay data points. The strong points of XAFS are: EXAFS monitors $\rho(r,t)$, the time dependent **partial** pair correlation function about the atom type whose absorption edge is being measured; and XANES monitors electronic structure variations, including allowing distinction between the crystalline and amorphous states. The XAFS, thus, allows the *direct* determination of: changes in the neighboring atom distances, in the electronic structure, in the temperature of a sample from the nearest neighbor bond vibration amplitude; and any laser irreversible damage or reversible changes by monitoring $\rho(r,t)$ and the absorption edge step height, changes in which monitor ablation. More detailed description of the apparatus with some of the preliminary results obtained during our commissioning are given in refs. [2, 3].

We have commissioned our facility by measuring the lattice-heating response to laser excitation for a 200nm thick Ge film supported on a 200nm thick SiOx film, and monitoring its XAFS with a time resolution of about 100ps. Our results are shown in Fig. 1.

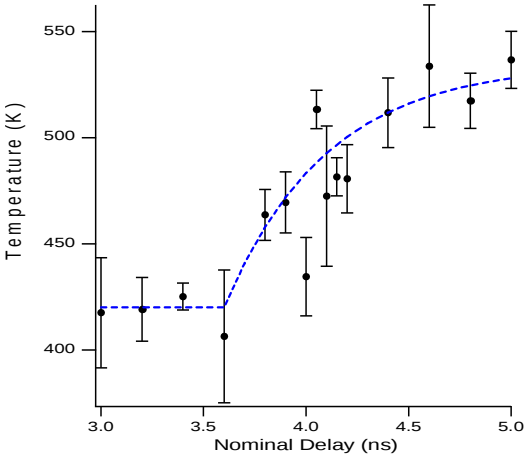

Fig. 1. The measured dynamics of the lattice heating of Ge after a 250 fs laser pulse. The nominal time delay is as measured on a fast oscilloscope. The true zero of the time delay is at ca. 3.6 ns where the heating starts rising. The points are the experimental data and the dotted curve is a best fit to an exponential with a relaxation time τ_{eT} of 0.5 ns.

The film rises to e^{-1} of its step in temperature in a time τ_{eT} of about 500 ps. A separate experiment [4] using a laser pump-laser probe of the transient reflectivity response indicates that the induced electronic excitation decays to e^{-1} of its equilibrium state in a shorter time of 275 ps, indicating that the electronic de-excitation requires some additional time to reach thermal equilibrium with the lattice.

With existing funding and additional funding requested from the Advanced Photon Source, improvements are being made to the facility that will significantly increase the signal-to-noise ratio of Fig. 1. The present limitation is the counting rate of a single fast avalanche photodiode (APD) detector. The incident x-ray intensity I_0 has to be attenuated by a factor of 100 in order to maintain the signal in the detectors' linear range (below 120kHz) for each of our I_0 and I_f detectors, where I_f is the fluorescent signal from the sample. This is required to eliminate systematic noise from the x-ray source in the output signal ratio I_0/I_f so that only random noise remains from the Poisson statistics of the finite x-ray photon counts. The non-linearity of the detector counting occurs when more than one photon per pulse occurs since the detector counts this as only one photon. We are presently making a numerical correction using Poisson statistics accurate to about 120 kHz, and we will increase the accuracy to higher counts but there is a limit since the reliability deteriorates as 272 kHz is approached. To understand the problem, the highest count rate from a single detector is 272 kHz when at every ring cycle the x-ray pulse emits at least one photon. The closer the detector counting rate gets to saturation at 272 kHz, the harder it is to accurately correct the signal since the change in the detector counting rate tends to zero. To increase the total counting rate while minimizing the need for corrections we are planning to use a 72 element APD array with total active area of 2949 mm^2 for the I_f detector, and a 64 element monolithic array with total active area of 64 mm^2 for the I_0 detector. By these means each detector can remain in its accurate counting range as the total counts increase by about two orders of magnitude, reducing the Poisson noise by one order of magnitude.

This facility will be used to investigate τ_{eT} of Ge (Fig. 1) as a function of T_i, the temperature before the laser induced temperature step. The τ_{eT} is expected to depend on T_i since anharmonic coupling between phonons is necessary to reach thermal equilibrium, and this coupling increases with T_i.

1.1.2 High-throughput Endstation for Nonresonant X-ray Raman Scattering

As is discussed in more detail below, non-resonant inelastic x-ray scattering (XRS) provides an important and in some cases unique window on core-shell spectroscopies. In particular, it can be used to study the final-state symmetry in the XANES of low-Z elements and can also be used to measure the XANES and/or EXAFS from low-Z elements in systems which are incompatible with soft x-rays (i.e., liquids with high vapor pressure or materials in high-pressure cells).

Motivated by our XRS studies on final-state effects [5, 6] (see section **1.2.5**) and with the concomitant goal of developing a novel user-facility at sector 20 of the Advanced Photon Source, we have constructed, and are commissioning of a high-throughput endstation for measurement of the momentum-transfer dependence of non-resonant x-ray Raman scattering at better than 1 eV resolution. A perspective-rendered schematic of the apparatus is shown in Figure 2. The scattering plane defined by the sample-analyzer-detector path for each analyzer is normal to the vertical scattering plane for the sample. This allows enough space to have independent detectors for each analyzer with only a modest deviation from the Rowland circle. Our previous work (and common practice) has shown that small deviations from the Rowland circle will not significantly degrade the final energy resolution, which is far less stringent than would be achieved by a Darwin-width limited, unstrained crystal. This multi-**q** configuration is quite different from all previous multi-crystal analyzers for XRS [7, 8], which have had all analyzers focusing radiation onto a single detector.

Each analyzer will be a spherically-bent Si (111) wafer with a 10-cm diameter and a 1-m radius of curvature. We will generally operate with the (555) reflection from the Si analyzer. These have been purchased from Dr. Trevor Tyson of NJIT – Dr. Tyson has recently developed a better method for making these analyzers which results in a greatly improved efficiency by reducing the distortion from bending strain near the edges of the analyzer. Each analyzer will be tuned to operate at approximately 9890 eV and the existing monochromator at Sector 20 will then be energy-scanned so that each analyzer-detector pair will then provide an independent energy-loss spectrum at successively larger momentum transfers. The apparatus will collect data from approximately 0.6 inverse Angstrom to 10 inverse Angstroms, spaced roughly every 0.5 inverse Angstroms. For low-Z elements (up to at least oxygen) this will provide enough range in momentum transfer to safely escape the pure dipole scattering limit, thus yielding information which is inaccessible to direct soft x-ray measurements of XANES. In addition, the large total solid angle will make practical many measurements of the extended XRS fine structure using the Si (111) monochromator and toroidal mirror with a flux of nearly 10^{13}/second and a final energy resolution of approximately 1.1 eV, or using the Si (311) monochromator without the focusing mirror for a reduced flux but improved final energy resolution of approximately 0.6 eV.

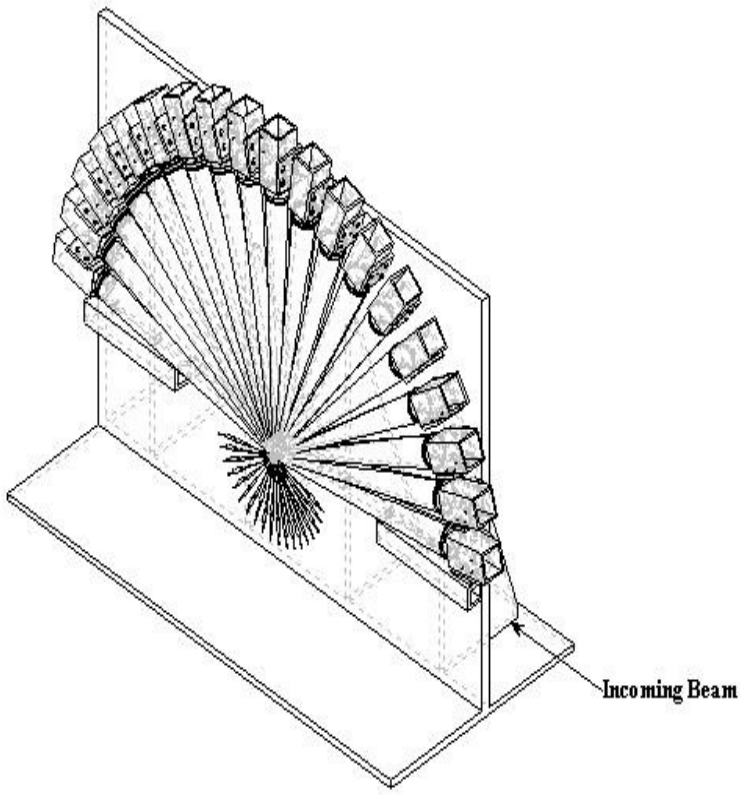

Fig. 2: A perspective rendering of the multi-crytal analyzer under construction for high-throughput measurements of q-dependent non-resonant x-ray Raman scattering. The final system will consist of 19 spherically-bent Si (555) analyzers focused on independent detectors. The length along the longest axis of the figure is about 220 cm. For the sake of clarity, many details have been omitted, including several radiation baffles, a helium-filled box to eliminate air-scattering, and the complete beam-pipe.

While these resolutions are much poorer than the planned resolutions for the new IXS/XOR sector under construction at APS for inelastic x-ray scattering measurements, they are extremely well-suited for the core-shell photoelectron spectroscopies described here. The energy resolutions and scientific goals of the two facilities are quite different, a fact which has been fully endorsed by the APS directorate.

The design of this apparatus makes use of much of the detailed work of others on multi-crystal analyzers (especially Peter Eng at GEO-CARS), but also adds an important new detail in the presence of independent detectors for each momentum-transfer out to near-backscattering from the sample.

In summary, the multi-crystal multi-detector apparatus will make XRS measurements at APS frequently competitive with the dipole-limited analogous measurements of XANES at soft x-ray synchrotrons, while allowing measurements of systems incompatible with the

experiment-environmental constraints of soft x-rays and also providing extra (non-dipole limit) detail. Hence, this is a highly ambitious project with concomitantly high potential pay-off. This project was essentially completed at the end of the grant.

Additional discussion of the applications of q-dependent XRS is provided in **1.2.2.**

1.1.3 Workforce Development, Education and supported Collaborator

During the tenure of the grant we supervised two students, Brandon D. Chapman and Yejun Feng, who completed their Ph. D. theses entitled "The Role of Disorder in Structural Phase Transitions in Perovskite Ferroelectrics" (Chapman) and "Exciton Spectroscopy Using Non-resonant X-ray Raman Scattering" (Feng). They are each now in postdoc positions which involve synchrotron radiation studies: Chapman at NSLS and Feng at the University of Chicago.

Two 2nd-year graduate students are working towards their Ph. D., Tim Fister and Michael Groves. They are making rapid progress toward their respective general exams. Mr. Fister has already completed an XAFS study of $Pb_2(PO_4)_3$, and is finishing analyzing the results, which support the order-disorder model for the ferroelastic phase transition in this material. Mr.Fister has also taken the lead in the design and construction of the high-throughput XRS endstation, described in **1.1.2**. His thesis research will utilized the high-throughput XRS endstation to research topics described in **3.1.2**. Mr. Groves has completed an XAFS study of the respective core-shell spectra of various perovskites, with the goal of readdressing a 1970 classic experiment [49] which aimed to separate the short-range from long-range theories of XAFS but did not succeed. He will work on the proposed time-resolved XAFS measurements described in **3.1.1**. for his thesis research.

One postdoc, Sang-Wook Han completed his tenure on the grant and is now an Assistant Professor at a South Korean University. His successor as a postdoc is Debdutta Lahiri who finished her tenure at the end of the grant and has a research position at a lab in India.

In addition, undergraduate student Lucas Wharton assisted with the design, construction, and commissioning of the high-throughput XRS endstation.

Special mention should be made of Prof. Y. Yacoby of Hebrew University in Jerusalem Israel. In the present grant Prof. Yacoby has been a close collaborator. He has visited with the PI and been funded in the present grant every summer and during a sabbatical leave at which time the COBRA technique (see **1.2.1**, below), that Prof. Yacoby conceived, was fully developed.

1.2 Highlights of Research Results for Grant

1.2.1 COBRA: A New Method for the Determination of Structure at Interfaces

Obtaining accurate structural information on epitaxial films and interfaces is nowhere more critical than in semiconductor passivation layers, where details of the atomic structure and bonding determine the nature of the interface electronic states. Various non-destructive methods have been used to investigate the structure of films and interfaces, but their interpretation is model-dependent, leading occasionally to wrong conclusions. We have developed [9-11] a new

x-ray method for 3D imaging of epitaxial structures, coherent Bragg rod analysis (COBRA). The usefulness of our technique is demonstrated by mapping, with atomic precision, the structure of the interfacial region of a Gd_2O_3 film grown epitaxially on a (100) GaAs substrate. Our findings reveal interesting behavior not previously suggested by existing structural methods, in particular a lock-in of the in-plane Gd atomic positions to those of the Ga/As atoms of the substrate. Moreover, we find that the bulk stacking of the Gd_2O_3 atomic layers is abandoned in favor of a new structure that is directly correlated with the stacking sequence of the substrate. These results have important implications for Gd_2O_3as an effective passivation layer for GaAs. Our work shows that the COBRA technique, taking advantage of the brilliance of insertion device synchrotron X-ray sources, is widely applicable to epitaxial films and interfaces.

1.2.2 Order-Disorder Character of the Ferroelectric Phase Transition in $BaTiO_3$

The PRL [12] clarifies a long-standing issue of the character of the changes of the atomic positions in BaTiO3 as it loses its ferroelectricity on heating. Ferroelectricity occurs in those materials where positive and negative charged atoms are displaced such that their average charges do not lie on top of one another. The long-standing question is how the displacement disappears when ferroelectricity is lost. One model was that the displacement goes to zero throughout the whole material (displacive model) while the other was that the displacement remains in very small regions but reverses its direction so that it averages to zero (order-disorder model). Different experiments have suggested apparent contradictory results that $BaTiO_3$ has either displacive or order-disorder character as ferroelectricity is lost. This Letter [12] resolves the apparent paradox. The reversal of the displacements with constant magnitude in small regions gives an order-disorder character while the small reorientation of the displacements gives a displacive character to the changes of the atomic positions as $BaTiO_3$ loses its ferroelectricity.

1.2.3 Diffuse x-ray Scattering From ABO_3 Perovskites

The ABO_3 perovskite ferroelectrics have a prominent role in our understanding of structural phase transitions in condensed matter systems because of their simple unit cell structure and their importance in applications. Despite extensive studies of these ferroelectrics, the origin of the reciprocal lattice space diffuse x-ray scattering (DXS) sheets in the paraelectric cubic phases of $BaTiO_3$ and $KNbO_3$ is still a matter of debate. In paper [13] diffuse x-ray scattering (DXS) measurements on the cubic paraelectric phase of single-crystal $PbTiO_3$ are presented. No diffuse scattering sheets are found, in contrast to sheets observed in the cubic paraelectric phases of $BaTiO_3$ and $KNbO_3$. A *quantitative* analysis of the diffuse scattering indicates that the transverse optical soft mode contribution is small in all three ferroelectric perovskites and the acoustic modes dominate the phonon diffuse scattering. Differences in the diffuse scattering are explained by differences in the disordering of the local displacements; this important result resolves a long-standing controversy about the source of the DXS in these perovskites. The lack of DXS sheets in $PbTiO_3$ is because its local displacements are not correlated over many units cells, in contrast to those of $BaTiO_3$ and $KNbO_3$, and cause a featureless DXS.

1.2.4 Final-state Effects Probed by Non-resonant x-ray Raman Scattering

The physics of low-energy photoelectrons in solids is a complex, many body problem. All aspects of the electronic structure of the material must be taken into account, including the interaction between the photoelectron and the complementary hole. This latter effect allows for Fermi-edge singularities in metals and excitons in insulators. As a canonical example of a many body problem in condensed matter physics, core-excitons are a topic of continuing interest.

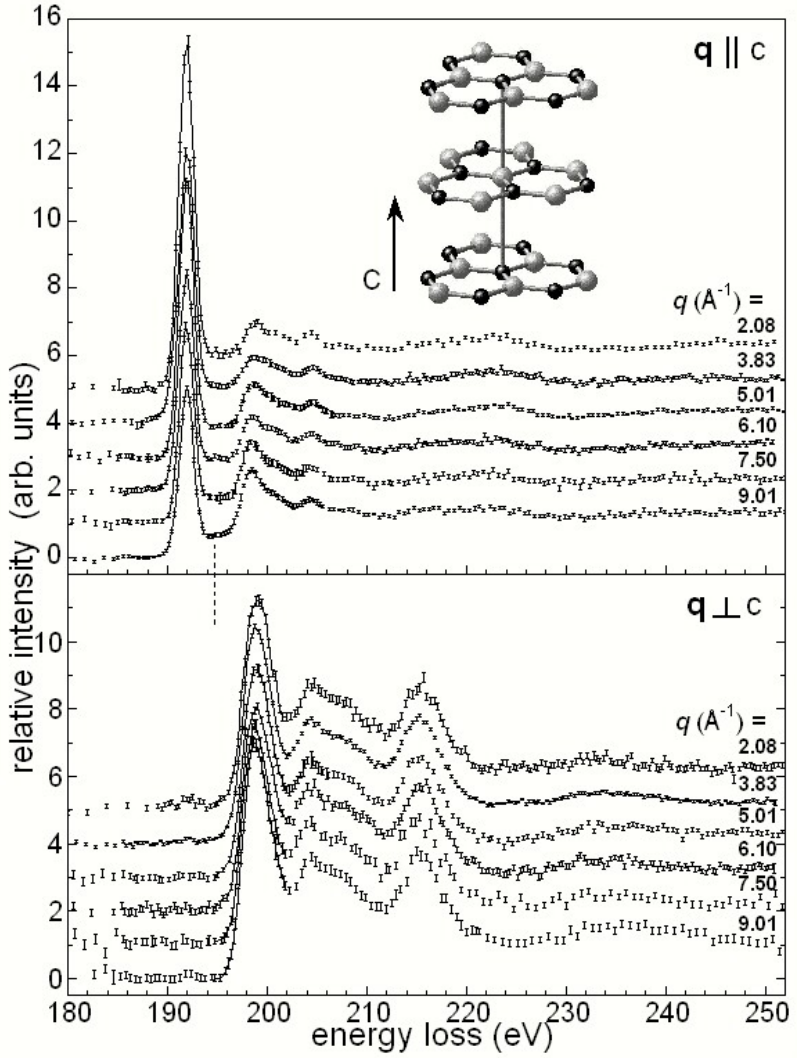

Figure 3: **q**-dependent x-ray Raman scattering (XRS) measurements of hexagonal boron nitride. (Inset): The crystalline structure of h-BN is 2-D hexagonal sheets stacked directly on top of each other, with the boron (black) and nitrogen (gray) always being nearest neighbors. (Main figure): The normalized XRS spectra from h-BN for (top panel) and (bottom panel).

The present synergy between steadily progressing *ab initio* theoretical treatments and on-going improvements in studies of non-resonant x-ray Raman scattering (XRS) shows strong potential for rapid progress on this old problem and other final-state effects in photoelectron

spectroscopies. [14-16] XRS is the inelastic scattering of hard x-rays from the K-shell of low-Z atoms. This combination of theory and experiment has shown itself to be especially suitable for spectroscopy of the angular characteristics of core excitons. Recent XRS studies on LiF [14] and our own work on icosahedral B_4C [15] convincingly demonstrated *s*-, and *p*-type excitons at the F and B K-edges, respectively. This latter study [15] in fact solves a significant part of a long-standing problem of site-substitutional disorder in icosahedral B_4C.

Motivated by that success, we subsequently extended this nascent exciton spectroscopy by demonstrating that for some systems one can learn not only the Δl selection rule for the exciton but also a full description of the final state characteristics in terms of spherical harmonics, Y_{lm}. This information is inherently unavailable from direct measurement of XANES and is in difficult (but possible, with the right materials and enough effort) to acquire from EELS measurements, which seldom use momentum transfers larger than a few inverse Angstroms.

As the first example of this improved spectroscopy, we show for the model system of hexagonal BN [16] that **q**-dependent XRS unequivocally identifies a large pre-edge feature as a Y_{10}-type core exciton. In Figure 3, we show the q-dependent XRS for both principal orientations of the direction of the momentum transfer. Notice the strong pre-edge resonance in the top panel. In our paper we use three independent and mutually-consistent arguments to identify the final-state characteristics associated with this resonance: first a qualitative, but powerful, symmetry-based argument which relies on the absence of q-dependence for the spectra with **q** aligned in the basal plane of the h-BN, second an *ab initio* calculation of the partial projected density of states, and third an independent *ab initio* calculation of the **q**-dependent XRS cross-section.

1.2.5 Time-resolved EXAFS: Thermalization of Electronic Excitations in Ge

As mentioned in **1.1.1**, we have developed a unique facility at sector 20 of the Advanced Photon Source that measures with better than 100 picosecond (ps) time resolution both x-ray absorption fine structure (XAFS) and diffraction on femtosecond laser-excited samples [17, 18]. This facility measures XAFS with two orders more efficiency than competing apparatus. The key aspect of this instrument is the combinations of gated detectors and a Ti-sapphire pump-laser which is synchronized to the 272 kHz natural frequency of the storage ring, so that data can be collected from a 95 ps FWHM x-ray-probe pulse on *each* cycle of the ring.

XAFS allows the determination of: the time for the laser excitation to couple to the lattice, the sample temperature after reaching thermal equilibrium, any ablation of the sample with time, and, in many cases, allows distinction between amorphous and crystalline states. Preliminary measurements on 200nm thick polycrystal Ge films indicate that the laser excitation is transferred to thermal heating of the lattice with a time constant of about 500 ps. Because of the two orders of magnitude increased efficiency it became feasible for the first time to measure *extended* XAFS with ps time-resolution *while scanning the time-delay* between the x-ray and laser pulses, making possible the determination of the 500 ps time constant. Such a facility opens up the possibility of investigating many exciting new physical phenomena,

1.3 Research Results for Drs. Brewe and Cross

Drs. Dale Brewe and Julie Cross, the beamline scientists supported under the present grant, have both performed exceptionally in all of their many roles. In particular, they have had an extremely productive 2.5 years as co-authors and occasionally as principal authors of research publications.

Given that, as per the directive of the DOE, this renewal proposal does not request funds to continue to support the salaries of Drs. Brewe and Cross we will confine the section of the progress report to two examples of their excellent work:

In PRL [19] diffraction anomalous fine-structure (DAFS) and extended x-ray absorption fine-structure (EXAFS) measurements were combined to determine short range order (SRO) about a single atomic type in a sample of mixed amorphous and nanocrystalline phases of germanium. EXAFS yields information about the SRO of all Ge atoms in the sample, while DAFS determines the SRO of only the ordered fraction. We determine that the first-shell distance distribution is bimodal; the nanocrystalline distance is the same as the bulk crystal, to within 0.01(2) Angstrom, but the mean amorphous Ge-Ge bond length is expanded by 0.076(19) Angstrom. This approach can be applied to many systems of mixed amorphous and nanocrystalline phases.

In article [20], it is shown how basic crystallography can be combined with resonant scattering of circularly polarized (CP) x-rays to extract element- and site-specific magnetism in crystals. This is achieved by combining the inherent element specificity of resonance scattering with the symmetry properties of the crystal, which results in enhanced/suppressed scattering amplitudes from certain lattice sites under particular diffraction conditions. This method is used to measure the magnetic response of inequivalent Nd sites in $Nd_2Fe_{14}B$ single crystal (4f and 4g sites in Wyckoff notation) through the crystal's magnetization reversal at room temperature and through the spin reorientation transition at lower temperatures. This approach might prove very valuable in studies of magneto-crystalline anisotropy (MCA) in complex materials with multiple elements and differing crystal sites as well. This has broad implications, not only for understanding the atomic origin of MCA in this material but for the mechanism of the spin-reorientation transition from c-axis towards the basal plane at T = 130 K, since the magnetic signals from these inequivalent sites can now be separated.

1.4 Publications from the present grant

We present here references to 28 papers which have either appeared in print or been submitted during the last 2.5 years or which will soon be submitted and which were both directly supported by this grant and have at least one person supported by this grant (Stern, Seidler, Brewe, Cross) as author or coauthor. The general research support for sector 20 provided by this grant has led to numerous other publications by general users who may not have needed the support of Brewe and/or Cross, or may not (for whatever reasons) have chosen to include them as co-authors.

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