

SNS Single-Crystal Diffractometer Workshop

March 1, 2002

Argonne National Laboratory

EXECUTIVE SUMMARY

This report summarizes the activities of the SNS Single-Crystal Diffractometer Workshop held on March 1, 2002, at Argonne National Laboratory. The purpose of the workshop was to bring together a broad cross section of the interested community, to seek their input on the desirability of moving forward with the formation of an Instrument Development Team (IDT) for the SNS SCD and to assemble the scientific case for this instrument. The workshop was convened by an organizing committee consisting of Professor Robert Bau, Chair (University of Southern California), Dr. Christina Hoffmann, SNS SCD Instrument Scientist (Oak Ridge National Laboratory), Dr. Thomas Koetzle (Argonne and Brookhaven National Laboratories), and Dr. Arthur Schultz (Argonne National Laboratory). The workshop agenda and the list of attendees are attached to this workshop report as Appendices.

The assembled group unanimously favored the formation of an IDT and strongly recommended that high priority be given to building the SNS SCD. *This instrument promises to revolutionize single-crystal neutron diffraction.* The ability to work with much smaller crystals, approaching the size that are now commonly used for laboratory single-crystal X-ray studies, together with the greatly increased throughput will open up many new areas of investigation, which is expected to stimulate rapid growth in the user community. The SCD instrument should be optimized for rapid Bragg intensity measurements on materials with moderate-sized unit cells (up to, say, 50 Å). To accomplish this objective, the instrument should have as wide detector coverage as possible. In addition, in order to maximize the scientific impact, the SCD should include provision for magnetic scattering experiments using polarized neutron beams, and for diffuse scattering measurements. The workshop participants recommended the construction of a separate, dedicated instrument for macromolecular crystallography at SNS, since the technical requirements for samples with large unit cells are quite different than those of the “small-molecule studies,” together with magnetic and diffuse scattering, that are targeted here for SCD.

The scientific case for the SCD instrument is detailed in the body of this report. The report is organized into seven sections, as follows: I. Coordination Chemistry and Metal Hydrogen Interactions; II. Hydrogen Bonding; III. Thermoelectrics; IV. Parametric Studies (the study of structure as a function of temperature, pressure, applied fields, etc.); V. Earth Science; VI. Magnetism; and VII. Diffuse Scattering. In each area of research, applications are envisioned that would significantly advance the state-of-the-art at currently available facilities. *The SCD promises an increase of at least two orders of magnitude in detectable neutron scattering intensity over existing single-crystal instruments in the U.S.A., thus greatly expanding the range of materials that can be explored.*

I. COORDINATION CHEMISTRY AND METAL HYDROGEN INTERACTIONS

The development of the SCD instrument at SNS will revolutionize single-crystal neutron diffraction as we know it, especially from the viewpoint of the practicing synthetic chemist. There are innumerable important chemical problems, especially those involving the location of hydrogen atoms in molecules, that cannot be tackled because of the severe difficulties in growing the large single crystals, in excess of 1 mm³ in volume, that currently are necessary for neutron diffraction analysis. The capabilities of the proposed SCD at SNS will change this situation radically. If, as we expect, the crystal size requirement can be cut down by a factor of 10, to a volume of about 0.1 mm³, a large number of critically important scientific problems can be solved. Some of these will be described below. Obviously, a further reduction in the minimum crystal volume, say down to 0.03 mm³ or so, would be even better. In the latter case, in fact, we predict that user demand would be so overwhelming that pressure to build a second single-crystal instrument at SNS would become a real possibility.

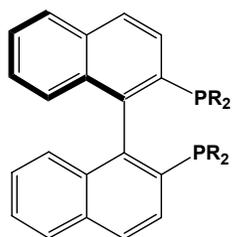
The SCD at SNS in its base configuration (two detectors for the point of comparison) is expected to provide two orders of magnitude more intensity than the existing SCD at IPNS, which dates from the early 1980's and was the first instrument of its kind to become operational. A full complement of detectors, as described in the conceptual design report for the SCD at SNS, will come very close to adding another order of magnitude because of the proposed ca. 50% coverage of reciprocal space. As has been mentioned above, the capabilities of this new instrument with its greatly increased throughput will fill a void in the chemical crystallography community. It will provide rapid access for important problems where only neutrons can give the desired information. On average, the IPNS SCD instrument can only accommodate approximately 25 worthy experiments per year. However, the pace of chemical crystallography is much faster than that. Recent numbers provided by the Cambridge Structural Database (Allen and Kennard, 1993) indicate a nearly exponential growth in the number of published X-ray crystal structure determinations. This recent growth is in large part due to the acquisition of modern CCD (charge-coupled device) detector diffractometers at major universities. A great number of worthwhile single-crystal neutron diffraction experiments are simply not considered because there is a dearth of instrument time available, while the pressure to publish important results only increases. Although the majority of these chemical problems may be studied by other techniques, few provide the confidence that can be obtained with single-crystal neutron diffraction.

Two of the most interesting areas of research that are expected to benefit enormously from the SNS are discussed in some detail below:

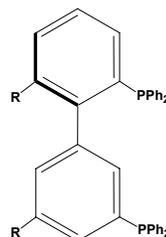
- (1) Systematic studies of chemical bonding and reactivity in classical and non-classical transition metal hydrides and related compounds, and
- (2) Metal hydride cluster complexes.

Systematic studies of chemical bonding and reactivity

The knowledge obtained in highly accurate structural work is needed to provide synthetic chemists with a rationale for choosing both the metal and the ligands necessary to achieve a desired synthetic target. For example, the catalytic activity of a hydrogenation catalyst may be fine-tuned by choosing a particular set of ligands, yielding an activated, stretched dihydrogen molecule or a weakly bound, easily substituted dihydrogen, or chirality transfer to a substrate may be achieved or enhanced by designing more rigid chiral auxiliary ligands (modified BINAP and BIPHEP ligands are good examples of this). It should be noted that most of these enhanced ligands take advantage of weak intramolecular interactions, often involving hydrogen atoms.



BINAP



BIPHEP

A systematic study of a series of related complexes is needed to achieve the abovementioned goal. This type of parametric approach is common in X-ray diffraction, and it has led to important insights into the reactivity pattern of ligands or the taxonomy of ligands or small molecules to be used in the so-called lego-chemistry, and to build supramolecular aggregates. (For additional examples of parametric studies, see Section IV.) All of this has been impossible to achieve with neutron diffraction due to the long data collection times and the need for crystals that are far larger than those required for X-ray crystallography. The advent of the new generation neutron sources will lead to a quantum leap in experimental capabilities that will open up new frontiers, since it will become possible to carry out neutron diffraction studies using samples almost comparable in size to those used for X-ray diffraction.

It is important to note that X-ray diffraction, even with state of the art data collections at low temperature on synchrotron radiation sources, cannot compete with the accuracy obtained from neutron diffraction when interactions involving hydrogen atoms are of interest. Many cases can be found in the literature where incorrect structures have been assigned based on refined positions of hydrogen atoms that eventually were shown to be erroneous when neutron diffraction results became available.

A particular instance where this type of study is critical to understanding the bonding and reaction mechanisms are transition metal hydrido complexes. Transition metal hydrides are critically involved in many stoichiometric and catalytic processes of organometallic chemistry. They display a broad reactivity pattern, some of them behaving as hydride donors whereas others may act as protonating reagents or may transfer hydrogen through a radical mechanism.

In recent years much work has been devoted to the study of novel bonding modes between metals and hydrido ligands in transition metal complexes. Moreover, other interactions have been characterized involving the hydrido ligand and a group within the first coordination sphere of the complex. These span

a wide range of possibilities from true covalent interactions, to hydrogen bonds, to the so-called "agostic" and "remote" interactions.

The discovery by Kubas, in 1984, that transition metals can bind molecular hydrogen forming the so called " η -H₂ complexes" or "non-classical hydrides" has opened a new field of investigation and has allowed some earlier reaction mechanisms or reactivity patterns, involving molecular hydrogen, to be more precisely defined or even reconsidered (Kubas, 2001).

The importance of transition metal hydrido complexes (both classical and non-classical) in hydrogenations is well known. The crucial step in the reaction path is the coordination to the metal center of an H₂ molecule and its activation via the formation of a non-classical η -H₂ complex, with the subsequent cleavage of the H-H bond (oxidative addition) leading to a classical M-(H)₂ hydrido complex.

For a better understanding of these reactions, a detailed knowledge of the metal-hydrogen interaction is essential. This can be obtained from the structures and the dynamics of classical and non-classical hydrides (Eckert and Kubas, 1993; Koetzle, 1995). In order to obtain this detailed insight, accurate structural parameters on the M-H and M-(H₂) moieties are needed.

Single-crystal neutron diffraction determinations of (H₂) complexes at low temperatures (< 25 K) have established that the H-H separation can cover a wide range of distances, from ~ 0.8 Å (strong H-H bond) to ~ 1.4 Å (weak H-H bond), thus neatly spanning the oxidative addition pathway and giving support to the mechanistic studies of this most important reaction. It should be noted that neutron diffraction provided the first unambiguous experimental proof of the existence of the so-called "stretched" (i.e., activated) H-H bonds (>1.0 Å) (Koetzle, 1995; Kubas, 2001).

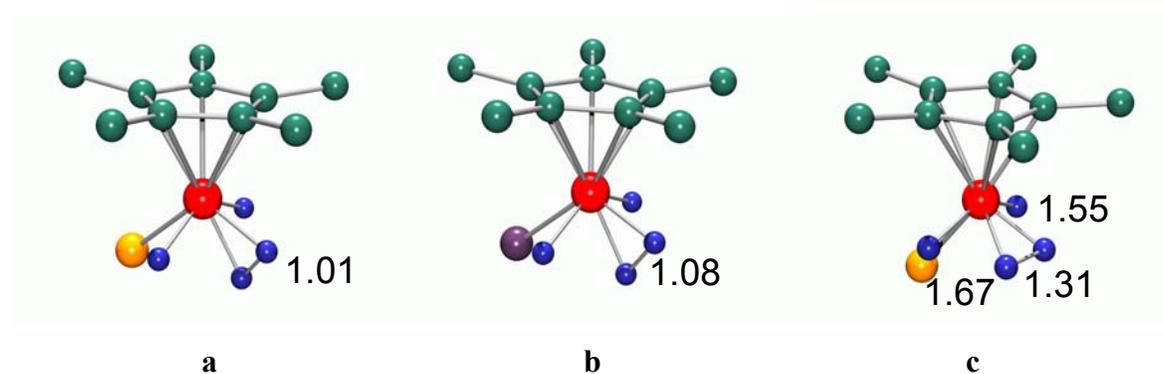


Figure 1. Molecular structures of a) **1**, $[(C_5Me_5)Os(\eta^2-H_2)(H)_2(PPh_3)]^+$, b) **2**, $[(C_5Me_5)Os(\eta^2-H_2)(H)_2(AsPh_3)]^+$, and c) **3**, $[(C_5Me_5)Os(\eta^2-H_2)(H)_2(P(c-Hx)_3)]^+$. The view of the molecule is the same in each case. The phenyl and cyclohexyl groups bound to phosphorus and arsenic, and the methyl hydrogen atoms on the C₅Me₅ ligand, are not shown for clarity.

Recently a series of osmium complexes (see Figure 1) containing hydrides and dihydrogen in varying degrees of activation were analyzed by single-crystal neutron diffraction (Gross et al., 1997). The reason for the rotation and activation of the H₂ ligand is not clear from just these three structures. In order to understand the relative contributions of electronic and steric properties of the ancillary ligands, a question still open to discussion, the series needs to be expanded to include other ligands such as trimethylphosphine. Unfortunately, it has not been possible to produce suitable crystals for neutron

diffraction. However, a single-crystal diffractometer at the SNS would provide the capability to probe many additional compositions of this molecule using ca. 0.1 mm³ crystals, which are readily available, and to use the experimentally observed trends as a check of high level quantum mechanical calculations.

In another interesting research project, a series of zirconium complexes were synthesized to study the Haber-Bosch process wherein H₂ acts as both the reductant and the source of H in the formation of NH₃ from N₂. This work provides an example of a problem where single-crystal neutron diffraction should have been used to provide the critical information relating to the positions of two hydrogen atoms in an important structural determination *before* the initial publication. The dinuclear N₂ complex {[P₂N₂]Zr}₂(μ-η²-N₂), where P₂N₂ = PhP(CH₂SiMe₂NSiMe₂CH₂)₂PPh (Fryzuk et al., 1993; Cohen et al., 1994) was reacted with both H₂ and BuⁿSiH₃, where Buⁿ = n-butane (Fryzuk et al., 1997). Both materials were studied with solution NMR, which indicated that H₂ reacted with N₂ to form {[P₂N₂]Zr}₂(μ-η²-HN₂)(μ-H) (**3**) and BuⁿSiH₃ formed the trapped intermediate {[P₂N₂]Zr}₂(μ-η²-BuⁿSiH₂N₂)(μ-H) (**2**). Both of these reactions formed the expected products. The X-ray single-crystal structure determination of **2** provided the same structure in the solid state as was observed in solution. However, the X-ray single-crystal structure determination of **3** did not indicate the same bridging motif. The putative structure was the unreduced, bridging dihydrogen adduct {[P₂N₂]Zr}₂(μ-η²-N₂)(μ-η²-H₂) (**1**). It was surmised that **3** existed in solution and was in equilibrium with **1** in the solid state, as shown in Figure 2.

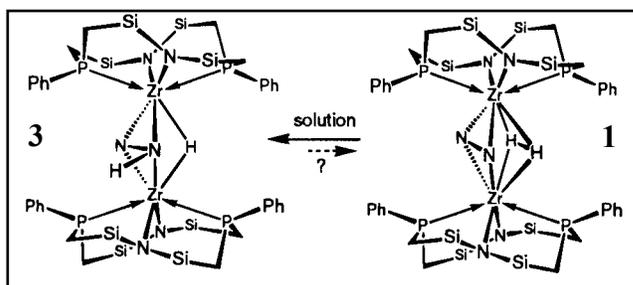


Figure 2. Putative solution and solid-state equilibrium between **1** and **3**.

Two years later, single-crystal neutron diffraction and inelastic neutron scattering studies (Basch et al., 1999) conclusively showed that the initial publication of the structure of **1** is incorrect. The correct structure is **3**, identical to that proposed by solution NMR, as shown in Figure 3.

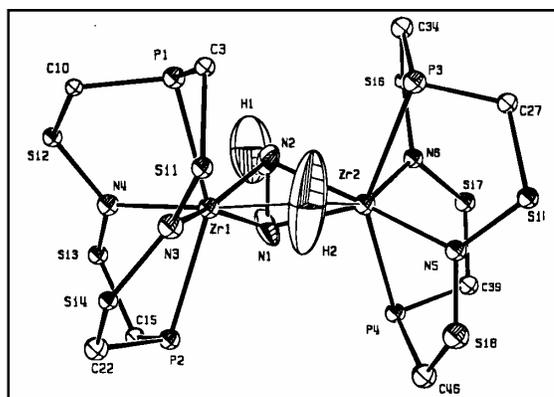


Figure 3. ORTEP diagram of **3** showing the inner core and the positions of the hydrogen atoms as determined by neutron diffraction. The silyl methyl groups and the phosphorus phenyl substituents have been removed for the sake of clarity.

The putative structure **1** was an artifact of X-ray analysis. In retrospect, if this X-ray result had been obtained while there was an instrument available of the likes of the proposed SNS SCD, it is very likely that the initial, incorrect X-ray structure would have been quickly corrected with a complementary neutron structure. Instead, the neutron result was bypassed for several years until instrument time became available for this problem at the ILL.

Metal hydride cluster complexes

The question of how hydrogen atoms are distributed in the interstitial cavities of metal clusters is an important one, and one that is ideally suited for neutron diffraction precisely because the X-ray diffraction technique is unable to accurately characterize (and in most cases unable even to detect) the presence of hydrogen atoms when they are surrounded by an array of metal atoms. Over the years, six-coordinate hydrogen (i.e., hydrogen atoms in octahedral cavities) and five-coordinate hydrogen (hydrogen atoms in square pyramidal sites; see Figure 4 for an example of this type of coordination) have been definitively characterized in molecular complexes (Hart et al., 1979; Hart et al., 1981; Bau et al., 1997), but four-coordinate hydrogen (i.e., hydrogen atoms in tetrahedral sites) and hydrogen atoms in higher coordination states (seven, eight or higher) are still unknown among molecular compounds.

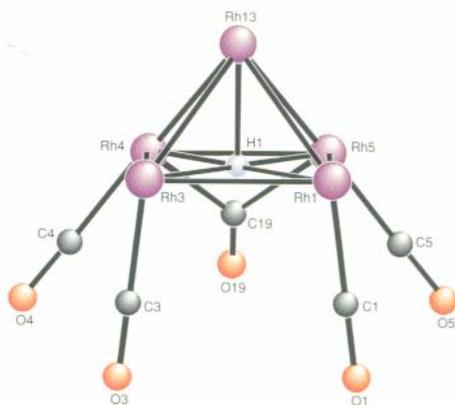


Figure 4. Partial view of the $[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]^{3-}$ cluster anion showing the square pyramidal coordination of hydride H1.

Target compounds that could be studied include the clusters $[\text{HRu}_{10}\text{C}(\text{CO})_{24}]^-$ and $[\text{HOs}_{10}\text{C}(\text{CO})_{24}]^-$ (Jackson et al., 1982; Bailey et al., 1989), which are strongly suspected to harbor four-coordinate hydrogen atoms, and the clusters $[\text{HRh}_{12}\text{N}_2(\text{CO})_{23}]^{3-}$ and $[\text{HNI}_{38}\text{C}_6(\text{CO})_{42}]^{5-}$ (Martinengo et al., 1986; Ceriotti et al., 1986), which are likely candidates for seven-coordinate and eight-coordinate hydrogen, respectively. All of these target clusters have been analyzed by X-ray diffraction, and it has been possible to grow crystals as large as 0.2 mm^3 of some of these compounds. As mentioned above, these crystal sizes are far too small to be handled by currently available neutron instrumentation, but with the advent of the proposed SNS SCD equipment we would be able to answer the question of whether four-, seven- or eight-coordinate hydrogen atoms can exist in metal cluster complexes. (Incidentally it should be pointed out that four-coordinate hydrogens, i.e., hydrogen atoms in tetrahedral interstitial sites, are known to exist in bimetallic solid-state systems such as uranium hydride and thorium hydride (Rundle, 1951; Mueller et al., 1977) but have never been found in soluble molecular species.)

The scientific significance of this work stems from the fact that hydrogen is generally thought of as an element that normally forms only one bond although in certain cases, e.g., hydrogen bonds, it forms two. Thus, many scientists are not aware that hydrogen atoms can be attached to three, five or six other atoms simultaneously, but as is mentioned above it has been shown that this unusual type of bonding does in fact occur in metal cluster compounds (Teller and Bau, 1981; Bau and Drabnis, 1997). The bonding situation in these complexes is similar to what occurs when hydrogen atoms become chemisorbed into the bulk of a metal lattice, as in palladium hydride and related systems. As a final note, it should be pointed out that hydrogen-containing materials are important in applications such as the nickel/metal-hydride batteries used in cellular phones, and intensive efforts are being made to develop binary and ternary metal hydrides for use as hydrogen-storage materials. Here, it is anticipated that neutron structural studies will continue to make major contributions to improved understanding of the structure and bonding of hydrogen in metal lattices.

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II. HYDROGEN BONDING

Fundamental studies of bonding

The Atoms in Molecules approach of Bader (1990) and the analysis of charge density that it employs (Popelier, 2000) have led to a fundamental gain in understanding of covalent and non-covalent bonding. However, the direct observation of experimental charge density also plays a vital role in improving our theoretical understanding of the bonding in organic, inorganic, and organometallic systems. The acquisition of very accurate neutron diffraction data is necessary for a complete experimental description of the charge density, since it allows accurate determination of atomic nuclear positions and displacement parameters (ADPs). Higher flux instruments are needed so that these studies can be extended to more weakly diffracting systems; already, small proteins are being modeled, and there is no reason why many other equally large organic and inorganic systems should not be studied, as there are no fundamental theoretical barriers.

Strong and weak hydrogen bonding

The hydrogen bond (HB) has a very special status in chemistry. It is a relatively weak interaction when compared with covalent bonds between atoms in molecules, but it is the strongest and probably the most important intermolecular interaction. Besides being vital in much of the chemistry related to the life sciences, it is also important in the “inorganic world and in the earth sciences.” The literature on hydrogen bonding is truly enormous, and even extensive reviews can only treat portions of the field (see, e.g., Jeffrey, 1997; Steiner, 2002). However, many fundamental questions remain open; for example, even though much research has focused on short hydrogen bonds, this is an area where the fundamental understanding (i.e., predictive power in a given chemical system) is still rather limited.

One of the most important issues in biological chemistry is the nature of enzyme catalysis. While the understanding of, for example, the genetic code and protein folding has seen great progress, the elucidation of the essential characteristics of enzymatic catalysis is in many cases far less advanced. If one can obtain a better insight into the nature of enzyme catalysis, the rewards may be enormous. We could potentially mimic the chemical environment of active enzymes in synthetically prepared complexes and thereby harvest the benefits of the chemical “tricks” that nature has developed over millions of years of evolution. Hydrogen bonds are known to play a pivotal role in many enzymatic reactions, and studying fundamental aspects of hydrogen bonds as well as their role in the active sites of various enzymes is of paramount importance. One example is the cleavage of peptide bonds in digestive enzymes (e.g., serine proteases) where a strong hydrogen bond has been suggested to be a major factor in the stabilization of the transition state of the reaction. It is increasingly evident that the shape of the potential energy surface (PES) along the hydrogen bond coordinate is influenced by many effects in addition to the heteroatom distance, which has traditionally been used to characterize hydrogen bonds. In protein crystallography it is very often only the heteroatom distance that can be determined accurately, but conclusions concerning the hydrogen bond based on this distance are very difficult to make for short hydrogen bonds. An important topic for future hydrogen bonding studies is therefore to unravel and quantify what other factors affect the

PES. Clearly, only accurate structural information on the hydrogen bond geometry will form the basis for further developments in the fundamental understanding of these phenomena.

Another example is given by systems that contain dihydroxy groups, in which one HB is short and the other is long. Dihydroxy groups with very short hydrogen bonds are found at the active sites of many important biological molecules, including 2-acetyl-1,8-dihydroxy-3,6-dimethyl naphthalene (a natural product found in tree bark) and hypiricin (the active ingredient in St. Johns wort). Both of these products have been crystallized. However, even after extensive trials, the only samples that have been obtained are too small for single-crystal neutron diffraction using present facilities. The reduction in crystal size requirements anticipated at SNS will allow these kinds of materials to be investigated, and it will open up the possibility of examining an endless variety of new systems in systematic series of investigations.

Weak intermolecular interactions

Supramolecular chemistry is a rapidly expanding area with many applications in crystal engineering. Here, weak intermolecular interactions are of prime importance. Successful molecular modeling of these systems relies upon accurate structural information regarding the weak intermolecular hydrogen bonds. Neutron diffraction characterization of such interactions provides definitive structural parameters – precise bond and contact distances and angles, torsion angles, etc., for benchmarking theory and, increasingly, accurate temperature-dependent ADPs, which are useful both in attempting to understand the dynamics and in determining whether disorder is involved. However, current requirements for large crystals of $\sim 1 \text{ mm}^3$ or more contrast markedly with the tiny crystals now acceptable on X-ray facilities, and this severely limits the range of studies. For example, the first N-H... π interactions to be investigated by neutron diffraction were reported only in 1996 (Allen et al., 1996) and the first C-H... π even more recently (Davidson et al., 2000).

The advent of high power, new generation spallation neutron sources such as SNS will make it possible to investigate the interacting capabilities of a large number of different molecular aggregates that may form the base of a library of building blocks for combinatorial chemistry.

The increasing availability anticipated over the next five years of new, highly efficient single-crystal diffractometers (SXD-11 at ISIS; the thermal quasi-Laue image plate-based Vivaldi and the upgraded D19 at ILL; the PCS station at LANSCE; several image plate-based diffractometers in Japan, including BIX-3 and BIX-4 at JAERI and BIX-P1 and BIX-P2 at the future JSNS) promises to dramatically increase access of chemists and X-ray crystallographers to single-crystal neutron diffraction.

It is perhaps worth remarking that deuteration is not a requirement here, because with single crystals the signal-to-background ratio for hydrogenous samples, while not optimal, is quite adequate with good instrument design. Of course, where deuteration is easily possible, this produces a desirable decrease in the incoherent scattering background, yielding improved counting statistics and an even more precise structure. In cases where certain sites are preferentially exchanged or protected on deuteration, this new information gives additional insight into the accessibility of such sites, and into the energetics of exchange. A spectacular example of the use of this type of information is seen in the increasing number of

studies of partially deuterated macromolecules. To date there are sparse examples of such studies on smaller molecules, and these are frequently serendipitous rather than planned. In many cases, where deuteration is employed it is to provide contrast (H/D) between different parts of a molecule for unambiguous identification of hydrogen sites.

Template-directed solid-state organic synthesis

The field of organic synthetic chemistry traditionally has focused upon the molecule as a centerpiece for making and breaking covalent bonds. However, organic chemists are now at a stage where it is time to look beyond the molecule in order to devise new strategies for the construction of molecular and polymeric products. In this context, the recent emergence of the field of supramolecular chemistry provides a foundation upon which such a transformation may take place. With its roots stemming from biology, supramolecular chemistry suggests that, similar to Nature (e.g. proteins, DNA), it should be possible to control molecular and polymer syntheses using noncovalent forces (e.g., hydrogen bonds, π - π interactions) in a manner such that principles of molecular recognition and self-assembly are exploited to position reactants to form single, and multiple, covalent bonds. Indeed, since it is expected that the hydrogen bond will play a pivotal role in permitting chemists to control such reactivity (cf., DNA), it is anticipated that the proposed single-crystal neutron diffractometer at SNS will play an important role here in providing excellent throughput, with accurate structure information gained on a time-scale (i.e., hours) that is comparable to more popular structure techniques such as nuclear magnetic resonance spectroscopy (e.g., ^{13}C NMR).

A general approach to controlling chemical reactivity supramolecularly utilizes the solid state as a medium for reaction. For example, molecular solids may be utilized to control reactivity utilizing molecules that function as linear templates. Indeed, it is anticipated that the solid state should largely eliminate effects involving solvent that have made past approaches to template-directed synthesis cumbersome. In this way, a reliable means to control reactivity supramolecularly may be achieved. An initial report (MacGillivray et al., 2000) has demonstrated that co-crystallization of resorcinol with trans-1,2-bis(4-pyridyl)ethylene (4,4'-bpe) gives the four-component molecular assembly, 2(resorcinol) \cdot 2(4,4'-bpe), where two molecules of the template resorcinol orient two molecules of 4,4'-bpe, by way of four O-H \cdots N hydrogen-bonds, for a [2+2] photoinduced cycloaddition (Figure 5). UV-irradiation produced the expected photoproduct, rctt-tetrakis(4-pyridyl)cyclobutane (4,4-tpcb), stereospecifically (yield: 100%).

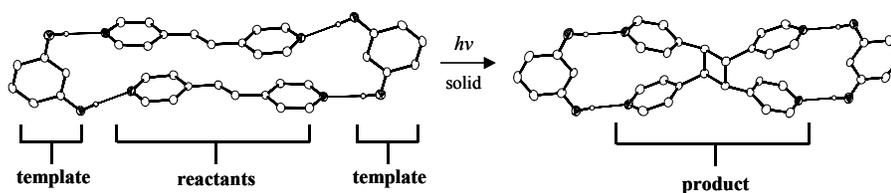


Figure 5. Perspective views of (a) 2(resorcinol) \cdot 2(4,4'-bpe) and (b) 2(resorcinol) \cdot (4,4-tpcb).

The product, in a similar way to the reactants, interacts with the resorcinol templates by way of O-H \cdots N hydrogen bonds. This result demonstrates the ability to control reactivity. It also has been possible to conduct a molecular synthesis by design, initially targeting a cyclophane product (Figure 6). Specifically, co-crystallization of 5-methoxyresorcinol (5-OMe-resorcinol) with 1,4-bis[2-(4-pyridyl)ethenyl]benzene (1,4-bpeb) produced 2(5-OMe-resorcinol) \cdot 2(1,4-bpeb), with four olefins organized for photoreaction (Figure 6). UV irradiation of the solid (Hg lamp) produced a product with a structure reminiscent of a [2.2]paracyclophane.

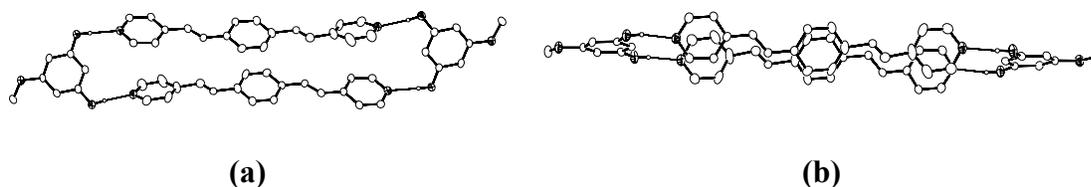


Figure 6. Perspective views of 2(5-OMe-resorcinol) \cdot 2(1,4-bpeb): (a) side-on, and (b) overhead.

The proposed SCD at SNS would benefit this research into the supramolecular control of reactivity in the solid state in two general ways. First, the instrument would make it possible to access data concerning the hydrogen bonding interaction between the templates and reactants (and/or products) without the need to grow large crystals. The ability to locate the position of the hydrogen atoms would provide a more realistic representation of the interaction between the template and reactants. This may, in some cases, make it possible to rationalize the observed reactivity (e.g., product yield) and to engineer additional template and reactant molecules (e.g., strong-acid templates). Second, the SCD at SNS would make it possible to conduct *in situ* solid-state reactions and to directly follow the transformation of reactants to products. Information concerning reactant and product geometries, as well as changes in phase of targeted crystal structures, may be obtained with potential widespread implications in both synthetic chemistry and materials science (e.g., photochromic materials). Complete and accurate characterization of geometries and phase transitions can only be obtained with the inclusion of accurate hydrogen positions and atomic displacement parameters, which can only be derived from neutron diffraction data.

It is recognized that the field of organic synthetic chemistry is beginning to undergo a transformation wherein chemists are looking beyond the molecule to control reactivity. Here, the proposed SCD at SNS could be exploited to probe the ability to control such reactions in the organized environment of the solid state. Moreover, as these and similar synthetic strategies continue to emerge, it is anticipated that the proposed instrument will become a tool to enable routine access to structure information that, in the context of both X-ray diffraction and solution-phase spectroscopy, may not be realized or simply inferred.

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III. THERMOELECTRICS

Thermoelectric materials possess the unique property that application of a temperature gradient induces a separation of charge. These materials are of great practical importance, for example because of their widespread applications in power sources and in cooling devices. Thermoelectricity is an extremely complex property that is dependent on many variables. Recently, new materials, including open framework structures such as skutterudites and clathrates, have been studied intensively in relationship to thermoelectric energy conversion (Bentien et al., 2000; Chakoumakos et al., 2001; DiSalvo, 1998; Kuznetsov et al., 2000; Nolas et al., 1998; Paschen et al., 2001; Sales et al., 1996, 2001). The basic hypothesis for the thermoelectric properties of host-guest structures is that the conducting framework provides a high Seebeck coefficient (S) and electrical conductivity (σ), while low-lying optical modes, associated with the vibration of the guest atoms, hybridize with the acoustic modes. The thermal conductivity (κ) is thus lowered significantly due to the resonant scattering of the heat carrying phonons. Together this leads to high values of the thermoelectric figure of merit $ZT = TS^2\sigma/\kappa$. Structural characterization, including description of the lattice dynamics of the system, is essential for understanding the thermoelectric properties of a material, and also for any rational design of new materials.

A large number of studies have focused on the thermal conductivity of thermoelectric framework structures and have attempted to understand the role played by the guest atoms in determining the thermal properties (Dong et al., 2001; Sales et al., 1999, 2000; Keppens et al., 2000). In this respect, well-tested models of thermal vibrations and lattice dynamics in solids have experienced a remarkable renaissance. By applying the Debye model, Sales and coworkers have shown that even the most basic crystallographic parameter, the average isotropic mean square displacement parameter ($\langle U^2 \rangle$) for the framework atoms, can provide a quite accurate estimate of the thermal conductivity. Moreover, the $\langle U^2 \rangle$ of the “rattler” guest provides an estimate of its Einstein temperature. Analysis of atomic displacements is best done using neutron diffraction. Neutrons are scattered by the point-like nuclei, and neutron data accordingly are not biased by the spatial distribution of the electrons as is the case for X-ray data. The structure-property relationship for the thermal conductivity obtained from the neutron studies is a very useful one, and it is now employed to guide the search for new thermoelectric materials.

Accurate neutron crystallographic data allow evaluation of not only the harmonic components of the atomic motion, but also the anharmonic effects (Iversen et al., 1995). The conventional approach to thermal motion analysis is reciprocal space structure factor fitting, where parameters describing harmonic as well as anharmonic components of the atomic motion are introduced in the structure factor expression. Iversen and coworkers have developed an alternative approach using the maximum entropy method (MEM). MEM analysis of neutron diffraction data yields the direct space nuclear density distribution (NDD), which corresponds to the distribution of point nuclei smeared by the thermal motion. The NDD can be directly fitted to probability density function (pdf) models in direct space, and this avoids the approximation related to Fourier transformation of the pdf to obtain the temperature factor expression in reciprocal space. It is important to note that neutron diffraction data can be used in this way for the determination of lattice dynamical force constants of very complex solids.

It should be mentioned that the temperature dependence of the atomic displacement parameters (ADPs) provides an effective means for detecting subtle structural disorder, which can nevertheless have substantial effects on the transport properties of the solid. This is so, because such disorder is “absorbed” into the ADPs in least squares modeling yet is temperature independent. A good example is provided in a recent study of the thermoelectric clathrate, $\text{Ba}_8\text{Ga}_{16}\text{Si}_{30}$, where slight disorder of the Ba guest atoms is very difficult to prove experimentally (Bentien et al, 2002). However, the temperature dependence of the Ba ADPs measured with neutron diffraction at ten different temperatures can only be satisfactorily modeled if a small ($\sim 0.1 \text{ \AA}^2$) disorder term is included in the Einstein model. This is an example of a so-called “parametric study”; for additional examples, see section IV.

Another important advantage of neutron diffraction in research on thermoelectric materials stems from cross-section variation. Doping of thermoelectric cage structures can lead to large changes in transport properties, but very often it is difficult from X-ray diffraction to determine the exact location of the dopants. An example is Ni doping in skutterudite, CoSb_3 . Differing only by a single electron, Ni and Co are very difficult to distinguish with X-ray diffraction, but with neutrons there is a factor of four difference in scattering length. Similarly, Ga/Ge/As clathrates structures have very small X-ray scattering contrast, and their detailed structure is thus best established with neutron diffraction methods.

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IV. PARAMETRIC STUDIES

Molecular shape tuning in a coordination complex with supramolecular aggregation in the solid state

The second-order phase transformation in *trans*-[Ni(cyan)₂(NH₃)₄] provides an example of how a single-crystal diffractometer at a next-generation neutron source could improve the search for solutions to intriguing problems in coordination chemistry that have ramifications in hydrogen bonding, phase transformations, and parametric studies (Falvello et al., 1999). This simple coordination complex is linked in the crystalline state to an intrinsically crystal-based phenomenon, namely a second-order phase transformation that compels the molecule to undergo a smooth, non-destructive shape change, as temperature is varied in the range of 10 – 300 K (Figure 7). The crystal structure, which is built up beginning with the nickel-centered molecule, is dominated by an unbounded ribbon of cyanurates mediated by intermolecular hydrogen bonds formed in a self-recognition interaction as shown in Figure 8 (Falvello et al., 1997). At the upper end of the operative temperature range of the transformation, a first-order component produces rotation of half of the ammonia ligands with concomitant reorganization of the critical hydrogen-bonding pattern that they form at intermolecular junctions. A complete characterization of this system, which was achieved using both X-ray and neutron diffraction, involved measuring a number of complete sets of single-crystal diffraction data over the range 10 – 300 K. At each temperature, an accurate structure determination was necessary in order to derive parameters for the hydrogen atoms involved in the interactions across intermolecular space. In the temperature range 223 – 300 K, in which the first-order component produces disorder in the ammonia moieties, the use of neutron diffraction was decisive – that is, no technique other than single-crystal neutron diffraction with carefully controlled sample environmental parameters could have been used to characterize the system properly. In fact, accurate refinement of the parameters of half-occupied hydrogen atom sites was necessary.

The characterization of the behavior of *trans*-[Ni(cyan)₂(NH₃)₄] in the solid state, unprecedented in molecular materials, has taken several years and is still ongoing; and with wide-ranging implications that have yet to be fully understood. A single-crystal diffractometer at a high-intensity neutron source, with a programmable variable sample environment, would have reduced the time required by an order of magnitude. The most salient features of this system could have been revealed by a series of about twenty full datasets, measured at various temperatures. We estimate that the proposed instrument at SNS would be capable of realizing these measurements, completely and accurately, in about three days.

At the upper end of the phase transition, a qualitative change is produced in the symmetry of the crystal, in such a way that the structure gives the appearance of disorder between two slight molecular distortions of opposite sense. This is observed in the form of elongation of the anisotropic displacement parameters (ADPs) of the atoms involved, in the direction of the distortion coordinate (Figure 9). A thorough analysis of the anisotropic displacement parameters requires high-accuracy and high-resolution diffraction data of the sort that we fully expect will be produced by the proposed SCD at SNS.

Compared with the possibilities provided by the proposed instrument, the limitations of current facilities have retarded the elucidation of the causes of the phase transformation in solid-state *trans*-[Ni(cyan)₂(NH₃)₄], and by implication the development of further molecular materials with this striking new behavior.

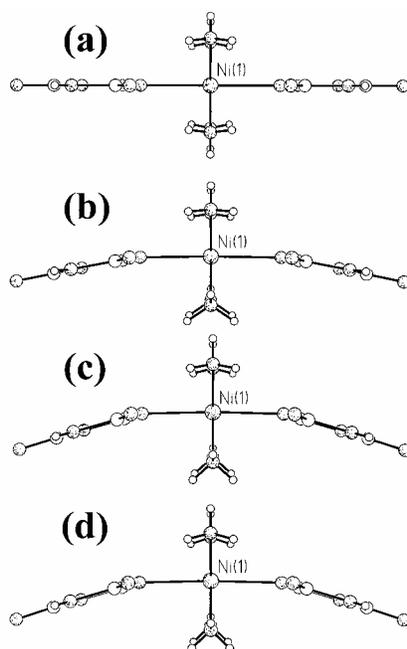


Figure 7. Lateral view of one molecule of *trans*-[Ni(cyan- κ N)₂(NH₃)₄] at various temperatures, showing the changing dihedral angle between the cyanate groups: (a) 298 K, dihedral angle = 0°; (b) 223 K, dihedral = 21.61(4)°; (c) 139 K, dihedral = 32.14(5)°; (d) 100 K, dihedral angle = 33.28(8)°.

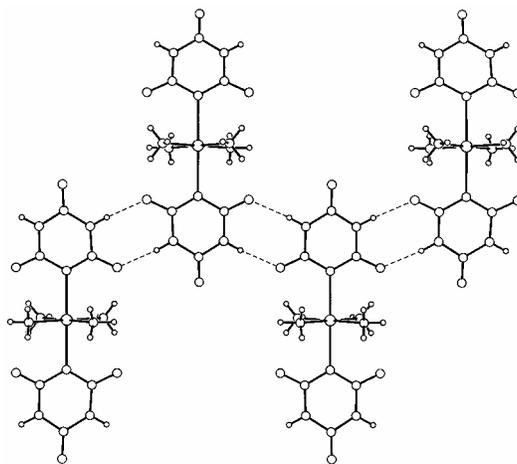


Figure 8. Section of the cyanurate ribbon from the crystal structure of *trans*-[Ni(cyan- κ N)₂(NH₃)₄] at 139 K.

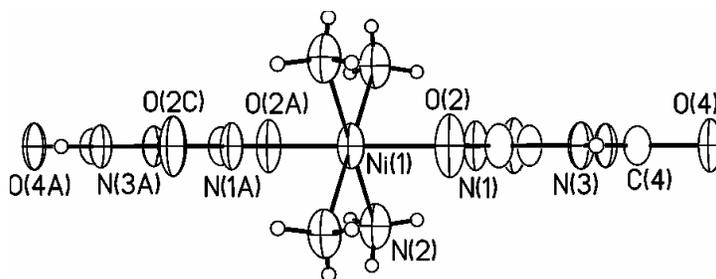


Figure 9. Side view of one molecule of *trans*-[Ni(cyan- κ N)₂(NH₃)₄] at 298 K. Non-hydrogen atoms are represented by their 50% probability ellipsoids.

The copper/saccharinate/aqua/ammonia reaction system: Versatility of saccharinate in coordination and intermolecular communication: Four different coordination modes of saccharinate and a dominant hydrogen-bonded supramolecular aggregate from a single reaction system

The fundamental metal-complexing and molecular recognition properties of the economically important compound saccharine were characterized in a complex reaction system involving a series of coordination compounds of copper (Figure 10) (Falvello et al., 2001). Beginning with *trans*-[Cu(sacch)₂(H₂O)₄], in which saccharinate is bonded to the metal through its deprotonated imido nitrogen atom, variation of the auxiliary ligand was used to produce a series of complexes in which saccharinate changed coordination mode among (a) binding through the imido nitrogen, (b) binding through the carbonyl oxygen, (c) bridging two copper centers using both the imido nitrogen and the carbonyl oxygen, and finally (d) through a weak interaction to copper involving the least basic of the functional groups, namely a sulfonyl oxygen atom. The final, intrinsically unflavored coordination mode is achieved in a highly stable crystal through the imposition of a structurally dominant supramolecular aggregate held together by a complex pattern of hydrogen bonds involving saccharinate, coordinated ammonia, and unligated water (Figure 11).

The full characterization of the versatility of saccharinate (an entity whose importance is unquestionable) in this unique reaction system could not have been achieved without the use of single-crystal neutron diffraction for elucidating the structure of two critical components. For the final product, involving sulfonyl coordination and hydrogen-bond-mediated supramolecular aggregation, the identification of the hydrogen atoms, the accurate characterization of the hydrogen bonding, and an unequivocal distinction between water and ammonia, required single-crystal neutron diffraction at relatively high resolution. The triclinic data set was measured in fourteen days on the SCD instrument at IPNS – the only single-crystal neutron diffractometer available in the U.S.A. at the time that these measurements were made. Furthermore, since the role of the auxiliary ligand is critical to the nature of the products formed and their stability, it was of utmost importance to establish that the first product indeed possessed all aqua moieties (seven days on the IPNS SCD) while the final product possessed precisely four ammonia ligands and

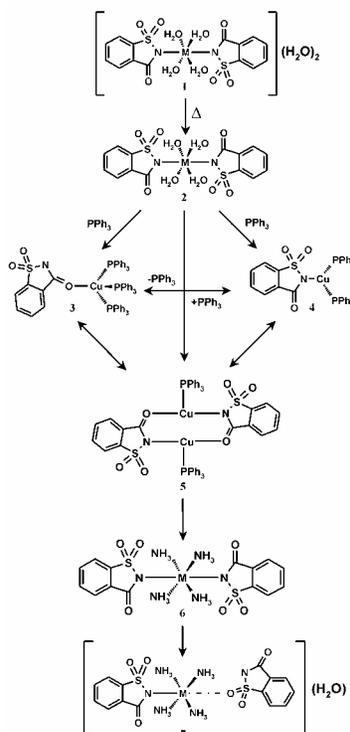


Figure 10. The Cu/saccharinate/ PPh_3 reaction system, with water and ammonia as secondary ligands.

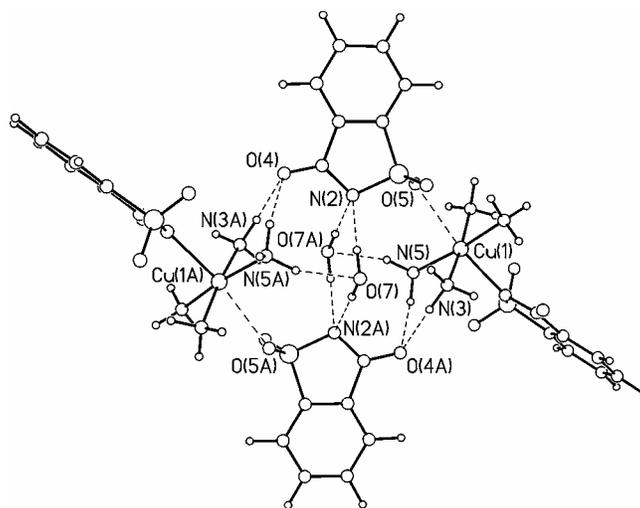


Figure 11. Drawing of the supramolecular aggregate formed by two asymmetric units of $[\text{Cu}(\text{sacch})(\text{NH}_3)_4](\text{sacch})\cdot\text{H}_2\text{O}$, from the neutron diffraction analysis. Atoms with "A" appended to their names are related to their congeners by a crystallographic inversion center.

unligated water. This is a good example of the added value brought to the scientific enterprise by single-crystal neutron diffraction in situations where no other technique suffices.

We estimate that the two data sets involved in this case could have been measured on the proposed SNS SCD instrument, with the necessary accuracy, in a total time of not more than two days.

Molecular solid solutions of Jahn-Teller complexes in non-Jahn-Teller-active host matrices

Six-coordinate, high-spin complexes of Cr(II) are Jahn-Teller active, and are usually observed to have a significant distortion produced by elongation of one mutually *trans*- pair of metal-ligand bonds. A typical complex possessing this property is the cation $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, as observed in the Tutton salt $(\text{NH}_4)_2[\text{Cr}(\text{H}_2\text{O})_6](\text{SO}_4)_2$, a molecular solid that gains its stability through an extensive network of hydrogen bonds that counter the intrinsic instability of Cr(II) to oxidation under normal ambient conditions.

In a manner analogous to the observed response of the deuterated copper Tutton salt under pressure, it was observed that the chromium Tutton salt undergoes a Jahn-Teller switch when doped with even a small proportion of the analogous zinc complex, which is not Jahn-Teller active. The Jahn-Teller switch is a change in the direction of the distortion, from elongation of one pair of mutually *trans*- bonds to elongation of another. A subtle change in the hydrogen-bonding pattern that endows the molecular solid with its stability is also produced.

Ideally a complete study of the molecular solid solution, $(\text{NH}_4)_2[\text{Cr}_x\text{Zn}_{(1-x)}(\text{H}_2\text{O})_6](\text{SO}_4)_2$, would involve high-accuracy single-crystal structure analyses at a series of several temperatures in the range of 10-300 K, of each of a series of samples in which the composition parameter x were varied from about 0.05 to 0.95. This would mean, in practical terms, roughly ten sets of data from each of about seven samples.

Using the facilities currently available in the U.S.A., one data set was gathered from each of two samples, providing a minimal, but still useful, characterization of the behavior of the affected ligands with a change of composition parameter (Araya et al., 1993; Cotton et al., 1994). It is important to note that high-accuracy data are necessary, because the Jahn-Teller effect becomes dynamic at certain values of temperature and composition parameter; and proper characterization of the system requires analysis of the ADPs of the ligands affected by Jahn-Teller distortion.

Fortunately, crystals of sufficient volume for use with currently existing neutron sources were available for the two analyses performed for the Cr/Zn Tutton salt system. An even more interesting system, *trans*- $[\text{Cr}_x\text{Zn}_{(1-x)}(\text{nic})_2(\text{H}_2\text{O})_4]$ (*nic* = nicotinate), in which the Jahn-Teller effect at the chromium center becomes dynamic upon doping, and which has been characterized in a preliminary fashion using single-crystal X-ray diffraction, will be fully characterizable only with the proposed SNS SCD instrument.

From the above examples, the importance of having the capability to rapidly obtain high-resolution neutron diffraction data, while removing the requirement for a large crystal, cannot be overestimated. This possibility will open up new horizons and increase our understanding of the basic science behind

applications of new smart materials and nano-machines based on fast molecular processes like molecular distortions.

Migrating intramolecular protons

In complexes of methylpyridines (MePy) with pentachlorophenol (PCP), the proton position in the very short $N\cdots H\cdots O$ hydrogen bond can be tuned, either chemically by shifting the methyl substituent, or by changing the temperature (Steiner et al., 2001). The availability of a large crystal meant that neutron diffraction data could be obtained in a reasonable time at seven temperatures from 20 K to 200 K. The mean proton position was found to change smoothly with temperature by 0.1 Å, from being at 1.206 Å from N at 20K (and 1.309 Å from O) to a distance of 1.306 Å from N (and 1.228 Å from O) at 200 K.

Complemented by very accurate studies of the structure at key temperatures – for example somewhere above 100K where the proton is centered - this parametric study provides reliable information for theoretical studies of hydrogen bond potentials in a simple model system. Extending these studies to larger systems with larger unit cells, and to smaller crystals, requires a dramatic increase in the availability of single-crystal neutron diffractometer capacity. Note that high-angle diffraction data become increasingly weak as temperature increases. Accordingly, for any given desired precision, considerably longer measuring times generally are required at higher temperatures.

Phase transition of a spin-crossover tricobalt coordination compound

The versatile chemical and physical properties of polynuclear transition metal complexes have generated interest in the areas of molecule-based electronic, photochemical, and magnetic materials. Understanding the metal-to-metal interactions in these polynuclear complexes is pivotal for the rational design and synthesis of molecules with intended properties. In a class of linear trinuclear complexes supported by the anion of di(2-pyridyl)amine, one remarkable feature is the tunable metal-to-metal interactions within the linear trinuclear unit. For the tricobalt compound $Co_3(dpa)_4Cl_2$ (**1**), there are "bond stretch" isomers that can be isolated from the same solution as crystals in either symmetrical $s-Co_3(dpa)_4Cl_2 \cdot CH_2Cl_2$ or unsymmetrical $u-Co_3(dpa)_4Cl_2 \cdot 2CH_2Cl_2$ forms (Chart I), as reported by Clerac et al. (2000). The former isomer has metal-metal bonding delocalized over the three cobalt atoms, whereas the latter has a singly bonded Co_2^{4+} unit and a separated Co^{2+} ion. In the solid state, these isomers exhibit a doublet ground state at low temperatures. When the temperature is increased, the two forms undergo gradual one-step spin crossover processes to higher spin states.

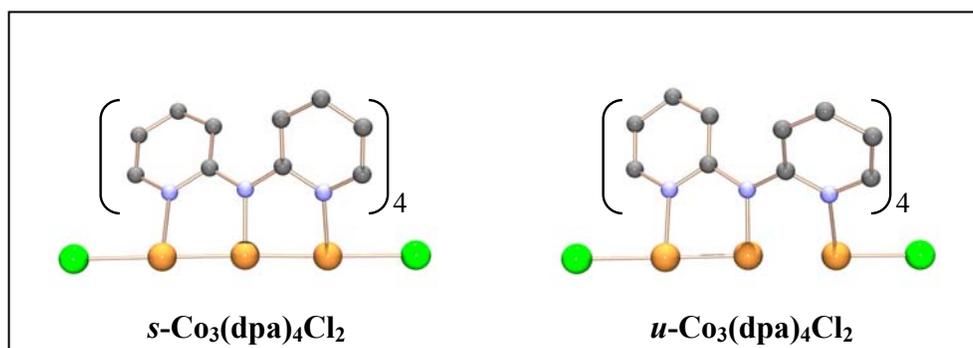


Chart I

Though the spin-crossover model is consistent with the structure of $u\text{-1}\cdot 2\text{CH}_2\text{Cl}_2$, the symmetrical $s\text{-1}$ molecule in $\mathbf{1}\cdot\text{CH}_2\text{Cl}_2$ remains symmetrical at all temperatures. A neutron diffraction study showed that the tricobalt compound exhibited an order-disorder transition involving a hydrogen bond to a metal-bound ligand. A reversible second-order phase transition from orthorhombic ($Pnn2$) to monoclinic (Pn) symmetry for the crystal of $\mathbf{1}\cdot\text{CH}_2\text{Cl}_2$ has been documented by neutron diffraction studies. As shown in Figure 12a, at 20 K one of the axial Cl atoms is involved in hydrogen bonding with the ordered CH_2Cl_2 solvent molecule in the solid state. A drawing of the structure at 296 K showing the solvent, which is now disordered, is presented in Figure 12b for comparison. It is seen that a displacive ordering of the solvent

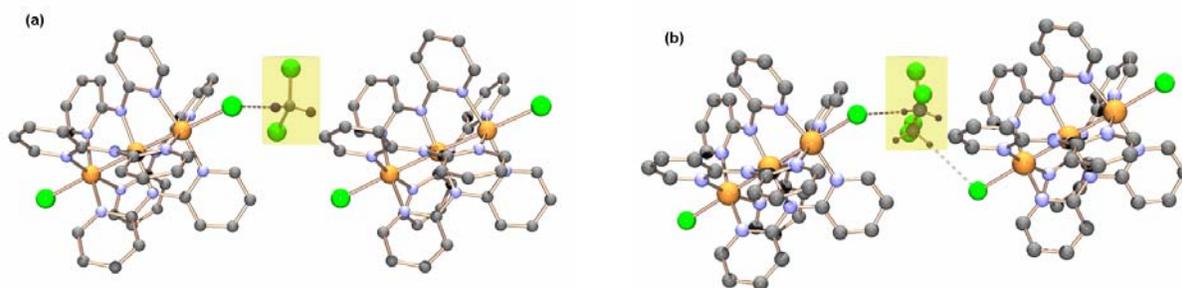


Figure 12. (a) A drawing of the extended structure of the monoclinic crystal of $s\text{-1}\cdot\text{CH}_2\text{Cl}_2$ along the bc plane at 20 K. One of the axial Cl atoms is hydrogen-bonded to an interstitial dichloromethane molecule with a $\text{Cl}\cdots\text{H}$ distance of 2.635(7) Å. (b) A drawing of the extended structure of the orthorhombic crystal of $s\text{-1}\cdot\text{CH}_2\text{Cl}_2$ at 296 K. Here the interstitial dichloromethane molecules are disordered in two positions.

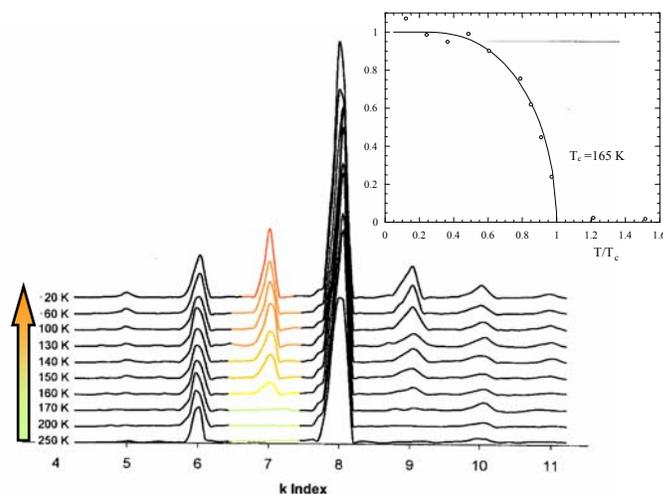


Figure 13. Plot of neutron diffraction intensities for $0k0$ reflections in space group $Pnn2$ versus temperature for $s\text{-1}\cdot\text{CH}_2\text{Cl}_2$. Systematic absence violations for reflections $0k0$, where $k = 3, 7, 9, 11$, at low temperature are consistent with a phase transition to monoclinic Pn symmetry. Inset: thermal variation of the normalized intensity of the 070 reflection; the black line is the fitting obtained with an Ising model.

molecule at lower temperature leads to a phase transition. Despite this, the molecules of *s-1* remain essentially, if not rigorously, symmetrical throughout the temperature range 20-296 K. This second-order phase transition is associated with the ordering of the solvent molecules and their hydrogen-bonding interactions.

Further insight into the phase transition process of *s-1*·CH₂Cl₂ was achieved by monitoring the change of neutron diffraction intensities of *0k0* reflections in the temperature range 20-250 K. The results are shown in Figure 13. The intensity of the 070 reflection at various temperatures is directly proportional to the square of the order parameter defined by an Ising model. This feature allows us to conclude that the displacive transition occurs around 165 K.

The *s-1*·CH₂Cl₂ compound in the *Pn* form has 92 atoms in the asymmetric unit, and seven days were required for data collection on the SCD instrument at IPNS. The relatively large unit-cell size of 2000 Å³ has pushed the limits of current instrumentation, resulting in a low data-to-parameter ratio for structure refinement. The new SNS SCD diffractometer will allow each data set to be collected within at most a few hours of beam time, so that a complete data collection and structure analysis could be obtained at each temperature shown in Figure 13. This will allow for temperature dependence studies of single-crystal structures. In addition, the SNS SCD will make magnetic structure measurement on these systems a reality. The capabilities provided by the SNS SCD will make it possible for the first time to study coordination compounds with complex physical properties, including phase transition, spin-crossover and magnetism.

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V. EARTH SCIENCE

Neutron scattering studies of materials of importance to the earth sciences are on the increase, largely because the low absorption coefficient for neutrons of most materials makes possible the construction of geologically realistic sample environments utilizing devices including furnaces, cryostats and pressure cells. There is a critical need to know the thermodynamics and kinetics of cation ordering in a variety of important rock-forming minerals, over a wide range of temperature and pressure. High-quality data on site occupancies for complex minerals such as pyroxene, amphibole, mica, and spinel can be derived from neutron diffraction and thereby provide the basis of geothermometers and geospeedometers for natural systems. Neighboring elements in the periodic table, or iso-electronic ions, may have significantly different neutron scattering cross-sections, thus allowing ordering/disordering processes within structurally different sites to be fully characterized by neutron diffraction more readily than by X-ray diffraction. These types of studies have more frequently been done using powder neutron diffraction, but single-crystal studies can offer additional information in many cases, and have been underutilized in the past because of the crystal size limitations. As in many other chemical systems, the unique character of the neutron interaction with matter is naturally exploited in a number of geoscience applications: (1) The location of light atoms in the presence of heavy atoms in the structure; (2) The determination of the distribution of elements with similar atomic number over symmetry-independent crystallographic sites; (3) The determination of the position of the atomic nuclei for the extraction of the electron-density distribution utilizing X-N maps; (4) The capacity for detailed study of the thermal components of the atomic-displacement parameters, which makes neutron scattering an excellent choice for *in situ* studies under non-ambient conditions (Artioli, 2002). Minerals are a special class of materials, but they offer the full range of interests as in other materials, including phase transitions, magnetism, order-disorder, hydrogen bonding, and diffuse scattering.

Water in the Earth's mantle

Water (hydrogen) is an important component of minerals and rocks that make up the Earth's mantle. In fact, models for the solar system suggest that mantle water accounts for about 10% of all water on the planet (the remainder resides in the oceans and the crust). The exact chemical form of this water and its distribution within the mantle have been the subject of debate within the earth science community (Thompson 1992). The problem is important, because water has a dramatic effect on the physical and chemical properties of mantle materials. For example, the presence of water significantly lowers the melting temperatures of rocks, decreases the viscosity of magma, affects the character of volcanic activity (explosive or non-explosive), and may even generate the forces within the Earth that produce earthquakes. The water stored within the mantle could exist within the crystal structures of minerals as hydroxyl ions (OH⁻), or be present in dissolved form (H₂O) in high-temperature melts. In the case of minerals, the structurally-incorporated water would be released as the ocean floor (slab) descends several hundred kilometers into the mantle at continental margins. During this process, called subduction, the temperature and pressure of the slab increases, causing minerals to either dehydrate or change symmetry without dehydration. The released ("dehydration") water is recycled back into the overlying Earth layer through volcanic activity that occurs along the continental margins. Recent experimental studies (e.g., Stalder and Ulmer 2001) have shown that dehydration-rehydration reactions involving hydrous magnesium silicates could be an important mechanism for transporting water into the transition zone (400 km). Phase transitions that occur within the subducted slab can also cause a change in volume, generating stresses that may be responsible for faulting and earthquakes. Based upon infrared spectroscopic measurements,

Faust and Williams (1996) have proposed that the high-pressure phase transition in hydrous magnesium silicate (phase B) may be related to a change in the hydrogen bonding.

Because it is not possible to directly sample material in the mantle, crystallographic studies of high-pressure minerals have focussed on synthetic phases in the system MgO-SiO₂-H₂O. These phases are synthesized in piston-cylinder devices at high temperatures and pressures. Maximum crystal size is generally less than 100 μm, which is inadequate for single-crystal neutron diffraction at current facilities. Consequently, the hydrogen atom positions have not been accurately determined for many of the hydrous magnesium silicates. The development of an SCD instrument at the SNS would enable mineral physicists to determine the hydrogen-bond geometry in these structures and to learn more about the role of the O···H bond in mantle processes. This in turn would be expected to lead to a refinement of geophysical models of the Earth's interior.

Gas clathrate hydrates

The tendency of certain gases to form solid compounds with water at low temperatures and modest pressures has been known for nearly 200 years (Sloan 1998), but these compounds were largely of academic interest until the oil and gas industry recognized that gas hydrate formation under certain conditions may block pipelines. This discovery motivated structural studies of hydrates of methane and other gases, which revealed them to be clathrates, or 'guest-host' inclusion compounds. The 'host' lattice consists of an ice-like hydrogen-bonded network of water molecules with polyhedral cavities large enough to accommodate a variety of 'guest' molecules. Clathrate hydrates are known to form with many different guest molecules and are generally stable at low temperatures and/or elevated confining pressures. These clathrates occur naturally in seafloor deposits, in permafrost, in fluid inclusions of other minerals, and as major phases of icy parts of planetary bodies in the solar system. They are widespread and abundant, and diverse technological and scientific interests motivate their study. In particular, methane hydrate on the seafloor and in permafrost sediments constitutes the largest fossil energy reserve, and several countries are pursuing its recovery to use the methane as a clean-burning fuel. To mitigate the build-up of greenhouse gases in the atmosphere, the feasibility and impact of sequestration of industrial waste carbon dioxide in clathrate hydrate on the seafloor also is being explored.

The gas clathrate hydrates are amenable to study by neutron diffraction because they are composed mostly of water molecules. Their hydrogen bonding, proton disorder, and guest molecule disorder can be directly probed by various neutron scattering techniques. Single-crystal neutron diffraction studies are the method of choice for locating the atomic positions, determining the cage filling, and modeling the guest molecule disorder. The orientationally disordered guest molecules give rise to the anomalously low, glass-like thermal conductivity of the clathrate hydrates. Single-crystal neutron diffraction studies of the clathrate hydrates (McMullan and Kvik, 1990) are rare, because large crystals are generally quite difficult to grow and to maintain them requires elevated pressures and/or low temperatures. The SNS single-crystal instrument will provide the resources that are needed to study hydrates under geologically relevant conditions and provide much needed physical and thermodynamic properties descriptions.

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VI. MAGNETISM

In magnetism, the determination of the spatial magnetization distributions around magnetic atoms and ions plays a crucial role in developing new magnetic materials. For example, the changes in the distribution of unpaired electrons that occur during phase transitions can explain metal-to-insulator transformations, and the deviation of the distribution from spherical symmetry may show which of the sub-bands are active at the Fermi level or the atoms, orbitals and spin densities due to covalent bonding in molecules.

Molecular and organic magnets

Research in magnetic materials has exploded in recent years due to the development of new molecular and organic magnets, i.e., solids that are built up from structurally well-defined clusters containing magnetic ions in a complex environment (Schweitzer and Ressouche, 2001). Since the discovery of the first ferromagnetic molecular compound (decamethylferrocenium tetracyanoethylene, $T_c = 4.8$ K) in 1986, enormous progress has been made in this area. These molecular magnets are typically polynuclear transition metal complexes, and they can be termed “single molecule magnets.” The unpaired electron responsible for the magnetism sits in a molecular orbital built up from the orbitals of the atoms constituting the molecule. The magnetization tends to be smeared out across the molecule, though perhaps concentrated on certain atoms. Measuring the magnetization distribution across a molecule reveals precious information on the nature of the molecular orbitals responsible for the magnetism and the interactions with neighboring molecules in the solid, as well as the chemical bonding and how the electron spin is spread out and oriented. This makes it possible to test the underlying theories of molecular bonding and magnetism, and to create new magnetic materials with predicted properties. Molecular magnets can also be viewed as single-domain magnets with a domain size in the nano limit. Thus, they can be used for studies of magnetic phenomena on the nano scale.

A typical example of a molecular magnet is the room-temperature magnet combining a hexacyanometalate $[M(CN)_6]^{4-}$ with a Lewis acid L^{P+} (Ferlay et. al., 1995), see Figure 14. If L and M are

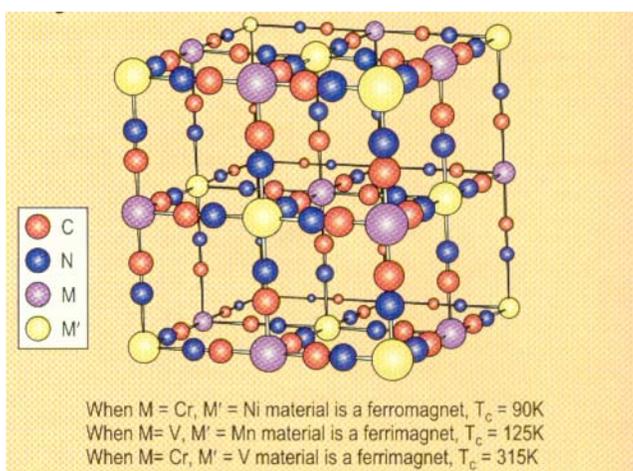


Figure 14. Nuclear structure of the hexacyanometalate $[M(CN)_6]^{4-}$ with a Lewis acid L^{P+} .

transition metal ions, the orbital interactions in the resulting compound can be described by well-understood principles, and it is therefore possible to tune the compound's magnetic properties.

Interest in these compounds is currently mainly scientific rather than practical, and one of the challenges here is to find new applications that will exploit their specific properties such as lightness, transparency, solubility, optical properties, and biocompatibility. Molecular magnets with total spin number $S = 10$ also display numerous excited spin states and open the way to a novel class of information storage systems.

Studies of the magnetic properties of such systems aim at understanding both the materials properties (e.g., magnetic coupling mechanisms) and the fundamental chemistry, such as reactivity in coordination complexes and its dependence on electronic structure. An area of research where neutron diffraction has not yet shown its full potential, due to the flux limitations of the present sources, is to combine charge density analyses with magnetic studies, in order to obtain an explanation for various magnetic phenomena in terms of electronic structure. An example where this would be useful is the large molecular magnet or "chromium wheel" system, $\text{Cr}_8\text{F}_8(\text{C}_5\text{H}_9\text{O}_2)_{16}$, containing 272 unique atoms (Overgard et al., 2002). For this structure the charge density has been determined from synchrotron X-ray data, and a detailed topological analysis of the electron density has been carried out. Figure 15 shows the experimentally determined electrostatic potential, which is used for predicting the inclusion properties of the molecule. A combination of magnetic neutron diffraction data, which may be obtained from future sources such as SNS, and synchrotron X-ray data may provide electronic information on complex molecular systems such as this, which is very difficult to obtain by other methods, e.g., theoretical calculations.

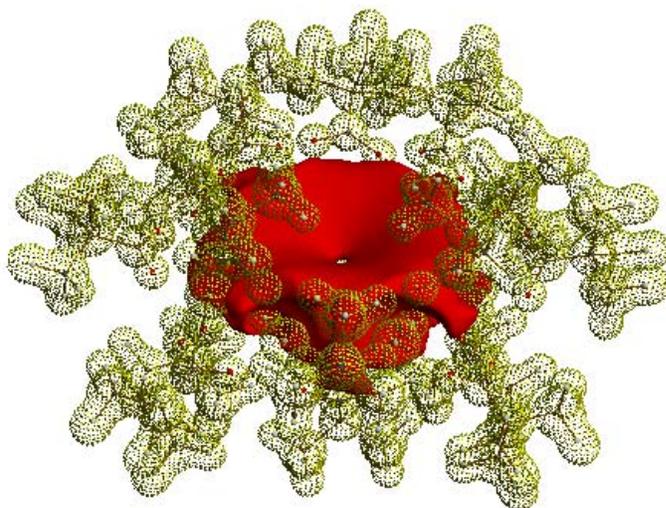


Figure 15. The experimentally determined electrostatic potential of the "chromium wheel" $[\text{Cr}_8\text{F}_8(\text{C}_5\text{H}_9\text{O}_2)_{16}]$.

In the area of molecular magnetism, the number of studies of organic radicals has also increased dramatically. Even though radicals are chemically reactive, there are many examples of materials where

radicals are trapped in the solid phase, such as nitroxides (Pillet et al., 2001; see Figure 16). These materials exhibit many different types of magnetic phenomena, which to a large extent are determined by the crystal packing and the detailed nature of the intermolecular interactions. Thus, the field of organic radicals will be particularly well suited for research with next-generation neutron sources such as SNS.

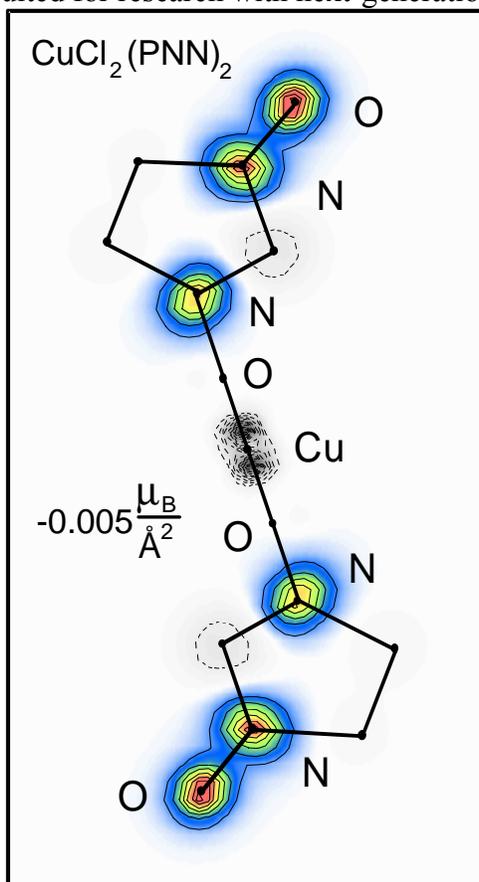


Figure 16. Spin density of the Cu complex $\text{CuCl}_2(\text{NitPh})_2$ projected along the π direction of the Nit (nitronyl nitroxide) ligand. The density is positive on most of the atoms on the two NitPh ligands and is negative on the copper. The lack of magnetization on the oxygens shows that this system represents an extreme case, where the spin distribution of the nitronyl nitroxide has been completely upset by the magnetic interaction with the copper.

As will be clear from the discussion above, neutron diffraction remains the technique of choice for studying magnetism. It is the classical polarized neutron diffraction technique that permits investigation of the distribution of the magnetization, which contains essential information on the electronic structure of materials: the nature of the magnetic orbitals, the interactions with neighboring molecules in the solid, and effects such as chemical bonding, spin delocalization or spin polarization. Up to now, this technique has only been used at continuous neutron sources such as the ILL (D3) because there was no device able to simultaneously polarize a beam efficiently at short wavelengths and maintain the bandwidth. Today, thanks to the progress made on ^3He neutron spin filters that make use of the spin dependency of the ^3He absorption cross-section, one can successfully apply this technique to a pulsed neutron source. Such filters, being developed at NIST and in Europe within the “European Neutron Polarization Initiative” network (a consortium of seven laboratories), are broadband, can have infinite divergence acceptance, do not influence the resolution of the instrument, and can create homogeneously polarized beams. Experiments are now routinely carried out at the ILL with such spin filters, and there is no doubt that a

polarized-beam option including a high-magnetic field cryomagnet for the SNS SCD instrument will lead to breakthroughs in molecular magnetism thanks to the high flux that will be available.

Magnetic moment configurations

For the determination of magnetic structures, powder diffraction is often limited because of the averaging of contributions of randomly oriented grains. For example, it is impossible to determine the moment configurations in a cubic lattice on the basis of powder diffraction only. In a single-crystal experiment, however, the anisotropic nature of the magnetic interaction can be used to separate the nuclear and magnetic contributions to the Bragg peaks, and it is possible to unambiguously determine the moment

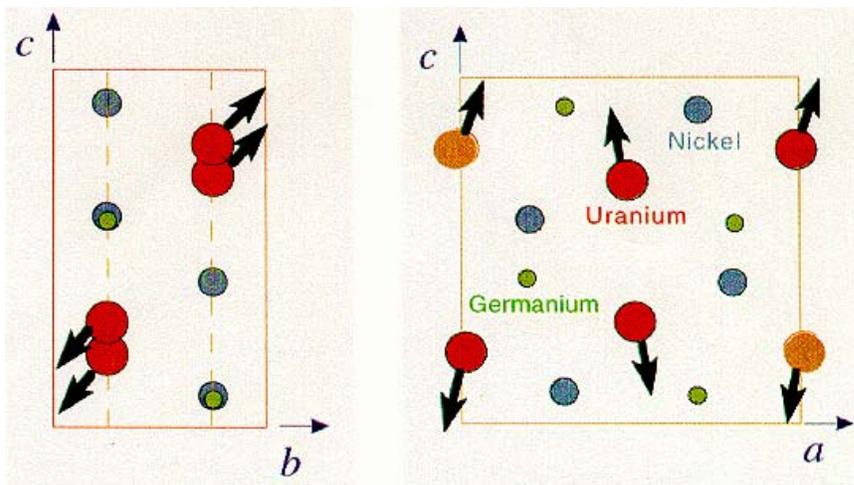


Figure 17. Moment configuration of one domain in UNiGe shown as projections on the orthorhombic *b-c* and *a-c* planes, respectively (Purwanto et al., 1996). The moment directions of the second domain are given by the images at the $y = 1/4$ and $3/4$ mirrors (dashed lines).

configurations even in ferromagnets (see, for example, Nakotte et al., 1999). In addition, single-crystal neutron diffraction makes it possible to separate co-existing magnetic phases in a single material (Radaelli et al., 2001). It can also distinguish between multiple-*k* and multi-domain, single-*k* magnetic structures, studies that cannot be done with powder diffraction. As an example of such studies, Figure 17 illustrates the proposed moment configuration in UNiGe. For this orthorhombic compound, time-of-flight single-crystal neutron diffraction revealed a complex configuration of uranium *5f* moments with a single-*k* propagation vector and the occurrence of two magnetic domains below $T_N = 42$ K (Purwanto et al., 1996). Polarized neutron diffraction experiments designed to measure the *x* component of the moment directly confirmed the non-collinear magnetic structure (Nakotte et al., 1996).

Small-moment systems

Compared to powder diffraction, another advantage of single-crystal neutron diffraction is its sensitivity to small magnetic moments. In general, powder diffraction experiments are limited to magnetic moments larger than about $0.2 \mu_B/\text{f.u.}$, while substantially greater sensitivity is achievable in a single-crystal experiment. However, to date neutron diffraction has made only a small contribution to the extensive research on small-moment systems, due to the sensitivity limitations of most diffractometers. The proposed SCD at SNS will make possible serious attempts to detect moments as small as $0.01 \mu_B/\text{f.u.}$, which should be sufficient to address many open questions regarding small-moment systems.

For example, many strongly correlated electron systems have inherently small moments that cannot be detected by existing single-crystal diffractometers. The proposed SNS SCD may be expected to provide valuable insight into the interactions of the so-called heavy fermion superconductors, such as UPt_3 (Keizer et al., 1999) where theoretical models propose the coexistence of tiny antiferromagnetic moments with the superconductivity. An additional example is the possibility opened up by the proposed SCD to distinguish between ‘true’ incommensurate structures and spin-slip structures where a coherent arrangement of spin-slip planes leads to a seemingly incommensurate propagation vector. For a spin-slip structure one should find magnetic third-order reflections, one order of magnitude weaker than the fundamentals. A spin-slip structure has been proposed, for example, for CePtSn (Kadowaki, 1999).

In addition to the examples enumerated above, the determination of magnetic structures plays a major role in the understanding of phenomena including low-dimensional systems, phase transitions, and geometrical frustrations. Because of the continuously evolving complexity of materials, the determination of antiferromagnetic structures is becoming less tractable. In contrast to powder diffraction and conventional monochromatic beam, single-crystal techniques, the time-of-flight Laue technique can overcome this difficulty. By providing large Laue maps of the reciprocal space, the determination of the propagation vectors becomes unambiguous: multi-domain and multi- k structures are distinguished, and the magnetic amplitudes are measured more rapidly.

Temperature, pressure and applied magnetic field

The properties of a magnetic material may be strongly modified by changing any of the thermodynamic parameters. Thus, changing the temperature, the external pressure or the applied magnetic field will provide valuable insight into the nature of the magnetic interactions. Since these interactions are generally highly anisotropic, only single-crystal experiments can provide complete information when changing vector quantities like external pressure and applied magnetic field.

Long-range magnetic order only occurs below the magnetic-ordering temperature, which for many materials of interest (for example, strongly-correlated-electron systems) can be quite low. In some cases, transition temperatures can be as low as a few hundred milli-Kelvin, and a dilution-refrigerator option for the SNS SCD would therefore be desirable, in order to accommodate such studies.

External pressure modifies the magnetic exchange and the hybridization effects in materials, which in turn can lead to suppression of zero-pressure magnetic phases and/or the appearance of new pressure-induced

phases (see, for example, Honda et al., 1997). In the majority of materials, the pressure effects are anisotropic, even in the case of hydrostatic pressure, because of anisotropic compressibilities. In general, higher pressures can be achieved for smaller sample volumes, and a reasonable long-range goal is to implement a 20-kilobar-pressure cell (with 1 mm³ sample volume) option for SCD.

While the temperature and pressure options should be easily accommodated in the design of the SCD instrument, the use of applied magnetic fields imposes additional design considerations, primarily because of the stray magnetic fields that arise from the magnet. However, by employing non-magnetic materials in the vicinity of the magnet, it should be possible to consider a superconducting magnet with a field up to about 8-10 Tesla without significant modification of the instrument. This should allow the study of field-induced magnetic structures in the majority of materials that are of interest for applications, and for basic studies (Sechovsky et al., 1995). In addition, application of a magnetic field will make possible domain population studies in antiferromagnetic systems. Unlike the case of ferromagnetic domains, there has been very little theoretical work to understand the properties of antiferromagnetic domains. For example, the

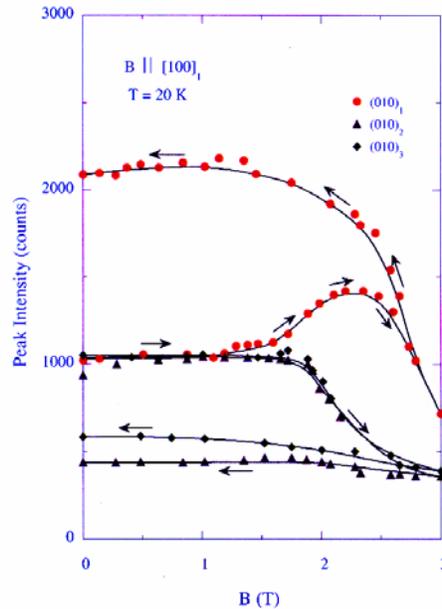


Figure 18. Magnetic intensities of the (010) reflection of three different magnetic domains (subscripts: 1, 2 and 3) of UPdSn as a function of the magnetic field applied along the *a* axis of domain 1 as measured at the Research Reactor, Chalk River Laboratories (Nakotte et al., 1998). Note that the magnetic intensities are almost equal before application of a magnetic field, while domain 1 has a substantially increased intensity after application of the field compared to domains 2 and 3. The arrows indicate the increase and decrease of the field. The lines are guides to the eye.

changes in domain occupancies in the antiferromagnetic compound UPdSn as a function of applied field (Nakotte et al., 1998) are shown in Figure 18 above. This compound forms three magnetic domains because of its hexagonal crystal symmetry and orthorhombic magnetic symmetry. As can be seen in the figure, all three domains are populated almost equally before application of a magnetic field. Application of a magnetic field along the principal axis of one of the three domains leads to domain repopulation, where one domain grows at the expense of the other two. A nearly single-domain sample remains, after releasing the field.

Concluding remarks

It must always be remembered that the magnetic structure factor is a vector quantity with complex components, and that much significant directional information is lost when only intensities are measured. The vector properties of the neutron polarization provide a unique way of recovering some of the lost information. The changes in direction of the neutron spin that take place on scattering by a magnetic interaction vector are highly dependent on their relative orientations. These changes can be measured using a neutron polarimeter that is presently unique to the ILL. Using this technique, called spherical polarimetry, it has been possible to solve a number of magnetic structure problems that had proven to be intractable when employing other techniques (Brown, 2001). Furthermore when the magnetic and nuclear scattering occurs at the same position in reciprocal space, this technique allows the precise determination of antiferromagnetic form factors, which is not possible by other means (Brown et al., 2002). Work is presently being done at the ILL to maintain bandwidth, a crucial feature in time-of-flight single-crystal diffraction. Taking advantage of the ^3He spin filter developments and the high neutron flux that will be provided by SNS, the SCD promises to be a unique world-leading instrument for investigating novel complex magnetic systems.

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VII. DIFFUSE SCATTERING

Properties of advanced materials (see also Section III on thermoelectrics) are often governed by defects and local atomic arrangements rather than by their long-range periodic structure. Any deviation from the average structure results in diffuse scattering holding the key to understanding the structure-property relationship.

Diffuse scattering is generally weak, and experiments require extensive detector coverage to allow for simultaneous measurement over large areas of reciprocal space. At the same time, low background scattering is essential, and one needs to be able to measure weak diffuse scattering signals adjacent to strong Bragg reflections.

Although single-crystal diffuse scattering measurements can be carried out using X-rays, neutrons have some unique advantages here:

- Neutrons allow the measurement of magnetic diffuse scattering, which contains information about magnetic short-range order. When the beam is polarized, one can separate the magnetic scattering from the nuclear coherent and nuclear spin incoherent ones (see D7 at ILL), and by making use of the neutron polarimeter cited in Section VI above, one should also be able to extract the nuclear/magnetic correlations that are expected in some advanced materials. This is an exciting and rapidly expanding area of research (see, e.g., Bramwell et al., 2001).
- Neutrons make it possible to study hydrogen in metals, which is of great importance in developing hydrogen-storage technology (see also Section I).
- Neutrons provide outstanding cross-section contrast. This may be essential for many applications, for example in studies of systems containing light elements. To cite another interesting case, a large class of quasicrystals is based on Ni-Co, which commonly cannot be distinguished using X-rays.
- Neutron scattering makes it possible to separate elastic from inelastic diffuse scattering contributions – this is *vital* especially for quantitative applications.

The study of cubic stabilized zirconia (CSZ) provides an excellent example in which diffuse neutron scattering measurements proved to be essential. CSZ material has extensive applications because of its ionic conductivity. Measurements on CSZ show strong diffuse scattering that can be explained by correlated oxygen vacancies, introduced by the doping and relaxation of the metals surrounding the vacancies (Neder et al., 1990; Proffen et al., 1996b). The diffuse scattering was investigated as a function of temperature (Figure 19, see Proffen et al., 1996a) using the state-of-the-art, time-of-flight Laue neutron scattering instrument SXD at ISIS (Rutherford Appleton Laboratory, U.K.). Analysis of these data showed that the width of the diffuse scattering remained virtually unchanged, implying that the correlation length of the oxygen vacancy ordering is basically temperature independent. The intensity, however, showed a sharp drop in the narrow temperature interval between 1250 and 1300 K (Figure 20). This temperature region corresponds to an anomaly in the Arrhenius behavior of the ionic conductivity (Strickler and Carlson, 1964). This can be qualitatively understood by a sudden transformation of correlated oxygen vacancies into “free” vacancies that are taking part in the conduction process.

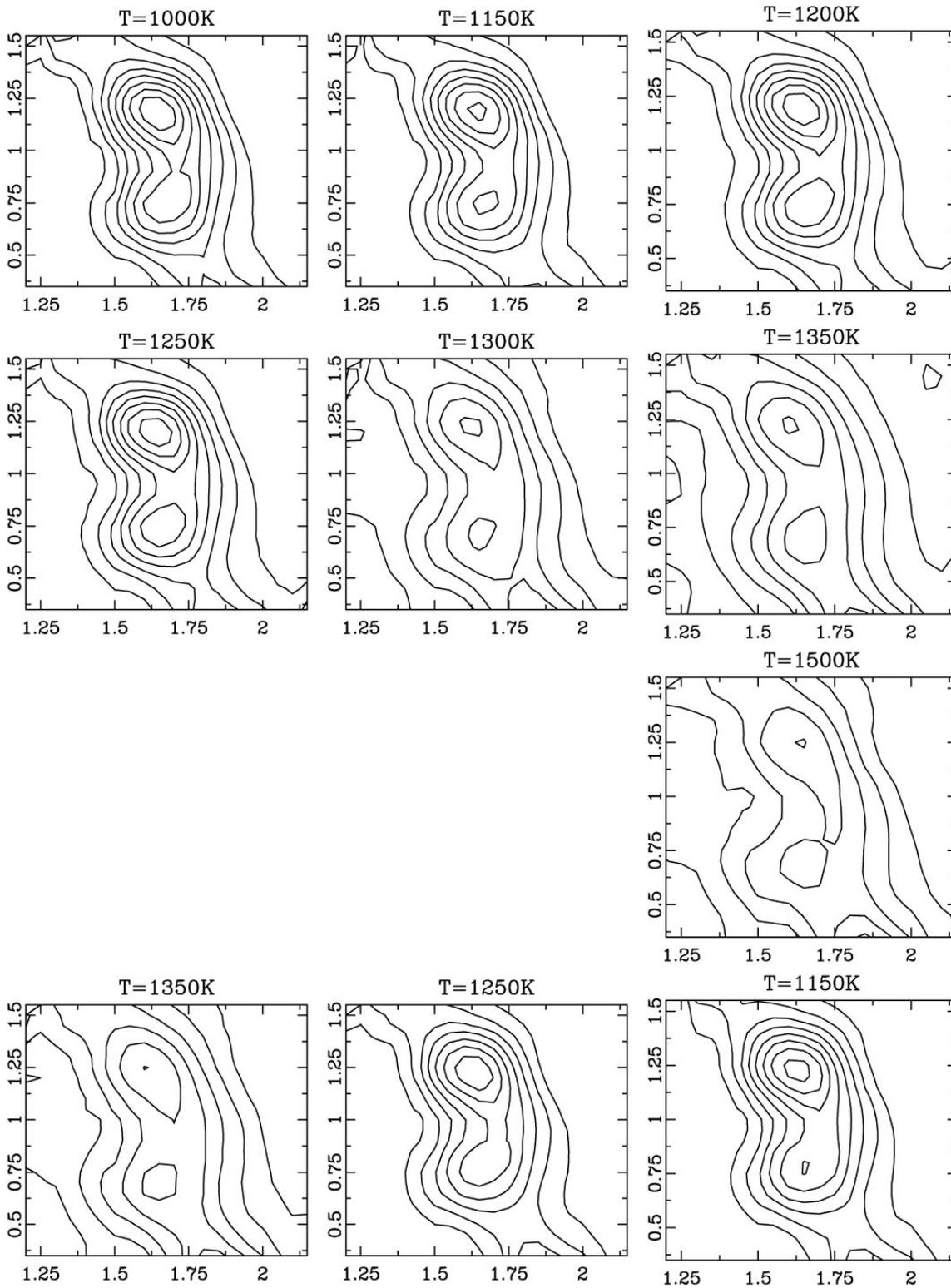


Figure 19. Diffuse scattering maxima in calcium-stabilized cubic zirconia, $Zr_{1.85}Ca_{0.15}O_{1.85}$, as function of temperature at the superlattice positions $(1.6\ 1.6\ 0.8)$ and $(1.6\ 1.6\ 1.2)$ related to oxygen vacancy ordering. The first seven panels correspond to measurements upon heating, and the last three panels to measurements upon cooling. Additional details can be found in Proffen et al., 1996a.

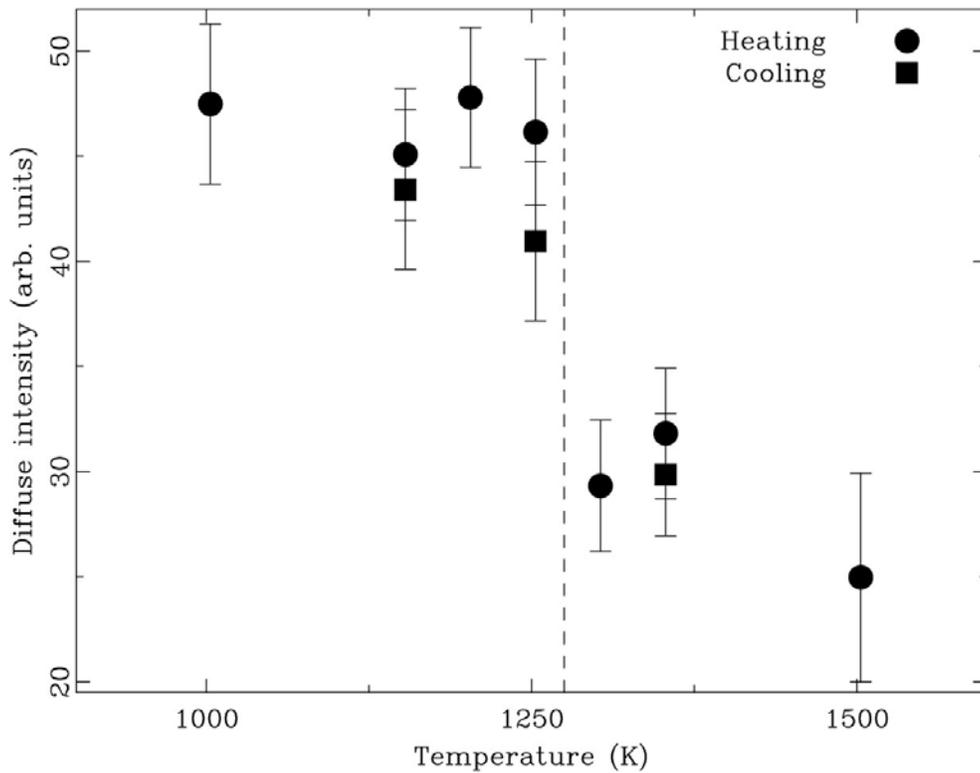


Figure 20. Intensity of diffuse maximum (1.6 1.6 1.2) in calcium-stabilized cubic zirconia, $Zr_{1.85}Ca_{0.15}O_{1.85}$, corrected for the decrease due to the Debye Waller factor. Details are given in Proffen et al., 1996a.

As an example of magnetic diffuse scattering, Figure 21 shows results from single-crystal diffraction experiments on the CMR material $La_{2-2x}Sr_{1+2x}Mn_2O_7$. The underlying physics of CMR materials is generally believed to involve polaronic degrees of freedom. As can be seen in the figure, the $x = 0.36$

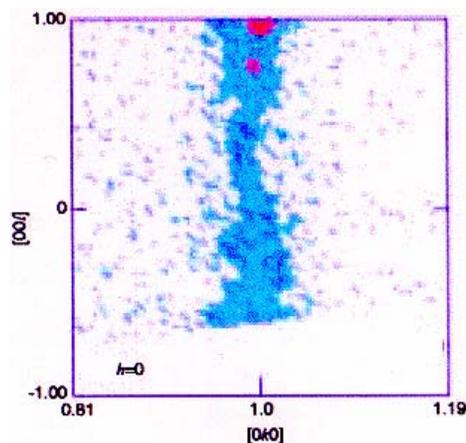


Figure 21. A portion of the time-of-flight neutron diffraction data taken on SCD at the Los Alamos Neutron Scattering Center from a single crystal of $La_{1.28}Sr_{1.72}Mn_2O_7$ at 120 K (Ling et al., 2000). The vertical strip of diffuse scattering extends along the c^* -direction, and it is indicative of two-dimensional ferromagnetic correlations within the Mn-O bilayers.

sample shows a rod-like diffuse scattering response (Ling et al., 2000). This observation is indicative of two-dimensional ferromagnetic correlations, which implies the presence of spin diffusion and in turn lends support to a polaronic model.

The proposed SCD at SNS, with its greatly reduced data collection times, undoubtedly will open the door to more extensive parametric studies of diffuse scattering than are currently feasible. At the same time, techniques for the quantitative analysis of diffuse scattering also are advancing rapidly. Recent studies have used Reverse-Monte-Carlo (RMC) simulations to model single-crystal diffuse scattering (Nield et al., 1995; Proffen and Welberry, 1997, 1998) and an automatic refinement process of interaction energies to match the observed scattering data (Welberry et al, 1998). There are also ongoing efforts in developing a general diffuse scattering modeling and analysis package, DISCUS (Proffen and Neder, 1997).

Although single-crystal diffuse scattering can be measured using X-rays, and many advances have been made using synchrotron radiation, neutron scattering has some unique advantages. As has been mentioned above, neutrons allow the measurement of magnetic diffuse scattering, which contains information about magnetic short-range order (see, e.g., Bramwell et al., 2001). Studies of this type currently are intensity limited, and the new SCD at SNS will open up exiting new possibilities in this field, especially if a polarized beam option is implemented.

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APPENDIX I. SNS SINGLE-CRYSTAL DIFFRACTOMETER WORKSHOP AGENDA

Friday, March 1, 2002

IPNS, Building 360, Argonne National Laboratory.

8:00 CONTINENTAL BREAKFAST

INTRODUCTION

8:45	Welcome and Opening Remarks (Function of Meeting; Goals; Possibilities)	R. Bau
9:00	The SNS Project – an Overview IAT/IDT Responsibilities	K. Crawford

INSTRUMENT CONTRIBUTIONS

9:30	Current Status of Single-Crystal Diffraction in the U.S.A.	A. Schultz
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10:00 BREAK

10:15	The Newly Updated SXD-11 at ISIS; Single-Crystal Diffraction in Europe	C. Wilson
10:45	Single-Crystal Diffraction in Japan and Plans for Instruments at the JSNS	I. Tanaka
11:15	Conceptual Design Effort for the SNS SCD	C. Hoffmann
11:45	Discussion	Participants

12:30 WORKING LUNCH

SCIENTIFIC DIRECTIONS

13:30	Studies of Transition Metal Coordination Complexes	G. Girolami
14:00	Single-Crystal Neutron Diffraction and Magnetism	E. Lelièvre-Berna
14:30	Accurate Neutron Crystallography in Chemistry and Materials Science	B. Iversen
15:00	Discussion	Participants

15:15 BREAK

VISION FOR THE FUTURE

15:30	Panel Discussion: Scientific Case; IAT/IDT Formation	Workshop Organizing Committee
17:00	Closing Remarks	T. Koetzle

APPENDIX II. SNS SINGLE-CRYSTAL DIFFRACTOMETER WORKSHOP ATTENDEES

March 1, 2002, Argonne National Laboratory

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