

DOE Report No. DOE/ER/45163-33
Annual Technical Progress Report

Title and Subtitle: **X-RAY AND γ -RAY SPECTROSCOPY
OF SOLIDS UNDER PRESSURE**

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Reporting Period: October 1990 - October 1993

Date Submitted: April 30, 1993

DOE Sponsorship
and Grant No.: Prepared for the U.S. Department of Energy
under Grant No. DE-FG06-84ER45163

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X-Ray and γ -Ray Spectroscopy of Solids under Pressure**I. Introduction**

This report briefly describes our studies of various materials at high pressures by means of x-ray and γ -ray absorption spectroscopy. High pressure provides a very effective means of studying materials. Virtually every property is altered, from the color and crystal structure, to the electrical and magnetic properties. The fundamental reason, of course, is that the quantum levels depend upon the atomic spacing so that both the electronic and vibrational structure are affected.

Synchrotron x-ray absorption spectroscopy, which probes materials on the microscopic level is quite well suited to high pressure studies. Moreover, since this field is still being developed, the ability to alter the microstructure of a material by means of high pressure aids in our understanding of the theory underlying the x-ray absorption spectra. Here we shall frequently refer to XAFS (x-ray absorption fine structure) which covers both XANES (x-ray absorption near-edge structure) as well as EXAFS (extended x-ray absorption fine structure). As the studies here show, this technique is especially sensitive to valence states, electronic structure, atomic vibrations, bond lengths, coordination numbers and atomic rearrangement during phase transitions. During this three year report period we have been able to obtain synchrotron beam time from Stanford Synchrotron Radiation Laboratory at a rate of approximately two weeks per year. Moreover conditions there have markedly improved over the course of this period.

Gamma-ray absorption spectroscopy, The Mössbauer effect, which is somewhat complementary to XAFS, is also well suited to high pressure science. It of course probes the effect of the solid state environment on a nuclear transition taking place in an atom or ion within that solid. This method then probes internal magnetic and electric fields, internal electron density at the nucleus as well as atomic vibrations. These quantities are generally

sensitive to the valence state and local atomic environment, and to changes such as those due to phase transitions.

Below we describe studies that were either completed during this three year report period or are well underway. In the latter case, they are further discussed in the main proposal. In either case they have been published in either a preliminary or final version as given in the list of publications.

II. XAFS Study of the Pressure-Induced Transition in Rubidium-Tungsten Bronze

We have measured the XAFS spectrum of the Rb K- and W L_{III} -edges in $\text{Rb}_{.31}\text{WO}_3$ as a function of pressure. This material has the simple hexagonal structure, composed of layers of corner-linked WO_6 octahedra. These octahedra are arranged in hexagonal rings of six, with each octahedron common to two rings. The c-axis repeat length is the width of a single layer. Since the rubidium ions occupy unusually large vacancies at the centers of hexagonal prisms, one might expect the material to be sensitive to rather modest pressures. Indeed, our observations of both of the above edges indicate a reversible phase transition in the vicinity of 2.0 GPa. This is primarily evident in the EXAFS oscillations due to back-scattering from the neighboring oxygens around the rubidium atoms, although in the high pressure phase, the mean-square deviations in both rubidium-oxygen and tungsten-oxygen bond lengths appear to decrease. A second series of experiments, recently performed, shows a progression of slightly changing spectra as one goes through the transition, somewhat reminiscent of the compressibility collapse in rhenium trioxide discussed below. Further experiments and analyses are planned to elucidate the nature of the transition and the high pressure phase.

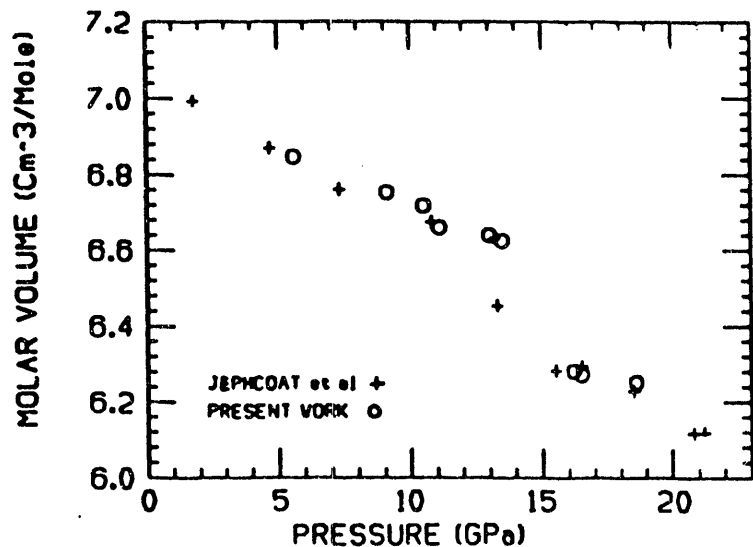
This is a collaboration with Prof. Brian Houser.

III. XAFS Study of the bcc-hcp Transition in Iron

The diffusionless (martensitic) bcc to hcp transition in iron occurs at about 13 GPa at room temperature, although there is a large two-phase region and considerable pressure hysteresis. x-ray diffraction studies have shown that in the two-phase region, c/a for hcp iron is different from what it is at the same pressure when single phase (i.e. obtained by lowering the pressure and taking advantage of the hysteresis). This may be due to some sort of epitaxy between the phases, or else, perhaps to the existence of some brief intermediate phase. We have obtained excellent data on this system, which is not feasible with diamond anvils not only because of too much absorption of the 7 keV x-rays but also because of the diamond glitches. Our boron-carbide anvils make the experiment possible not only because they are of lower Z material but also because we can drill out enough material so that the x-rays only have to go through about 2 mm of it. The experiment also requires pressures approaching the limit attainable with boron carbide, namely somewhere above 20 GPa. One drawback to such anvils in this case is that they contain small amounts of iron, the spectra of which have to be carefully subtracted from what is measured. Careful analysis, taking advantage of the FEFF analysis program due to our colleague, J.J. Rehr, which includes multiple scattering results is the pressure-volume relation shown in Fig. 1. Our results agree very well with, and are of a quality comparable to the best x-ray diffraction results. Still in progress is the unravelling of the data corresponding to the mixed-phase region which should tell us something about the transition mechanism.

This is part of the thesis research of Fuming Wang.

Fig. 1 Comparison of the molar volume of iron determined from the present XAFS results with the x-ray work of Jephcoat. et. al., J. Geoph. Res. **91**, 4677 (1986).

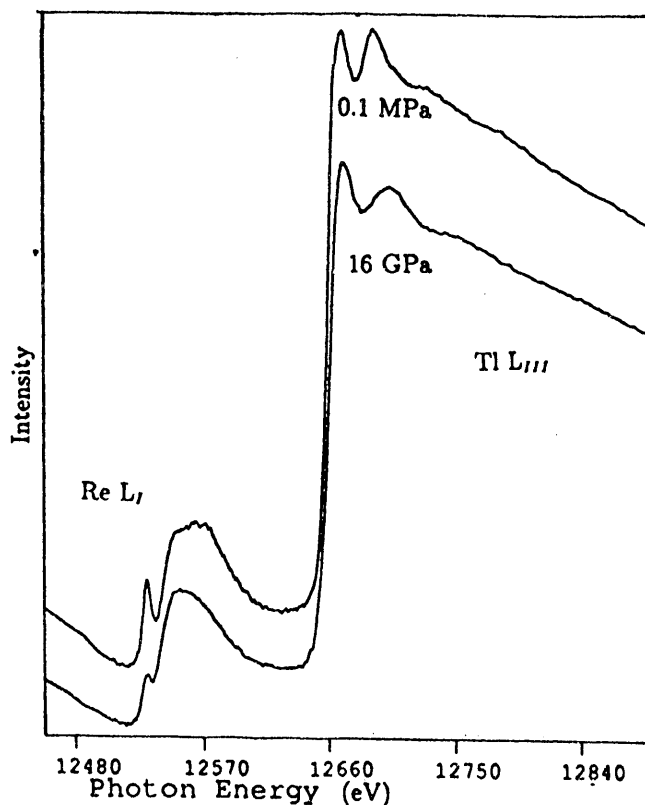


IV. XAFS Search for Valence Change in Thallium Perrhenate at High Pressure

We have studied the material, TlReO_4 , which undergoes a series of pressure-induced structural transitions. Raman studies indicate that only at the highest pressure transition discovered to date (at 9.7 GPa) is there a significant change. For the phase above that pressure, there is a dramatic color change as well as a marked change in the character of the Raman spectra. Because of this there was speculation that there may be a change in the electronic configuration from $\text{Tl}^+(\text{Re}^{+7}\text{O}_4)^{-}$ to $\text{Tl}^{3+}(\text{Re}^{+5}\text{O}_4)^{-3}$. Our XAFS measurements include a study of all the L-edges of both the rhenium and thallium ions to pressures exceeding 16 GPa. As expected, the highest pressure phase shows markedly different signatures at all the edges, although the L_{II} and L_{III} edges within each atomic species are very similar. The essential changes are that the oxygen coordination number about the rhenium decreases but the bond length stays relatively constant. In contrast there is a significant decrease in the Tl-O bond length, suggesting a large structural rearrangement. In Fig. 2 we show the change in the XANES at the Re- L_I and Tl- L_{III} edges. Although changes are evident, they are probably not large enough to account for the predicted valence change. Analysis of these results are continuing.

This is also part of the thesis research of Fuming Wang.

Fig. 2 Re L_I -edge and Tl L_{III} -edge in TlReO_4 above and below the 9.7 GPa phase transition.



V. XANES Analysis of the Alkali Halides

For the last several years we have been studying the XAFS of the alkali halides, NaBr, RbCl, KBr and RbBr. Indeed the former two compounds have played an important role as pressure calibrants. However these materials are of fundamental importance in their own right because of their relative simplicity. In addition, the latter three materials undergo pressure-induced transitions from the NaCl to the CsCl structure with a pronounced change in the character of the XANES. Recent advances in theoretical calculations of the XANES require that improvements in the determination of the experimental XAFS background function be pursued if detailed comparison between experiment and theory is to be made. We have begun such a program based upon the FEFF program, mentioned above, including multiple scattering which is highly important for the near edge. The procedure so far has relied heavily on simulated calculations in which the background is known. The agreement between experiment and theory is increasingly promising as our method evolves.

This work is a collaborative effort with Dr. P. Livins and Prof. J.J. Rehr.

VI. Pair Potentials in Alkali Halides Studied via EXAFS

A second approach, to analyze the EXAFS of these materials, also has been carried out. It used parameter fitting to extract the change of nearest-neighbor distance and thus the pressure, as well as the absolute values of the second cumulant as a function of pressure and the third cumulant at atmospheric pressure. For all the materials, a sharp reduction with pressure of the second cumulant was found. Classical statistical mechanics was then invoked to calculate the first, second and third moments of the nearest-neighbor distance and thus their second and third cumulants. The integration was done with the Monte Carlo technique. For the potential energy U in the Boltzmann factor, the generalized Huggins-Meyer pair potential was used along with a three-body potential term due to charge transfer. Generally, model calculations and the EXAFS data match well, so that high-pressure EXAFS data can therefore be regarded as a help to assess and even exclude, potential parameters from the literature. For these materials, the resulting goodness-of-fit

parameters showed that incorporating anharmonic parameters into the fitting process was not justified.

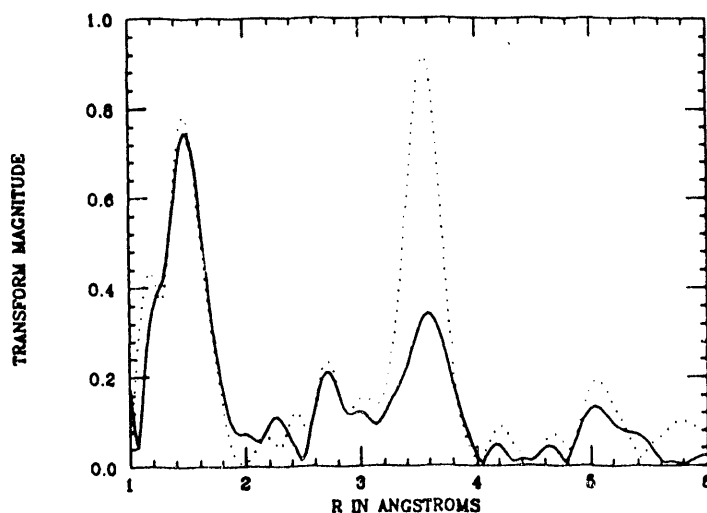
This research formed a part of the PhD thesis of Dr. Jürgen Freund.

VII. EXAFS Determination of Bond Angles in Rhenium Trioxide

An especially nice case of the EXAFS “focussing effect” occurs in the material ReO_3 . Such a behavior manifests itself as an enhancement in the backscattering from a second or third nearest neighbor atom when there is an intervening nearest neighbor atom. Rhenium trioxide undergoes a compressibility collapse at about 5 kbar, in which the nearest neighbor oxygen atoms move sideways from their positions which had been exactly in between two rheniums. Fig. 3 shows the change in the above enhancement with pressure in the EXAFS-derived radial distribution function. These results were analyzed using a new separable spherical wave approximation that included multiple scattering. It was found that a certain amount of structural disorder was assumed necessary in order to match the observed decrease in the multiple-scattering signal with the values of the bond angle taken from the literature. Ignoring such effects resulted in the overestimation of the pressure-induced bending of the Re-O bond.

This reseach formed a part of the PhD thesis of Dr. Brian Houser.

Fig. 3 Fourier transforms of ReO_3 EXAFS at one bar (dotted line) and 8.5 kbar (solid line).

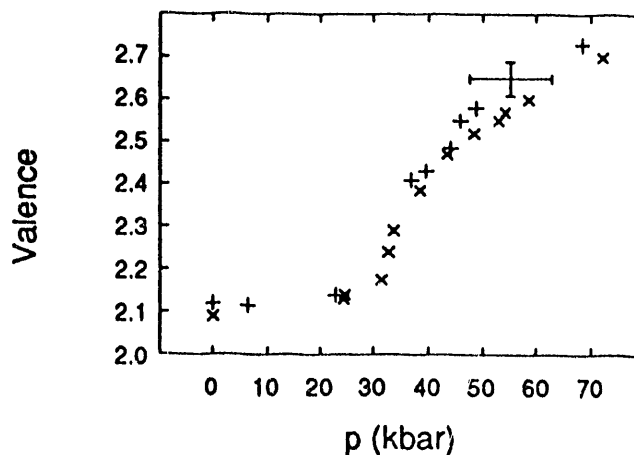


VIII. XAFS Study of the Mixed-Valence Transition in Samarium Selenide

High pressure induces a fluctuating valence in SmSe and many other rare earth systems. In this case there is a continuous valence transition around 3 GPa displaying a large decrease in volume while still retaining the same NaCl type structure. At low pressures it is semiconducting and the samarium is divalent. At high pressures it is metallic and the samarium becomes trivalent. In the transition region the valence fluctuates on a time scale of 10^{-13} s which is slower than the x-ray absorption process. Thus the XAFS spectrum provides a snapshot of the distribution of divalent and trivalent samarium ions. In this work we have found from the Se K-edge EXAFS at the pressure corresponding to a valence of 2.5 that the lattice does respond locally to the fluctuation producing a split radial distribution for the samarium nearest neighbor atoms surrounding the selenium. Analysis of the Sm- L_{III} EXAFS yields the continuous valence change as shown in Fig. 4. We find that the valence varies with pressure as $[(P - P_c)/P_c]^\alpha$ where the critical pressure is $P_c = 3.16$ GPa. The exponent α was found to have the value 0.44, which is somewhat less than the value $1/2$ expected for mean field theories.

This research formed a part of the PhD thesis of Dr. Rudolph Bauchspies in collaboration with Prof. E. D. Crozier.

Fig. 4 Valence versus pressure for SmSe as determined from the Sm L_{III} absorption edge at 300K (+) and 77K (x).

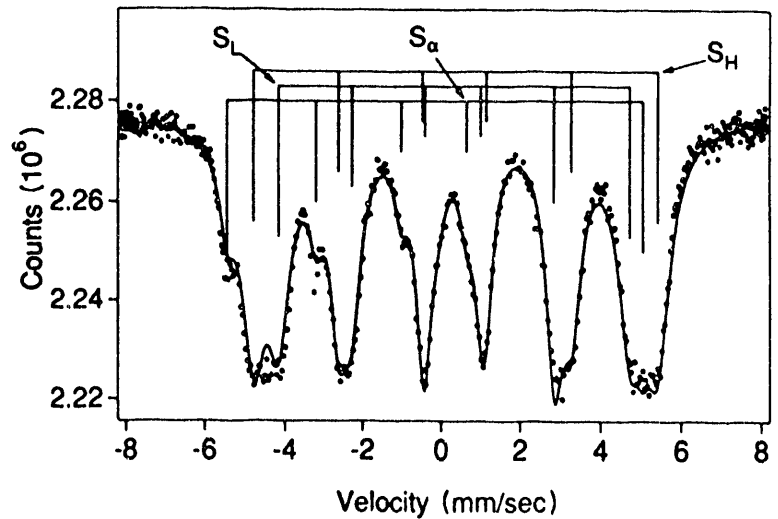


IX. Mössbauer Studies of Iron Hydride at High Pressure

We have measured as a function of pressure the Mössbauer spectra of iron hydride made in a diamond anvil cell at high pressure and room temperature. The spectra show a sudden change at 3.5 ± 0.5 GPa from a single hyperfine pattern to a superposition of three (Fig. 5). The former pattern results from normal bcc iron with negligible hydrogen content, while the latter from residual bcc iron plus newly formed iron hydride. X-ray diffraction studies on quenched samples have shown that iron hydride is of double hcp structure, whose two nonequivalent iron sites may account for the observation of two different patterns. Even allowing for the effect of volume expansion, the observed isomer shifts for the hydride are considerably more positive than those of other metallic phases of iron. At the same time, the hyperfine fields are slightly smaller than that of bcc iron. The fact that hydrated hexagonal iron is ferromagnetic is surprising in its own right because pure hcp iron is nonmagnetic down to milliKelvin temperatures. As a possible explanation for our results, one may expect a bonding of hydrogen with iron, which would result in a small reduction of 4s electrons, possibly accompanied by a small increase of 3d electrons compared with the neutral atom in the pure material. The differences between the hyperfine fields in the two spectra are presumably due to

This research forms a part of the PhD thesis of Mr. In-Jerng Choe.

Fig. 5 Fit of the Mössbauer spectrum of iron hydride at 3.5 GPa showing three sextets: S_α from the unmodified α -iron, S_L and S_H from the iron hydride.

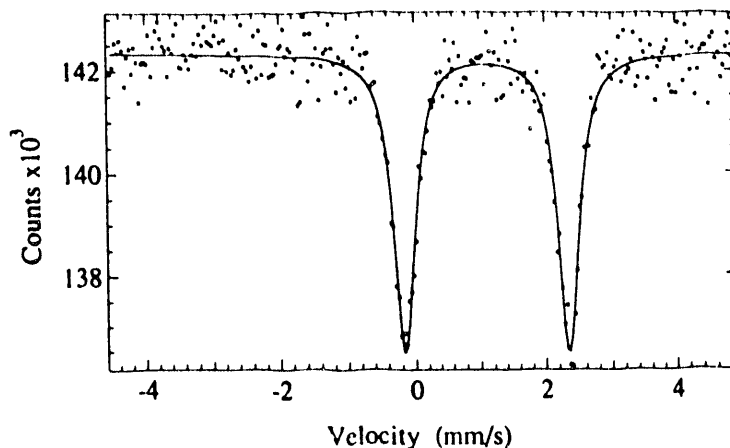


X. Mössbauer and X-ray Studies of Iron Silicate Spinel at High Pressure

We have also measured the Mössbauer spectra of $\gamma\text{-Fe}_2\text{SiO}_4$ in a diamond anvil cell at room temperature and pressures up to 16 GPa. It is well known that magnesium-iron spinel, is a high pressure polymorph of olivine, which exists under conditions like those in the mantle transition zone of the Earth. Also it has been shown that the olivine to spinel transition coincides with the condition at the 400 km seismic discontinuity. Therefore this study is of interest in order to help understand and constrain compositional models of the mantle transition zone. Our observed spectra on the present system show a doublet which is characteristic of the paramagnetic state (Fig. 6). Both the isomer shift and quadrupole splitting are slightly smaller than those of fayalite (the iron-rich member of the olivine phase) and decrease linearly with pressure. This simple linear trend suggests that no electronic nor polymorphic transitions occur under 16 GPa except those due to the small and continuous changes of volume and local symmetry under pressure. On the basis of a crystalline field calculation, the negative pressure derivative of the quadrupole splitting is associated with the trend of the oxygen atoms to form an ideal fcc sublattice. This would lead to a perfect octahedral arrangement around the iron atoms. The decreasing isomer shift with pressure indicates an increasing charge density at the nucleus. This is normal behavior in iron compounds and comes about not only because of increasing 4s electron density but also 3s density due to less screening from the 3d electrons. The later behavior is in turn due principally to an outward movement of the 3d electrons towards the oxygens.

This research also forms a part of the PhD thesis of Mr. In-Jerng Choe.

Fig. 6 Fit of the Mössbauer spectrum of $\gamma\text{-Fe}_2\text{SiO}_4$ at 5.7 GPa and room temperature.



XI. Publications

- “Extended X-Ray-Absorption Fine-Structure Study of Alkali-Metal Halides under High Pressure,” J. Freund, R. Ingalls and E. D. Crozier), *Phys. Rev.* **B43**, 9894 (1991).
- “EXAFS of Alkali Halides under High Pressure and Interatomic Potentials,” J. Freund and R. Ingalls, in *X-Ray Absorption Fine Structure*, S. Samar Hasnain, Ed. (Ellis Horwood, N. Y., 1991), p. 429.
- “Mössbauer Studies on Iron Hydride at High Pressure,” I. Choe, R. Ingalls, J. M. Brown, Y. Sato-Sorensen and R. Mills), *Phys. Rev. B* **44**, 1 (1991).
- “On the Determination of Interatomic Potential Anharmonicities from EXAFS Measurements,” J. Freund, *Phys. Lett.* **A157**, 256 (1991).
- “The Separable Spherical Wave Approximation: Application to XAFS Multiple Scattering in ReO_3 ,” B. Houser, R. Ingalls and J. J. Rehr, *Phys. Rev.* **B45**, 8097 (1992).
- “XAFS Studies of Perovskite Related Materials at High Pressure,” R. Ingalls, B. Houser and E. D. Crozier, in *Recent Trends in High Pressure Research*, A. K. Singh, Ed. (Oxford & IBH Co. PVT, LTD, New Dehli, 1992), p.223.
- “Static Compression of Iron Silicate Spinel: X-Ray and Mössbauer Studies at Room Temperature,” I. Choe, R. Ingalls, Q. Bi, J. M. Brown and Y. Sato-Sorensen,” *J. Phys. Chem. Miner.* **19**, 236 (1992).
- “Study of the Near Edge XAFS Background Determination in the Alkali Halides,” P. Livins and R. Ingalls, *Bull. Am. Phys. Soc.* **38**, 387 (1993).
- “Structural Transition in TlReO_4 Studied via XAFS,” R. Ingalls and F. Wang, *ibid.*, 457 (1993).
- “Pressure-Induced Transition in $\text{Rb}_{.31}\text{WO}_3$ as Measured by XAFS.” B. Houser, R. Ingalls and F. Wang, *ibid.*, 457 (1993).
- “EXAFS Study of the bcc-hcp Transition of Iron,” F. Wang and R. Ingalls, *ibid.*, 458 (1993).
- “Study of the Near Edge Background Determination in the Alkali Halides,” P. Livins, R. Ingalls and J.J. Rehr, *Jpn. J. Appl. Phys.* **32**, Suppl. 32-2, 116 (1993).
- “XAFS Study of the bcc-hcp Transition of Iron,” F. Wang and R. Ingalls, *ibid.*, 749 (1993).
- “The Valence of Samarium in the Mixed-Valence Transition in SmSe ,” K.R. Bauchspies E.D. Crozier and R. Ingalls, *ibid.*, 752 (1993).

XII. Papers in preparation for Physical Review B.

"XAFS Study of the Mixed Valence Compounds SmS and SmSe at High Pressure,"

K. R. Bauchspiess, E. D. Crozier and R. Ingalls.

"Focussed Multiple-Scattering EXAFS Analysis of Bond-Angle Changes in ReO_3 ."

B. Houser and R. Ingalls

XIII. Reports and Presentations

"XAFS Studies of Perovskite Related Materials at High Pressure," R. Ingalls B. Houser and E. D. Crozier, *XIII Airapt International High Pressure Conference*, Bangalore, India, October, 1991.

"XAFS Study of the bcc-hcp Transition of Iron," R. Ingalls and F. Wang, *VII International Conference on X-ray Absorption Fine Structure*, Kobe, Japan, August, 1992

"Study of the Near Edge Background Determination in the Alkali Halides," P. Livins R. Ingalls and J.J. Rehr, *ibid.*

"The Valence of Samarium in the Mixed-Valence Transition in SmSe," K.R. Bauchspiess E.D. Crozier and R. Ingalls, *ibid.*

"Study of the Near Edge XAFS Background Determination in the Alkali Halides." P. Livins and R. Ingalls, American Physical Society Conference, Seattle, Washington, March 1993.

"Pressure-Induced Transition in $\text{Rb}_{.31}\text{WO}_3$ as Measured by XAFS," B. Houser, R. Ingalls and F. Wang, *ibid.*

"Structural Transition in TlReO_4 Studied via XAFS," R. Ingalls and F. Wang, *ibid.*

"XAFS Study of the bcc-hcp Transition of Iron," F. Wang and R. Ingalls, *ibid.*

"Pressure-Induced Transition in $\text{Rb}_{.31}\text{WO}_3$ as Measured by XAFS," B. Houser and R. Ingalls *XIV Airapt International High Pressure Conference*, Colorado Springs, Colorado, July, 1993.

XIV. PhD Theses

“Study of Bond Angle Determination by XAFS using the Separable Spherical Wave Approximation”

Brian D. Houser

University of Washington, September, 1990.

“X-Ray Absorption Fine-Structure of Solids under High Pressure”

Jürgen Freund

University of Washington, December, 1990.

“A Study of the Pressure-induced Mixed-Valence Transition in SmSe and SmS by X-ray Absorption Spectroscopy”

Karl Rudolph Bauchspiess

Simon Fraser University. August, 1990.

XV. Personnel

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