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**COVER SHEET
FOR TRIP REPORTS SUBMITTED TO THE
OFFICE OF ENERGY RESEARCH**

Destination(s) and Dates for
Which Trip Report Being Submitted: Leuven, Belgium and Federal Republic of
Germany (9/4-29/90)

Name of Traveler: Richard G. Haire

Joint Trip Report ☐ Yes
☒ No

If so, Name of Other Traveler(s): _____

ORNL/FTR--3786

OAK RIDGE NATIONAL LABORATORY

OPERATED BY MARTIN MARIETTA ENERGY SYSTEMS, INC.
POST OFFICE BOX 2008, OAK RIDGE, TENNESSEE 37831-6285

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ORNL
FOREIGN TRIP REPORT

ORNL/FTR-3786

DATE: October 12, 1990

SUBJECT: Report of Foreign Travel of Richard G. Haire, a Staff
Research Chemist in the Chemistry Division

TO: B. R. Appleton

FROM: R. G. Haire

PURPOSE: There were two objectives for the foreign travel to Belgium and The Federal Republic of Germany. The major objective was to carry out a collaborative, structural investigation of curium bismuthide as a function of pressure at the European Institute for Transuranium Elements (EITU), located in Karlsruhe, FRG. An associated goal was to evaluate new instrumentation for resistivity measurements under high pressure being developed at this Institution. A second objective was to attend the First International Conference on f-elements, which was held in Leuven, Belgium, where the traveler was to present two papers (author/coauthor of four papers) and to chair an oral session dealing with solid state chemistry and physics.

SITES

VISITED:	9/4-8/90	Univ. of Leuven	Leuven, Belgium	Conference Attendees
	9/10-29/90	EITU	Karlsruhe, FRG	J. Fuger U. Benedict J. Spirlet J. Naegele M. Gensini J. Dancausse P. Link

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ABSTRACT:

The primary objective of the collaborative studies with EITU was to study curium bismuthide using energy dispersive X-ray diffraction to monitor its structure as a function of pressure. This objective was accomplished and the material was investigated up to 0.48 megabars of pressure. These studies were a continuation of established and productive collaborations between ORNL and EITU. The study of this curium compound is significant in that it is the first 5f-element bismuthide to be studied under pressure. Bismuth has the highest Z and the largest radius of the pnictogen group of elements (important for Hill Plot assessments) and has the greatest potential to form f-p type bonding with actinides under pressure. From a preliminary assessment of our experimental data it has been determined that two structural transitions occurred in the curium bismuthide sample as a result of the applied pressure.

The traveler also evaluated/compared new instrumentation being established at EITU for measuring resistivity under high pressure. At the present time, EITU is a major center for high pressure research on actinide elements and compounds, and the traveler gained considerable information about actinide research that will be beneficial in future work at ORNL.

In addition, the traveler participated in the First International Conference on f-Elements, held in Leuven, Belgium, where presentations and discussions were held concerning both experimental and theoretical aspects of lanthanide and actinide elements and compounds. Four research reports concerning research work in which the traveler was involved were presented, and the traveler also chaired a scientific session on solid state chemistry and physics at this meeting. This conference was well attended by some 300 scientists from a multitude of countries, which provided exposure of the attendees to a wide variety of scientific expertise.

SUMMARY OF ACTIVITIES

The traveler is engaged full time at the Transuranium Research Laboratory (Chemistry Division, ORNL) for carrying out basic research on actinide and lanthanide elements and compounds as part of the US DOE program for producing and studying the transuranium elements. One important aspect of such studies at ORNL has been the investigation of metals and compounds under high pressure by X-ray diffraction and spectrometry (absorption, Raman, and fluorescence). A number of these studies have been done in past collaborations with EITU.

Primary aims of such research have been to gain an understanding of the basic electronic nature of the 4f and 5f elements and to develop systematic relationships based on electronic configurations and f-electron participation in bonding. This area of study forms an important part of modern solid state research and has a high degree of visibility in the scientific community.

The scientific collaboration between ORNL and EITU discussed in this report combines the technical assets that exist at ORNL (special isotopes, expertise in microtechniques, and preparation of micro-sized samples in pure form) with those of EITU (facilities for high pressure research, as well as combining the high pressure technical expertise and the manpower of both institutions. In the present situation, the curium bismuthide was prepared by the traveler at ORNL, transported to EITU, and the traveler together with an EITU staff member used EITU's facilities to investigate the material under pressure.

The intrinsic effect of applying pressure on a solid material is to decrease interatomic distances which increases the probability for electronic interactions or orbital overlap. These conditions can lead to participation of the f-electrons in bonding, valence instabilities or changes, etc., which all provide important information about the electronic nature of the materials being studied.

The objective of the collaborative research carried out during this foreign travel was to investigate the structural behavior of curium bismuthide under pressure using energy dispersive X-ray diffraction. From such information it is possible to ascertain if structural changes occur, to determine the relative volume behavior with pressure, and to determine a bulk modulus for the material. The occurrence and nature of structural transformations and the nature of the relative volume behavior (e.g., the presence or absence of volume collapses) can be indicative of electronic changes induced in the material by the application of pressure. The bulk modulus of a material can be used for a group-type classification of the material and can be correlated with the nature of the bonding in material.

The pnictides and chalcogenides are two classes of materials that have the potential to display unusual bonding behavior under pressure. The pressure behavior of a few such lanthanide and actinide compounds have been studied by other investigators but the actinide bismuthides have not been studied to date. The study of curium bismuthide is therefore of interest not only because it was to be the first actinide bismuthide to be studied, but also because bismuth is the highest pnictogen (largest Z and having the largest radius)

that can be selected. Both the metal-metal distances and the pnictogen radius are important in the solid state behavior of these pnictides (e.g., Hill Plot assessment). These distances and the spatial extension of the orbitals of each component are important for potential f-p interactions. Systematic comparisons as a function of the actinide or pnictogen in such compounds allow identification and quantification of these critical parameters.

The curium bismuthide was studied under pressure using a diamond anvil pressure cell. It was determined that the material's normal pressure, NaCl-type structure transformed at about 17 GPa to a CsCl-type cubic structure, which was accompanied by about a 12% decrease in the relative volume. At about 25 GPa of pressure, the latter structure then transformed to a tetragonal structure which was retained up to 48 GPa, the maximum pressure reached in the study. The behavior of the curium bismuthide under pressure bears some similarity to the behavior of plutonium telluride under pressure, although the CsCl-type phase in curium bismuthide is stable over a much smaller pressure range. There has been considerable scientific interest in plutonium monotelluride as there does not appear to be a consistent description or explanation for several of its anomalous physical properties. A detailed analysis of the experimental data from the present work will now be required in order to successfully describe and interpret the behavior of curium bismuthide under pressure. Additional studies of other actinide bismuthides will eventually be needed to establish fully the systematics of these systems.

Evaluation of New Instrumentation for Resistivity

The apparatus and techniques used in high pressure research are periodically examined and either new or improved approaches are frequently developed to circumvent some of the current difficulties and limitations. During the past several months EITU has been developing instrumentation for measuring the low-temperature resistivity of materials as a function of pressure. During this foreign travel period the traveler had an opportunity to examine and evaluate this instrumentation.

The instrumentation for measuring resistivity actinide materials under pressure and at low temperatures will provide another dimension to EITU's capabilities for high pressure research. Such measurements will be very beneficial in probing the bonding and electronic properties of the actinides. Such measurements will be very difficult and time consuming, and at least initially, will be more limited in the magnitude of pressures that can be achieved. Due to the larger sample sizes that are needed, and the

electrical contacts that need to be made with the samples and reference material for pressure calibration (lead is one that is currently being employed), it is necessary to use sintered diamonds of larger dimensions. The cell used for applying pressure on these diamonds and the samples is quite large and massive compared to the DAC cells used for X-ray diffraction work. Since the resistivity cell will eventually (at least six more months development time will be necessary) be used with radioactive materials, it must be loaded/unloaded in a glove box and then removed for insertion in a cryostat for cooling with liquid helium and making the measurements. Considering the mechanics and required procedures, merely changing the pressure on a sample will take one to two days. This compares to a period of about one hour for the comparable adjustment with a conventional DAC. Even so, this new capability will be a valuable addition and will complement EITU's other high pressure capabilities. It should provide very interesting results with a variety of actinide materials. Of special interest for such studies will be heavy fermion-type materials.

The instrumentation for high pressure resistivity measurements adds to EITU's capabilities for high pressure spectral (absorbance and reflectivity) and X-ray diffraction measurements. This facility must be considered one of the centers for high pressure research on the actinides and high pressure research is strongly supported. ORNL should maintain its collaborative research arrangements with EITU in order to benefit from the expertise and developments that are made in this field, and to maintain ORNL's effort in this area of research.

First International Conference on f-Elements

During the first week of the foreign travel (September 4-8) the traveler attended the First International Conference of f-Elements, held at the University of Leuven, Leuven, Belgium, under the auspices of the Commission of the European Communities. This conference was a combination of the former European Rare Conferences (ICRE) with the previously f-element conference (ICLA) that was established a few years ago in Europe. The combined conference format will be continued (Finland, 1994) and will alternate with the American Rare Earth Conference (next scheduled, July, 1990) and the International Actinide Conferences (AN-93, Santa Fe, NM, September, 1993).

The conference in Leuven brought together chemists, physicists, and other scientists of related disciplines from many countries to discuss fundamental and technological aspects of these f-elements. The conference included

plenary lectures of more general interest followed by parallel session lectures on specific aspects of these materials. In addition, three large poster sessions dedicated to selected areas of interest were held in conjunction with the oral sessions, with the intent of encouraging discussions among the attendees. The conference scheduled about 60 oral lectures and about 200 poster presentations. Over 600 authors were listed and it was estimated that about half this number actually participated in the Conference. About 21 of the attendees were from universities and laboratories in the United States. A majority of the countries of the world were represented; the European nations were major participants.

The Conference was grouped into the following categories: analytical and environmental chemistry; superconductivity; nature and bonding of the f-elements; spectroscopy; solid state chemistry and physics; biological aspects of the elements; coordination chemistry; thermodynamics; and organometallics. A few of the prominent speakers were: J. G. Bedenorz and C. W. Chu (high TC's); B. R. Judd (bonding); L. Eyring (oxides systems); G. R. Choppin (environmental); B. Fegley (solar system); C. F. Meares (biological aspects); J. D. Corbett (cluster chemistry); R. G. Denning (spectroscopy); A. Streitwieser (catalysis); T. J. Marks (organometallic chemistry); and K. N. Raymond (ligand synthesis/complexation).

The traveler presented two posters: one on the high pressure behavior of Pm metal and an (Pm,Sm) alloy; and a second on the use of alloys for actinide research. He was also a coauthor on a poster dealing with the luminescence of actinide compounds, and a poster concerning structural and transport studies of actinide hydrides. The traveler also served as a chairman for an oral session on solid state chemistry and physics.

Evaluation of the Trip

The traveler found the foreign travel to be technologically and scientifically productive and informative. The First International Conference on f-elements dealt with recent findings and aspects of elements that constitute about one third of the Periodic Table. The conference provided an excellent opportunity to interact with scientists from a variety of organizations, and to acquire an awareness of scientific developments and approaches at other laboratories. In some instances, discussions may lead to future interactions or a rapid exchange of information.

The collaborative experiments at EITU were considered very successful, and will provide the first data on the high

pressure behavior of bismuthides, the heaviest pnictide that can be prepared and studied. These experiments will lead to additional studies of actinide bismuthides and the results of the curium bismuthide will have high visibility in the scientific community.

The efforts at EITU also served to update the traveler to the latest developments in high pressure work at EITU. As EITU also tends in general to be a center for European actinide research, where many experimental results and theoretical concepts are funneled, the trip allowed the traveler to be exposed to a variety of current and future aspects of actinide research in the European Communities.

Finally, the high pressure studies carried out during this travel period are not only valuable for their specific scientific value but also because they provide stimulation for future collaborative research between ORNL and EITU, which has been very productive and valuable in the past.

APPENDIX

Itinerary

9/2-3/90	Travel from Oak Ridge, TN to Frankfurt, FRG
9/4/90	Travel from Frankfurt, FRG to Leuven, Belgium
9/4-8/90	Conference in Leuven, Belgium
9/8/90	Travel to Karlsruhe, FRG
9/8-28/90	EITU in Karlsruhe, FRG
9/29/90	Travel from Karlsruhe, FRG to Oak Ridge, TN

Persons Contacted at the Conference

A. Blaise	CEN, Grenoble, France
W. T. Carnell	ANL, Argonne, IL
P. Caro	CEA, Paris, France
G. R. Choppin	Florida State University, Florida
K. Conder	ETH, Zurich, Switzerland
J. D. Corbett	Iowa St. Univ., Ames, IA
L. E. Cox	LANL, Los Alamos, NM
W. D'Olieslager	Univ. Leuven, Leuven, Belgium
G. D. Del Cul	ORNL, Oak Ridge, TN
N. Edelstein	UC, Berkeley, CA
D. D. Ensor	Tenn. Tech. Univ., Cookeville, TN

L. Eyring	Univ. Arizona, Tempe, AZ
B. Fegley, Jr.	Univ. Mainz, FRG
J. M. Fournier	CEN, Grenoble, France
C. Corller-Walrand	Univ. Leuven, Leuven, Belgium
J. E. Greedan	MacMaster Univ., Canada
K. A. Gschneider	Iowa St. Univ., Ames, IA
J. M. Haschke	LANL, Los Alamos, NM
R. Hoppe	Univ. Gressin, FRG
C. K. Jorgensen	Univ. Geneva, Switzerland
B. R. Judd	John Hopkins Univ., Maryland
E. Kaldis	ETH, Zurich, Switzerland
B. Kanellakopulos	HC, Karlsruhe, FRG
J. L. Kim	Tech. Univ., Munchen, FRG
T. J. Marks	Northwestern Univ., Chicago, IL
G. Meyer	Univ. Hanover, FRG
L. R. Morss	ANL, Argonne, IL
K. N. Raymond	UC, Berkeley, CA
H. B. Silber	San Jose St., San Jose, CA
E. Soulie	CEN, Saclay, France
Y. Suzuki	Meiji Univ., Wroclaw, Poland
T. Thevenin	CEN, France
J. Ward	LANL, Los Alamos, NM

[Conference: First International Conference on f-Elements,
University of Leuven, Leuven, Belgium]

Persons Contacted at EITU

J. van Geel	Director
J. Fuger	Scientific Coordinator
U. Benedict	Head, Actinide Research
J-C. Spirlet	Staff Scientist
J. Rebezant	Staff Scientist
H. J. Naegele	Staff Scientist
C. Walker	Staff Scientist
M. Gensini	Scientist
J-P. DanCausse	Scientist
P. Link	Scientist

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END

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