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The effect on crystallographic parameters of selenium for sulfur replacement has been studied in several series of ternary molybdenum chalcogenides of the Chevrel-Phase type. The magnetic and superconducting properties of these ternaries was investigated.

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FINAL REPORT

THIN FILM SYNTHESIS OF SUPERCONDUCTING

CHEMICAL COMPOUNDS

(AFOSR-83-0271)

November 11, 1985

Submitted to: Air Force Office of Scientific Research
Solid State Sciences Division
Bolling AFB, Building 410
Washington, D.C. 20332

Submitted by: Department of Chemistry
Cornell University
Ithaca, N.Y. 14853-1301

Principal Investigator: M. J. Sienko (deceased - 12/4/83)
Professor of Chemistry
15 July 1983 - 30 December 1983

Co-Principal Investigators: Roald Hoffmann
John A. Newman Professor of Physical Sciences

James M. Burlitch
Associate Professor of Chemistry

Period of Support: 1 January 1984 - 14 October 1984

OVERVIEW

Work has progressed on the superconducting thin film synthesis and analysis system in three separate areas: the characterization tools for measuring the DC conductivity and superconducting transition temperature of various samples have been assembled; further work has been done on various ternary molybenum chalcogenide systems to gain a more complete understanding of the reaction thermodynamics and the interrelationships between structure, composition and physical properties such as superconductivity; A thin film synthesis apparatus was designed, constructed and tested.

An A-C susceptibility device was constructed and used to measure the superconducting transition temperatures of many new samples. The design is based on a previous instrument (W. Fischer's Ph.D. thesis) with several modifications which were necessary to improve sensitivity and reduce the amount of liquid helium needed per sample. The major modification was to reduce the size of the primary and secondary coils, while increasing the number of windings in the secondary coils. This was accomplished by reducing the size of the sample space by a factor of 2, which resulted in an improved signal to noise ratio because the fraction of the coil filled with sample was increased by over 400%. The reduced size of the detection system made it possible to insert the entire device into a Janis "supervaritemp" liquid helium dewar. This enabled up to 20 samples to be measured with one transfer of liquid helium (8 liters of liquid used) while the previous device required up to 6 liters of helium per sample.

The second characterization device constructed was a 4-probe D-C conductivity device based on a design by Professor D. Holcomb. This design utilizes the high imput impedence (gigaohms) of a Keithly model 181 nanovoltmeter and an interfaced current source also purchased from Keithly. The temperature was controlled by inserting the conductivity probe into a Janis "supervaritemp" dewar which was equipped with temperature controllers and heaters to regulate the temperature between 2 and 400 K.

The most significant result obtained during this research period was the develpment of a novel synthetic approach to the ternary molybdenum chalcogenides. The method developed was first to synthesize the copper phase, $Cu_{1.8}Mo_6X_8$ {X=S and Se}, which is relatively easy to synthesize (thin films of this material have been reported in the literature and are the simplest of all the Chevrel phases to make). This material is then introduced to a solution of iodine in acetonitrile which reacts with the mobile copper in this structure to form CuI which then precipitates out of solution. In this way the binary phases (and the intermediate solid solution) Mo_6X_8 can be formed. It is then possible to diffuse the desired ternary metal into the binary phase at a relatively low temperature (T=500 C). This method produces high quality materials of known composition. The extension of this method to thin film synthesis is especially promising, because once an initial film of $Cu_{1.8}Mo_6X_8$ {X=S and Se} is prepared, it can be transformed into a film of a different ternary molybdenum chalcogenide. This method will produce films of many of the ternary molybdenum chalcogenides without having to develop customized ultra-high vacuum "recipes" for each compound.

The thin film synthesis apparatus consists of a conventional, evacuable dry box connected to a UHV system via an intermediate chamber holding an RF sputtergun. This system permits RF sputtering of a variety of metals and non-metals, including ternary molybdenum chalcogenides, described above, at moderate pressures and metal deposition at 10^{-10} Torr. Work on this part of the project is continuing.

Equipment Purchased under This Grant

Description	Manufacturer	Cost
(Film Deposition System)		
Vacuum System (Pump)	Perkin-Elmer (TNB-X)	15,685.00
Vacuum Chamber	Nor-Cal	7,491.00
UHV System	Cornell	26,203.56
Ionization Gage Controller	Varian	1,969.44
Purification System	Vacuum Atmospheres Co.	33,201.00
Sputtergun	US, Inc.	3,495.00
RF Power Supply	US, Inc.	6,985.00
Film Thickness Monitor	Inficon	4,340.73
(AC Susceptibility Measurement Device)		
Meter, Supervari Temp	Janis Research	8,974.13
Preamplifier	Ithaco	2,155.50
Minicomputer	Digital Equipment Corp.	7,026.60
Terminal	Digital Equipment Corp.	2,575.00
(DC Conductivity Measurement Device)		
Nanovoltmeter	Keithley	4,353.98
Temperature Controller	Oxford Instruments	2,190.06

Details of the synthetic work on ternary superconductors.

1. (David C. Johnson and Jean Marie Tarascon) The effect on crystallographic parameters of selenium for sulfur replacement has been studied in several series of ternary molybdenum chalcogenides of the Chevrel-phase type. In all the systems examined -- $MMo_6(S_{1-x}Se_x)_8$ with M=La, Ce, Sm, Eu, Yb, Pb, Ag and $0<x<1$ -- the hexagonal c/a ratio shows a minimum when plotted against the percent sulfur replaced. The minimum is shallowest for the case of Ag and deepest for the case of La and Ce. The apparent cause of the minimum is the strong preference by the selenium for occupancy of the general position chalcogen site rather than the special position site on the $\bar{3}$ axis. The preferred site ordering is greater for M^{3+} than for M^{2+} or M^{+}. Delocalization of M off the $\bar{3}$ axis decreases the ordering, as it tends to increase the bonding in the a direction.

2. (Jean Marie Tarascon, Martin R. Harrison, and David C. Johnson) Magnetic susceptibility measurements have been carried out by the Faraday method over the range 4.2-300 K on a series of phases of composition $Eu_{1.2}Mo_6(S_{1-x}Se_x)_8$ where $0<x<1$. No magnetic ordering and no superconductivity was observed; the europium is essentially divalent over the whole range of composition. Superconducting critical temperatures measured by an ac mutal inductance technique, show, for the series $La_{1-x}Wu_xMo_6Se_3$, roughly the same behavior as found for $La_{1-x}Yb_xMo_6Se_8$ and can be accounted for in terms of the theory of Abrikosov and Korkov. ESR spectra, measured from 4.2 to 300 K at X-band frequency, are quite different for $Eu_{1.2}Mo_6X_8$ and $Eu_{1.0}Mo_6X_8$. Furthermore, in

some of the $Eu_{1.2}Mo_6S_{8-x}Se_x$ samples, the temperature study reveals a phase change in the ESR signal around 110 K. The signals, quite surprising for Eu^{2+}, can be interpreted by assuming a spin Hamiltonian containing a crystal field term that is large compared to the Zeeman splitting.

3. (David C. Johnson and Jean Marie Tarascon) Magnetic susceptibility measurements have been carried out by the Faraday method over the range 4.2-300 K and superconducting critical temperatures measured for the solid solution $SmMo_6(S_{1-x}Se_x)_8$. The susceptibility studies indicated that the samarium is in the 3^+ oxidation state. The moment obtained for the samarium varies as the symmetry of the chalcogen cube changes throughout the solid solution. This indicates that crystal field effects are important in these materials.

4. (David C. Johnson) The silver solid solution, involving a mix of sulfur and selenium, was investigated and room temperature X-ray measurements showed that the solid solution was single phased. The c/a ratio in this series did not vary with composition. Susceptibility measurements over the temperature range 3-300 K were performed and the data suggest that a structural instability occurs in the selenium rich compositions. The anomaly, marked by a sharp decrease in the observed susceptibility, indicates a reduction in the density of states at the Fermi level. The structural instability is either a distortion in the molybdenum octahedron or a localization of the silver atom either on or off of the $\bar{3}$ axis.

5. (David C. Johnson and Nathalie Chevreau) The $M^{+2}Mo_5S_5$ compounds (M=Pb, Sn, Eu, Yb, Ba, Sr, Ca) all were found to have a lattice instability. The temperature at which the molybdenum octahedra distorts is a function of the bonding differences between the different ternary metals and is related to the electron polarizability of the cation. The lattice distortion temperature was found to be inversely proportional to the observed superconducting critical temperature as a result of the localization of electrons from the conduction band to intracluster molybdenum-molybdenum bonds when the structure distorts. This observation was then extended to the $PbMo_6(S_{1-x}Se_x)_8$ solid solution.

6. (Nathalie Chevreau and David C. Johnson) A new low temperature technique was devised to synthesize the previously unknown phases, $SbMo_6S_8$ and $BiFMo_6S_8$. The procedure used was to leach out the copper from the phases $Cu_{1.8}Mo_6S_8$ via a solution of iodine in acetonitrile. The resulting material, Mo_6S_8, was then heated with the ternary element, antimony or bismuth, up to 600°C in a sealed quartz tube. The resulting compounds were characterized by X-ray diffraction and DTA and found to be single phased.

7. (Natalie Chevreau) The above mentioned low temperature synthesis of ternary molybdenum chalcogenises has been used to prepare the new material $GaMo_6(S_{1-x}Se_x)_8$ (X=0, 0.1, ..., 1) and has also been extended to the known materials $MMo_6(S_{1-x}Se_x)$ (M=Zn, Cd, Sn, and Pb). These materials were characterized by X-ray diffraction and DTA analysis.

PUBLICATIONS

The following papers containing AFOSR acknowledgment were published, accepted for publication, or submitted for publication during the report period:

1. "$Hf(Se_{1-x}Te_x)_2$: Deviations from Vegard's Law in Mixed Systems," D.T. Hodul and M.J. Sienko. Inorg. Chem. 20, 3655-3659 (1981).

2. "Magnetic Behavior and Structural Chemistry of $RE(Os,IR)_4B_4$-Borides," K. Hiebl, P. Rogl, and M.J. Sienko, J. Less-Common Metals 82, 21-28.

3. "Phase Separation in Metal Solutions and Expanded Fluid Metals," P.P. Edwards and M.J. Sienko, J. Am. Soc. 103, 2967-2971 (1981).

4. "Temperature-Dependent Electron Spin Interactions in Lithium [2.1.1] Cryptate Electride Powders and Films, "J.S. Landers, J.L. Dye, A. Stacy, and M.J. Sienko, J. Phys. Chem. 85, 1096-1099 (1981).

5. "Superconductivity in the Pseudoternary System YRh_4B_4-$LuRh_4B_4$-$ThRh_4B_4$,: K. Hiebl, P. Rogl, and M.J. Sienko, J. Less-Common Metals 82, 201-210 (1981).

6. "Ambivalent Behavior of Ytterbium in the Pseudobinary System $YbMo_6S_8YbMO_6Se_8$," J.-M. Tarascon, D.C. Johnson, and M.J. Sienko, Inorg. Chem. 21, 1505-1511 (1982).

7. "Structural Chemistry and Magnetic Properties of the Compounds $EuOs_4B_4$ and $EuIr_4B_4$ and of the Solid Solution $REOs_4B_4$-$REIr_4B_4$ (RE = Ce, Pr, Sm)," K. Hiebl, P. Rogl, and M.J. Sienko, Inorg. Chem. 21, 1128-1133 (1982).

8. "The Transition to the Metallic State," P.P. Edwards and M.J. Sienko, Accts. Chem. Res. 15, 87-93 (1982).

9. "Conductivity Studies in Search of Liquid-Liquid Phase Separation by Solutions of Lithium in Methylamine," R. Hagedorn and M.J. Sienko, J. Phys. Chem. 86, 2094-2097 (1982).

10. "The Transition to the Metallic State," P.P. Edwards and M.J. Sienko, Acct. Chem. Res. 15, 1505-1511 (1982).

11. "Ambivalent Behavior of Ytterbium in the Pseudobinary System $YbMo_6S_8YbMO_6Se_8$," J.-M. Tarascon, D.C. Johnson, and M.J. Sienko, Inorg. Chem. 21, 1128-1133 (1982).

12. "Structural Chemistry and Magnetic Properties of the Compounds $EuOs_4B_4$ and $EuIn_4B_4$ and of the Solid Solutions $REOs_4B_4$-$REIn_4$ (RE = Ce, Pn, Sm)," K. Hiebl, P. Rogl, and M.J. Sienko, Inorg. Chem. 21, 1128-1133 (1982).

13. "Conductivity Studies in Search of Liquid-Liquid Phase Separation by Solutions of Lithium in Methylamine," R. Hagedorn and M.J. Sienko, J. Phys. Chem. 86, 2094-2097 (1982).

14. "Re-evaluation of the Crystal Structure Data on the Expanded-Metal Compounds $Li(NH_3)_4$ and $Li(ND_3)_4$," A.M. Stacy and M.J. Sienko, Inorg. Chem. 21, 2294-2297 (1982).

15. "Low-Temperature Magnetic Susceptibility of the Expanded-Metal Compounds $Li(NH_3)_4$ and $Li(ND_3)_4$," A.M. Stacy, and M.J. Sienko, Inorg. Chem. 76, 4248-4254 (1982).

16. "Crystal Chemistry and Superconductivity in Lithium-Intercalated Niobium Disulfide," C.S. McEwen and M.J. Sienko,

Rev. Chim. Minerale 19, 309-316 (1982).

17. "Electron-electron Interactions in Expanded-Metal Compounds," A.M. Stacy, P.P. Edwards, and M.J. Sienko, J. Solid State Chem. 45, 63-70 (1982).

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19. "Magnetic Susceptibility of Hydrozine Intercalated $TiSe_2$," D.R.P. Guy, R.H. Friend, D.C. Johnson, and M.J. Sienko, J. Phys. C. 15, L 1251 (1982).

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22. "Energy Density of Electronic States in Rare Earth Molybdenum Chalcogenides as Deduced from Studies of Chemical Substitution Effects on Superconductivity," J.-M. Tarascon, D.C. Johnson, and M.J. Sienko, Inorg. Chem. 22, 3769 (1983).

23. "Chalcogen Ordering on Special Position Sites in Ternary Molybdenum Chalcogenides," D.C. Johnson, J.-M. Tarascon, and M.J. Sienko, Inorg. Chem. 22, 3773 (1983).

24. "Magnetic, Magnetic Resonance, and Superconductivity Studies in the Pseudobinary Systems $Eu_{1.2}Mo_6S_8$-$Eu_{1.2}Mo_6Se_8$ and $LaMo_6Se_8$-$EuMo_6Se_8$," J.-M. Tarascon, M.R. Harrison, D.C.

Johnson, and M.J. Sienko, Inorg. Chem. 23, 1094 (1984).

25. "What is a Metal?" P.P. Edwards and M.J. Sienko, International Reviews in Physical Chemistry, submitted.