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PROGRESS REPORT

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AMENDMENT # A005

"Synthesis and Properties of Novel Cluster Phases"

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This report covers the last year of funding (ending June 30, 1993) under this three year grant. Since this is the final report, some discussion of the progress from the full period will be included with more a more detailed review of progress since the last report. Further this report provides some of the background that leads to a renewal proposal for a three year project for the period 7/1/93 to 6/30/96.

All the research performed is in the area of cluster compounds, those solid state compounds that contain metal clusters. Major goals of the research were to examine the solution chemistry of clusters and the materials that could be prepared from these solutions, to synthesize new cluster phases, and to examine the properties of the materials so produced. This is a large mandate that covers a potentially very large class of materials. We continue to uncover new compounds and composite materials, and to understand their properties at a deeper level.

This past three years was a particularly gratifying period of research in that our past discoveries were honored by my election to the American Academy of Arts and Sciences and to National Academy of Sciences. Further, I received the 1991 American Physical Society International Prize for New Materials.

Solution Chemistry of Clusters

We have studied two classes of materials: those based on the solutions formed by dissolving LiMo_3Se_3 in polar solvents, and those based on M_6X_8 clusters. We discuss the work on LiMo_3Se_3 first.

We have prepared solutions containing inorganic polyanionic chains of $(\text{Mo}_3\text{Se}_3)_n$ in polar solvents, from which solid films have been cast or from which films of organic polymer blends have also been produced. We are studying the properties of these systems in order to understand the range of behavior of single and aggregated

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(Mo₃Se₃) chains in bulk organic-inorganic polymer blends ("nano-composites").

Our studies have included: 1. preparative methods of inorganic chain solutions and the formation of blends, 2. electron microscopy of the resulting nano-composites, 3. physical properties of the composites. We discuss each in turn and indicate areas for future work.

1. Preparative Methods: LiMo₃Se₃ and Blends.

A new method of preparation of LiMo₃Se₃ has been developed. In the past an exchange method at 450°C taking several weeks was used. The reaction is: InMo₃Se₃ + LiI ----> LiMo₃Se₃ + InI(sublimes). We have found that treatment of InMo₃Se₃ with tertiarybutyllithium causes intercalation of Li and eventual displacement of In. The latter process is quite slow at room temperature, but is greatly speeded up by dissolution of the product in a polar solvent. The solution is centrifuged to remove In particles and small amounts of degradation products.

Our initial method of making polymer blends was to mix two solutions, one of LiMo₃Se₃ (usually in DMSO) and the other of a polar organic polymer in DMSO or other suitable solvent. TEM studies showed that even after several days of stirring, the mixture is inhomogeneous. The inhomogeneity appears to increase as the molecular weight of either polymer increases. This suggests that the process of interdiffusion of the two polymers is quite slow. Recently we have circumvented this difficulty by mixing a solution of polar organic monomers with the LiMo₃Se₃ and then initiating polymerization. This process produces much more homogeneous blends. These materials will be used in future studies.

A collaboration with a polymer chemist in the department, Professor Jean Frechet, is underway through a joint student to develop suitable polar monomers that will also be resistant H₂O and O₂ in-diffusion. These polymers will decrease the already slow decomposition of the LiMo₃Se₃ in air. We will also produce ordered blends where all the Mo₃Se₃ chains are parallel, so that the anisotropy in electrical and mechanical properties can be determined. We are studying the properties of the solutions and blends by ⁷Li, ⁶Li, and ⁷⁷Se NMR, UV-Vis spectroscopy, and for the blends only the electrical and magnetic properties. (See the renewal proposal for further details.

2. Electron Microscopy of LiMo₃Se₃ Foils and Blends.

We are collaborating with Prof. J. Silcox in Applied Physics, who has the current state of the art STEM in his laboratory. This apparatus will not only resolve atomic spacings below 2Å but also has an energy loss spectrometer attached, allowing us to study composition and electronic excitations in Mo₃Se₃ solutions and blends as a function chain aggregation. These studies are essential

if the chemical, electrical and mechanical properties of the blends are to be understood and exploited.

In the last yearly report, images from the STEM were presented which showed the locally highly ordered nature of the individual Mo_3Se_3 chains. We have also successfully measured electron energy loss spectra for small chain aggregates (≈ 10 nm in diameter). We have discovered that a known absorption in the LiMo_3Se_3 solutions at 2.5 eV is thickness dependent, becoming stronger as the wire thickness decreases. This absorption may therefore be a surface or waveguide type mode in the wire. We have also discovered a plasmon resonance at 23 eV and preliminary results indicate that this resonance may have a linear dispersion relation. These studies both prove that we can prepare the world's thinnest wires and begin to give us some idea of their electronic properties.

STEM and TEM studies will continue both to understand the structure of the blends at the molecular level and to understand some of the properties, especially the mechanical behavior. These latter studies will be very important in understanding the strength and fracture properties of the blends.

3. Properties of LiMo_3Se_3 Blends

Blends of up to 10:1 organic to inorganic (monomer ratio) are quite conducting, although the conductivity is activated. It is not clear if this activation is dominated by interchain electron hopping or possibly by some intrachain localization expected in low dimensional metals. However, at present measurements have only been conducted on blends produced by the mixing method. Studies are planned for the more homogeneous blends formed by in situ polymerization of organic monomers. Frequency dependent studies will help separate the electronic and ionic contributions (from the Li^+ ions in the blend) to the conductivity.

Studies of the mechanical properties and their dependence on chain alignment will be performed in collaboration with Professor Ed Kramer in the Materials Science Department. These will begin this summer when we have in hand highly homogeneous blends of various types.

4. Other Soluble Clusters: Nb_6I_{11} and Mo_6X_8

We originally proposed to prepare novel solids by linking clusters with bidentate ligands. Since the isolated molecular species $\text{Nb}_6\text{I}_8 \cdot 6\text{L}$ with $\text{L} = \text{RNH}_2$ were known, it seemed likely that extended coordination compounds could be prepared with bidentate ligands such as pyrazine. This should result in phases such as $\text{Nb}_6\text{I}_8 \cdot 3\text{pz}$ that are linked into a three dimensional array of clusters. While precipitates could be obtained with pyrazine, crystalline products could not be produced. Other approaches starting from $\text{W}_6\text{S}_8 \cdot 6\text{L}$ as reported by Saito et al similarly failed. The main problem was the lack of solubility of most complexes and

especially of the bridged species. Thus there was no driving force for crystallization. A great deal of effort was put into this aspect of the project with little progress and finally we put this part of the project on hold.

Recently the project has been restarted following the publication of a clever piece of work by Du Shriver and his students. They discovered how to make soluble, labile clusters based on $[\text{Mo}_6\text{Cl}_8 \cdot 6\text{O}_3\text{SCF}_3]^{-2}$. This cluster contains 24 metal bonding electrons, the usual number for M_6X_8 halides. While many neutral and anionic donor ligands can replace the triflate, we would also like to replace the rather inert inner chlorides on the cluster by sulfur so that the cluster can be oxidized. An molecular orbital analysis shows that clusters with fewer than 20 metal electrons would have significant π overlap with aromatic ligands such as pyrazine. If chlorides remain in the inner positions, the clusters cannot be oxidized all the way from 24 electrons to 19. On the other hand, Chevrel phases are known with only 20 electrons per cluster and Nb_6I_{11} has only 19. Thus it seems likely that if X is polarizable (S or I), 19 electron clusters will be possible.

From the starting point published by Shriver, we could easily prepare $[\text{Mo}_6\text{Cl}_8 \cdot 6\text{SR}]^{-2}$ anions. We have further found that under forcing conditions of temperature ($\approx 100^\circ\text{C}$) the terminal SR group will exchange with the Cl to produce $[\text{Mo}_6(\text{SR})_6\text{Cl}_2 \cdot 6\text{Cl}]^{-2}$. The terminal Cl can now be replaced by triflate as in the original synthesis. The sulfur is now protected by R from linking to adjacent clusters as in the solid state Chevrel phases. Note also that the solid state compound $\text{Mo}_6\text{S}_6\text{Cl}_2$ has been reported, since only 6 sulfurs are needed to bridge to adjacent clusters.

This is as far as we have proceeded to date with these clusters. Since the R group can be chosen to impart solubility to the cluster, we are excited about the possibility of linking these clusters to produce a crystalline compound and subsequently oxidizing them to produce intercluster overlap. It may also be possible, depending upon the dimensionality of the linked network, to remove the R group from the sulfur using standard organic chemistry techniques. All this will likely lead to novel materials with exciting properties which we hope to study in the renewal period.

New Solid State Cluster Compounds

In this area we continue to be particularly successful. We have synthesized and examined the properties of many new low dimensional compounds including: M_4ZTe_4 (with $\text{M} = \text{Ta}$ or Nb , and $\text{Z} = \text{Fe}$, Co , Ni , or Si), $\text{TaFe}_{1.25}\text{Te}_3$, Nb_3SiTe_6 , NbMTe_2 (with $\text{M} = \text{Fe}$ or Co), and $\text{Ba}_6\text{Co}_{25}\text{S}_{27}$. These all exhibit unusual clusters, condensed clusters, or metal-metal bonded one or two dimensional networks and most of the results have been published. The telluride chemistry of Nb and Ta appears extensive, while our attempts to prepare similar

or related phases using group IV or group VI metals have just started. There are a large variety of potential compounds to propose as target compositions that have not yet been synthetically explored and we are confident that a set of cluster or network phases must exist for the group IV and VI metals as well. Again, refer to the renewal proposal and publications for details

Research in the Next Year

The many avenues of research opened by the work reported above will be continued to the end of the term of this project, June 30, 1993, and hopefully beyond that with the success of a renewal proposal submitted for the period July 1, 1993 to June 30, 1996

PUBLICATIONS for three year grant period (full or partial DOE support is preceded with a *)

- *183. "Synthesis and Structure of Ta_4SiTe_4 , a New Low-Dimensional Material, M. E. Badding and F. J. DiSalvo, Inorganic Chemistry, 29, 3952 (1990)
- *184. "Electronic and Structural Properties of the Novel Chain Compound Ta_4Te_4Si " J. Li, R. Hoffmann, and F. J. DiSalvo, Inorganic Chemistry, 29, 3943 (1990)
- *185. "A Small, Inexpensive Apparatus for the Determination of the Density of Powdered Materials" M. Y. Chern, R. D. Mariani, D. A. Vennos and F. J. DiSalvo, Rev. of Scientific Instruments, 61, 1733 (1990)
- 186. "Synthesis, Structure, Electrical and Magnetic Properties of $CaNiN$ " M. Y. Chern and F. J. DiSalvo, J. Solid State Chemistry, 88, 459 (1990)
- 187. "Synthesis, Structure, and Properties of Ca_2ZnN_2 " M. Y. Chern and F. J. DiSalvo, J. Solid State Chemistry, 88, 528 (1990)
- 188. "Synthesis, Structure, and Properties of a New Ternary Metal Nitride: Ca_3CrN_3 " D. A. Vennos, M. E. Badding and F. J. DiSalvo, Inorganic Chemistry, 29, 4059 (1990)
- *189. "Preparation of a Novel Polymer Blend of Poly(ethylene oxide) and the Inorganic Polymer $(Mo_3Se_3)_n$: Infrared Absorption of Thin Films" J. K. Vassiliou, R. P. Ziebarth, F. J. DiSalvo, and A. Rosenberg, Chemistry of Materials, 2, 738 (1990)
- *190. "Synthesis and Properties of Some New Reduced Niobate Compounds" C. E. Michelson, P. E. Rauch and F. J. DiSalvo, Materials Research Bulletin, 25, 971 (1990)
- 191. "Synthesis, Structure and Properties of Anti-perovskite Nitrides Ca_3MN , with M = P, As, Sb, Bi, or Ge, Sn, and Pb." M. Y. Chern, D. A. Vennos and F. J. DiSalvo, J. Solid State Chemistry, 96, 415 (1992)
- 192. "The Structural Distortion of the Anti-perovskite Nitride $AsNCa_3$ " M. Y. Chern, F. J. DiSalvo, and J. B. Parise, J. Solid State Chemistry, 96, 426 (1992)
- 193. "The Structure of Ta_3N_3 at 16K by Time-of-Flight Neutron Diffraction" N. Brese, M. O'Keeffe, P. Rauch, and F. J. DiSalvo, Acta Cryst. C47, 2291 (1991)
- 194. "Synthesis, Structure and Properties of a New Intermetallic Compound, $Ca_3Ni_3Sn_3$ " D. A. Vennos, M. E. Badding and F. J. DiSalvo, J. less Common Metals, 175, 339 (1991)

- *195. "New Layered Ternary Niobium Tellurides: Synthesis, Structure and Properties of NbMTe₂ (M = Fe or Co)" J. Li, M. E. Badding and F. J. DiSalvo, Inorganic Chemistry, 31, 1050 (1992)
196. "Structure of Lithium Niobium Nitride" D. A. Vennos and F. J. DiSalvo, Acta Cryst., C48, 610 (1992)
197. "Synthesis and Characterization of a New Ternary Nitride, Ca₃VN₃," D. A. Vennos and F. J. DiSalvo, J. Solid State Chemistry, 98, 318 (1992)
198. "LiMoN₂: The First Metallic Layered Nitride" S. H. Elder, L. H. Doerrer and F. J. DiSalvo, Chem. of Materials, 4, 928 (1992)
- *199. "Characterization of TaFe_{1.3}Te₃, a New Layered Telluride with an Unusual Metal Network Structure" M. E. Badding, W. Zhou, P. P. Edwards, J. Li, and F. J. DiSalvo, J. Solid State Chemistry, 100, 313 (1992)
- *200. "Synthesis, Structure and Properties of the New Cluster Phase: Ba₆Co₂S₂₇" J. Snyder, M. E. Badding and F. J. DiSalvo, Inorg. Chemistry, 31, 2107 (1992)
- *201. "Synthesis and Structure of Nb₃SiTe₆, a New Layered Chalcogenide Compound" J. Li, M. E. Badding and F. J. DiSalvo, J. of Alloys and Compounds, 184, 257 (1992)
202. "Ambient Pressure Synthesis of Ternary Group (V) Nitrides" P. E. Rauch and F. J. DiSalvo, J. Solid State Chemistry, 100, 160 (1992)
- *203. "Synthesis and Structure of W₃S₄Cl₄," P. E. Rauch, F. J. DiSalvo, W. Zhou, D. Tang and P. P. Edwards, J. of Alloys and Compounds, 182, 253 (1992)
- *204. "Electrical and Magnetic Properties of Ta₄SiTe₆ and Isostructural Compounds" M. E. Badding, R. L. Gitzendanner, R. P. Ziebarth and F. J. DiSalvo, submitted to J. Solid State Chemistry
- *204. "The Magnetic Structure of TaFe_{1.3}Te₃: Magnetic Susceptibility, Mossbauer Spectra and Neutron Diffraction" M. E. Badding, F. J. DiSalvo, J. B. Parise and M. E. Eibschutz, in preparation
205. "Synthesis, Structure and Properties of M₂NiN₂ (M = Sr and Ba)" U. M. Bolle and F. J. DiSalvo., in preparation
- *206. "Sythesis and STEM Microscopy of Crystalline Nanometer Scale Wires" M. D. Hornbostel, S. Hillyard, J. Silcox and F. J. DiSalvo, in preparation
- *207. "One Dimensional Plasmon Dispersion in Nanometer Scale LiMo₃Se₃ Wires" M. D. Hornbostel, S. Hillyard, J. Silcox and F. J. DiSalvo, in preparation

NOTE: several more publications are expected to be written by the end of the grant period, June 30, 1993, but as of 1/15/92 these have not yet been started.

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