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FINAL REPORT

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"Synthesis and Characterization of New Low-Dimensional Metal
Complex Conductors"

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FINAL REPORT

Accomplishments and Conclusions

△ This research program was devoted to the synthesis and characterization of new transition metal complex electrical conductors. The primary objective of the program is to develop guidelines which will lead to the rational synthesis of electrical conductors with desired properties, with a secondary mandate being to solve important scientific problems that are encountered in the research. (18)

Mixed-valence compounds provide very good candidates for electrically conducting materials. Studies on the compounds KCu_4S , $\text{K}_3\text{Cu}_8\text{S}_6$, and KCu_3S_2 show that $\text{K}_3\text{Cu}_8\text{S}_6$ is a kinetic phase and displays behavior typical of systems with charge density waves. Magnetic, electrical, and X-ray studies on these compounds are discussed in detail in Technical Report No. 25 (Jan. 7, 1987). Magnetic, spectral, and electrical conductivity studies on the mixed-valence compounds with cationic copper complexes and donors such as TCNQ^- have permitted an evaluation of the transport mechanism in this series of compounds. For example, as discussed in Technical Reports Nos. 26 (May 15, 1987) and 27 (July 10, 1987), one-third of an electron (per formula unit) is transferred from TCNQ^- to $[\text{Cu}(\text{phen})_2]^{2+}$, E and t are of comparable magnitudes, the bandwidth is appreciable, and high electrical conductivities and low activation energies are expected and observed. Current ideas concerning significant problems in low-dimensional crystalline inorganic and organic solids have been identified (Technical Report No. 31).

The new high-temperature copper ceramic superconductors fit naturally in our program because these are good examples of mixed-valence systems. Magnetic and electrical studies on the 1-2-3 compounds revealed frustration and spin-glass behavior (Technical Report No. 30) and variable-range hopping in oxygen-depleted samples (Technical Report No. 29). Studies on the Bi-Ca-Sr-Cu-O superconducting ceramics revealed effects of composition and firing conditions on the properties of these materials (Technical Report No. 32). Current studies are devoted to Sn doped samples of the new bismuth superconductors. Here Mossbauer spectroscopy is being used to probe electronic structures.

As a part of our continuing effort to produce two-dimensional mixed-valence copper complexes, we studied a number of suitable candidates including a series of copper carboxylates. As discussed in Technical Report No. 34, the two-dimensional complex copper(II) maleate monohydrate undergoes a transition to a ferromagnetically ordered state at 4 K. The ferromagnetic interaction occurs as a result of the relative orientation of the magnetic orbitals and the orbitals of the bridging carboxylate group which transmits the superexchange mechanism. Unusual materials have been generated in this phase of our work, and characterization of them is still underway.

Much attention was paid to the bis(phthalocyanato)-lanthanides which have sandwich-like structures and are capable of existing in two oxidation states. The compounds may also be doped with iodine, and single crystals may be grown by using

electrochemical techniques. As discussed in Technical Report No. 34, the electrical conductivities of the iodine doped substances are several orders of magnitude higher than those of the undoped materials. The conductivity behavior may be explained in terms of the variable hopping mechanism for heavily doped semiconductors. Calculations using the angular overlap model were carried out the aim of reproducing magnetic properties, and as discussed in Technical Report No. 35, the results show that the pyrrolic nitrogen donor atoms are weak sigma donors and moderate pi donors. Some very exciting new magnetic results have been obtained for the oxidized $\text{Ln}(\text{Pc})_2$ compounds with Tb, Dy, Ho, Er, Tm, and Lu. These results form the basis for technical reports to be issued in the near future.

List of Publications:

M. Schwartz, W. E. Hatfield, M. D. Joesten, M. Hanack, and A. Datz, "Magnetic Exchange Interactions in the Linear Chain Chromium Compounds Catena-fluorophthalocyaninatochromium(III) and Catena-cyanophthalocyaninatochromium(III)", Inorg. Chem. 1985, 24, 4198.

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Schwartz, M.; Hatfield, W. E. "Spectroscopic and Magnetic Studies of Two Electrically Conducting Charge Transfer Compounds of 7,7,8,8-Tetracyanoquinodimethanide with Cationic Copper Chelates", Inorg. Chem., 1987, 26, 2823.

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Keller, H. J.; Bandrauk, A. D.; Bayon, J. C.; Bellito, C.; Clark, R. J. H.; Day, P.; Haasnoot, J. G.; Hatfield, W. E.; Jones, M. T.; Papavassiliou, G.; Robert, T.; von Schultz, J. U.; Underhill, A. E.; Whangbo, M.-H. "New Highly Conducting Systems", In Organic and Inorganic Low-Dimensional Crystalline Materials; Delhaes, P., Drillon, M., Eds.; Plenum: New York 1987; 457-461.

Hatfield, W. E.; Miller, J. H., Jr.; Editors; High-Temperature Superconducting Materials: Preparations, Properties, and Processing; Marcel Dekker, Inc.; New York 1988, 389 pages.

Hatfield, W. E.; Rohrs, B. R.; Kirk, M. L.; Helms, J. H.; Ro, H.; Williamson, E. J. "Magnetic Anomalies in the Rare Earth Oxide Superconductors $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{YbBa}_2\text{Cu}_3\text{O}_{7-x}$ "; In High Temperature Superconducting Materials: Preparations, Properties, and Processing; Hatfield, W. E., Miller, J. H., Jr., Eds; Marcel Dekker, Inc.: New York 1988; 313-320.

Miller, J. H., Jr.; Liu, B.; Riley, W. J.; Dibianca, A. N.; Holder, S. L.; Hunn, J. D.; Rohrs, B. R.; Hatfield, W. E. "Temperature-Dependent Conductivity of Oxygen-Depleted YBCO Ceramics"; In High Temperature Superconducting Materials: Preparations, Properties, and Processing;

Hatfield, W. E., Miller, J. H., Jr., Eds; Marcel Dekker, Inc.: New York 1988; 243-249.

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Padilla, J.; Hatfield, W. E. "Magnetic and Electrical Properties of Sandwich-Like Lanthanide Phthalocyanines", Synthetic Metals 1989, 29, F45-F50.

Miller, J. H., Jr.; Hatfield, W. E.; Rohrs, B. R.; Kirk, M. L.; Perkinson, J. L.; Trojan, K. L.; Hunn, J. D.; Zhang, Z. H.; Riley, W. J. "Synthesis and Characterization of BiCaSrCuO and BiSnCaSrCuO Superconducting Ceramics", In High Temperature Superconductivity - The First Two Years; Metzger, R. M., Editor; New York: Gordon and Breach Science Publishers; pp. 235-240.

List of Technical Reports:

ter Haar, L. W.; Di Salvo, F. J.; Bair, H. E.; Fleming, R. M.; Wasazczak, J. V.; Hatfield, W. E. "Charge Density Waves in the Mixed-Valence Two-Dimensional Metal, $K_3C^{u}_8S_6$ ", Technical Report No. 25.

Schwartz, M.; Hatfield, W. E. "Two Electrically Conducting Charge Transfer Compounds of 7,7,8,8-Tetracyanoquinodimethanide with Cationic Copper Chelates", Technical Report No. 26.

Schwartz, M.; Hatfield, W. E. "Correlation of Spectroscopic and Magnetic Data of Two Charge Transfer Compounds of TCNQ with Cationic Copper Chelates", Technical Report No. 27.

Hatfield, W. E. "The Advent of High Temperature Superconducting Materials: Chronology of Events and Hallmark Developments"; Technical Report No. 28.

Miller, J. H., Jr.; Liu, B.; Riley, W. J.; Dibianca, A. N.; Holder, S. L.; Hunn, J. D.; Rohrs, B. R.; Hatfield, W. E. "Temperature-Dependent Conductivity of Oxygen-Depleted YBCO Ceramics"; Technical Report No. 29.

Hatfield, W. E.; Rohrs, B. R.; Kirk, M. L.; Helms, J. H.; Ro, H.; Williamson, E. J. "Magnetic Anomalies in the Rare

Earth Oxide Superconductors $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{YbBa}_2\text{Cu}_3\text{O}_{7-x}$ ";
Technical Report No. 30.

Keller, H. J.; Bandrauk, A. D.; Bayon, J. C.; Bellito, C.; Clark, R. J. H.; Day, P.; Haasnoot, J. G.; Hatfield, W. E.; Jones, M. T.; Papavassiliou, G.; Robert, T.; von Schultz, J. U.; Underhill, A. E.; Whangbo, M.-H. "New Highly Conducting Systems", Technical Report No. 31.

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Padilla, J.; Hatfield, W. E.; Wasson, J. R.; Estes, W. E. - "Ferromagnetic Long Range Ordering in Copper(II) Maleate Monohydrate", Technical Report No. 33.

Padilla, J.; Hatfield, W. E. "Magnetic and Electrical Properties of Sandwich-Like Lanthanide Phthalocyanines", Technical Report No. 34.

Padilla, J.; Hatfield, W. E. "Application of the Angular Overlap Model to Lanthanide Phthalocyanines", Technical Report No. 35.

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who participated in the project:

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