A METALLURGICAL APPROACH TO HIGH TEMPERATURE SUPERCONDUCTIVITY

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A Metallurgical Approach to High Temperature Superconductivity

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Superconductivity
Lattice Instability
Metallurgy
Electrical Resistivity

A second system of ternary superconductors has been discovered. Their formula is $X(R_{II})B_2$ with X being almost any trivalent transition element. In addition the superconductor Er$B_2$ first becomes superconducting, then loses it and becomes ferromagnetic at a lower temperature. This phenomenon is a radically new feature for ordered compounds. The properties of these and some closely related superconductors and magnets have been investigated.

We have further results on Chevrel-phase compounds, the first ternary superconducting system ever discovered; we find three distinct low temperature phases.
within the room temperature homogeneity range of Cu$_x$Mo$_3$S$_4$. A non-linear pressure variation of the superconducting transition temperature ($T_c$) correlates with the crystallographic instabilities of ZnMo$_5$S$_6$, ZnMo$_5$Se$_6$ and Cu$_{0.7}$Mo$_3$Se$_4$.

A correlation between $T_c$ and the composition induced metal-insulator transition in AgSn$_{1-x}$Sb$_x$Se$_2$ has been found.

We provide an explanation for the low temperature resistance behavior of a number of high $T_c$ A-15 superconductors, and a formalism for isolating the aspherical Coulomb scattering contribution to the electrical resistivity of metals has been developed. This leads to a principal understanding of the resistivity of superconductors above their transition temperature.

Low temperature x-ray measurements have been completed on crystallographically unstable systems (La,Ce)Ru$_2$ and (Hf,Zr)V$_2$, and these instabilities correlated with $T_c$. 

[Diagram or figure here]
ACHIEVEMENT

Contract No: USAF/F49620-77-C-0009

A Metallurgical Approach to High Temperature Superconductivity

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Research achievements for the period 1 October 1976 – 31 December 1977 are detailed below with reference to the "Statement of Work" of the proposal.

a) Work on New Multicomponent Superconductors

We have now discovered the second system of superconducting ternary compounds. They are the double Rh borides. The system is XRh$_4$B$_4$ in which X = Y, Nd, Sm, Er, Tm, Lu and Th.\textsuperscript{1,2} The superconducting transition temperatures ($T_c$) are shown in Table I. For X = Gd, Th, Dy and Ho, the isomorphous compounds become ferromagnetic instead (see Table I). Of particular interest are the high $T_c$'s of the Er and Tm compounds. Never before have such high superconducting transition temperatures been observed in compounds with elements having magnetic moments as high as 9.6$\mu_B$.

The erbium compound is particularly interesting. The superconducting $T_c$ is at 8.6K as pointed out before. Below 0.9K the compound loses its superconductivity and becomes magnetic instead.\textsuperscript{3}

It is astonishing that even though the effective moments of Ho (10.6$\mu_B$) and of neighboring Er (9.6$\mu_B$) differ by only 10%, HoRh$_4$B$_4$ is ferromagnetic whereas ErRh$_4$B$_4$ is superconducting. Therefore, we explored the superconducting properties of the pseudoternary alloys (Er,Ho)Rh$_4$B$_4$ to clarify the reasons for this striking juxtaposition. Our results for this system...
are shown in Fig. 1. Here, we found that for up to 89% dilution of Er by Ho the superconducting transition temperatures are only weakly dependent on the Ho content and that the disappearance of superconductivity observed for pure ErRh$_4$B$_4$ also persists over this concentration range. For higher Ho concentrations, only ferromagnetic transitions were observed. Other ternary systems in which superconductivity has recently been discovered include the Y-Os-Si$^5$ and Sc-Rh-Si$^6$ systems, with superconducting transition temperatures up to 10K and 9K, respectively. The composition and structure of each of the superconducting phases remain to be determined.

b) Work on Metastable Superconductors

Our work on the metallurgy of the above RERh$_4$B$_4$ compounds led to the discovery of a structurally distinct high temperature modification (with the same stoichiometry) which could be obtained as a single phase by substituting small amounts of Ru for Rh. The superconducting and magnetic transition temperatures obtained for this body-centered-tetragonal series RE(Rh$_{0.85}$Ru$_{0.15}$)$_4$B$_4$ and for the pure Ru series of isostructural compounds, RERu$_4$B$_4$, are shown in Figs. 2a and 2b, respectively.$^7$ The $T_c$'s among the former series of compounds range from 4.0K for the Dy member to 9.6K for the Y compound, and no transitions into a magnetically ordered state were found above 1.5K; these materials thus constitute only the third known true ternary structure type to exhibit superconductivity in the presence of a large concentration of highly magnetic rare earth ions. Again, the presence of large concentrations of these highly magnetic rare earth ions does not severely interfere with the superconducting behavior.
A factor has been identified which correlates with the divergence in the superconducting properties of the two series of compounds shown in Fig. 2. Whereas the members of the superconducting RE(Rh$_{0.85}$Ru$_{0.15}$)$_4$B$_4$ series of compounds all exhibit c/a ratios less than 2.00, the RERu$_4$B$_4$ series shows c/a ratios greater than 2.00, even though the unit cell volumes of corresponding members of each series are nearly the same (see Fig. 3). In order to study this correlation further and to determine the manner in which the shift from high $T_c$'s to low $T_c$'s comes about, we studied the crystallographic and superconducting properties of the Y(Rh$_{1-x}$Ru$_x$)$_4$B$_4$ pseudoternary system. Our results, shown in Fig. 4, indicate that the transition is quite abrupt, and that the transition does indeed occur at the composition ($x \approx 0.5$) at which the c/a ratio increases past 2.00 with increasing $x$. The reasons for this correlation have not yet been identified.

$T_c$ data for the series of pseudoternary NaCl-type compounds AgSn$_{1-x}$Sb$_x$Se$_x$, shown in Fig. 5, support the contention that there exists some as-yet-unknown mechanism which enhances $T_c$ for systems exhibiting abrupt composition-induced metal-semiconductor transitions. Whereas a monotonic decrease in $T_c$ with increasing $x$ is predicted on the basis of carrier concentration considerations, $T_c$ increases initially, reaches a peak for $x = 0.15$, and finally decreases precipitously to < 1.5K as a metal-semiconductor transition sets in at $x = 0.4$. This behavior is reminiscent of that observed previously for the Li$_{1+x}$Ti$_{2-x}$O$_4$ spinel system.

In the course of a continuing study of the relationship between high-temperature superconductivity and low-temperature lattice instability, we observed a very unusual variation of $T_c$ with composition $x$ (Fig. 6a) for the Chevrel-phase compounds Cu$_x$Mo$_3$S$_4$. Results of low-temperature x-ray and electrical resistivity measurements (Fig. 6b and 6c) revealed that...
the three \( T_c \) ranges of Fig. 6a are those of three distinct low temperature phases which are stable within the room temperature homogeneity range of rhombohedral \( \text{Cu}_x\text{Mo}_3\text{S}_4 \). Pressure-induced discontinuities in \( T_c \) were also found (Fig. 7), corresponding to transformations between the three phases. From the data of Figs. 6 and 7, the pressure-composition phase diagram in Fig. 8 was constructed.

c) Electrical and Magnetic Measurements on Superconducting Materials at Normal and High Pressures

We have identified one factor contributing to the anomalous pressure dependencies of \( T_c \) in the ternary molybdenum chalcogenides through hydrostatic compressibility measurements up to 29.8 kbar on eleven of these compounds.\(^{13}\) Data for the ternary sulfides are shown in Fig. 9. Analysis of the data reveals a small bulk modulus (\( B_o \)) for each compound, with values comparable to those found in simple s-p elements such as indium. In contrast, the magnitude of the first pressure derivative of \( B_o \) is nearly three times as large as the largest reported values for elements.

The proposed relationship between the occurrence of nonlinear pressure variation of \( T_c \) and crystallographic instability\(^{14}\) has been further verified through measurements on the Chevrel-phase compounds \( \text{ZnMo}_5\text{S}_6 \), \( \text{ZnMo}_5\text{Se}_6 \) and \( \text{Cu}_{0.7}\text{Mo}_3\text{Se}_4 \).\(^{15}\)

Powder neutron diffraction data\(^{16}\) have confirmed the existence of long-range magnetic order in the compound \( \text{HoMo}_6\text{S}_8 \). For this material, the type of order is ferromagnetic (Fig. 10), commensurate with the crystallographic unit cell and is coincident with the destruction of superconductivity.
Thus, the competitive interplay between the two cooperative phenomena of magnetism and superconductivity yields similar results for HoMo$_6$S$_8$ and ErRh$_4$B$_4$. In contrast, low temperature neutron diffraction data$^1$ for ErMo$_6$Se$_8$ reveal the presence of magnetic Bragg peaks which are not compatible with a simple ferromagnetic structure and this ternary compound remains superconducting below the temperature at which this magnetic structure occurs. Thus, ternary superconducting systems continue to display a rich variety of properties not previously observed in binary compounds.

One interesting feature of the magnetic behavior of the (RE)Rh$_4$B$_4$ compounds is that the Gd member does not have the highest magnetic ordering temperature, contrary to what one expects for magnetic exchange via conduction electrons. Other, simpler, borides (e.g. (RE)B$_6$ and (RE)B$_4$) also behave in this same anomalous way. We are investigating this behavior in these simpler borides and have grown single crystals of several (RE)B$_4$'s for magnetic and electrical measurements. These measurements are not complete.

Electrical resistivity measurements have been made on a number of the (RE)Rh$_4$B$_4$ compounds. Figure (11) shows the data for HoRh$_4$B$_4$. An anomaly at the magnetic ordering temperature is evident, as well as the negative curvature at higher temperatures, characteristic of superconducting materials.

We have found that an unusual phonon-spectrum (e.g., non-Debye like) is reflected, in the case of A-15 superconductors, by resistivity behavior which varies with $T^2$ at low temperature.$^1$ We have observed that the resistivity of Zr$_2$Rh ($T_c = 11$K) also fits such a power law above $T_c$, suggesting a similar cause for the unusual properties$^2$ of Zr$_2$Rh.
Theoretical work by Fulde and co-workers predicts that scattering of conduction electrons by the aspherical part of the 4f electron orbits of rare earth ions can be a new coupling mechanism for superconductivity. We have presented a method for determining the magnitude of this scattering mechanism from electrical resistivity measurements on materials containing rare earth ions, and have successfully applied this method to PrB$_6$ for which the effect was found to be relatively large.

**d) Low Temperature X-ray Diffraction Measurements**

The occurrence of low-temperature lattice distortion in Cu$_x$Mo$_3$S$_4$ for $x \approx 2$ was found to increase $T_c$ above that of the room-temperature rhombohedral phase. This behavior is just the opposite to that previously observed for most other materials; for the latter, distortions to a less symmetric structure invariably reduced $T_c$.

Other systems exhibiting lattice transformations on which we have now completed measurements are (La,Ce)Ru$_2$ (correlation of $dT_c/dp$ with the cubic-tetragonal transformation) and (Hf,Zr)V$_2$ (detailed investigation of lattice distortions and their correlation with $T_c$).
REFERENCES


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<th>Compound</th>
<th>Superconducting Transition Temperature (K)</th>
<th>Magnetic Ordering Temperature (K)</th>
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<tr>
<td>YRh₄B₄</td>
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<tr>
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<tr>
<td>Sc₀.75Th₀.25Rh₄B₄</td>
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</table>
Fig. 1. Low temperature phase diagram for \( (E_{1-x}H_{x})Rh_4B_4 \) compounds possessing the primitive tetragonal \( YRh_4B_4 \) structure.
Fig. 2  Superconducting (o) and magnetic (o) transition temperatures for the isostructural series of compounds $RE(Rh_{0.85}Ru_{0.15})_4B_4$ (Fig. 2a) and $RERu_4B_4$ (Fig. 2b) which crystallize in the body-centered-tetragonal LuRu$_4$B$_4$ structure. The arrows indicate temperatures above which no transitions were observed by ac magnetic susceptibility measurements, and the symbol X indicates that the element below it does not form the phase.
Fig. 3. Crystallographic data for two series of body-centered tetragonal compounds.
Fig. 4. Superconducting and crystallographic properties of the pseudoternary system $Y(Rh_{1-x}Ru_x)_4B_4$. 
Fig. 5. Composition dependence of the superconducting transition temperature for the NaCl-type system $\text{AgSn}_{1-x}\text{Sb}_x\text{Se}_2$. 
Fig. 6  Superconducting transition temperature (Fig. 6a), lattice transformation temperature (Fig. 6b), and residual resistance ratio (Fig. 6c) vs. composition for Cu$_x$Mo$_3$S$_4$. 
Fig. 7  Hydrostatic pressure dependence of the superconducting transition temperature for Cu$_x$Mo$_3$S$_4$. 
Fig. 8. Pressure-composition phase diagram for Cu$_x$Mo$_3$S$_4$ derived from the $T_c$ data in Figs. 6a and 7.
Fig. 9. Compressibility data for Chevrel-phase sulfides.
Fig. 10. Magnetic diffraction pattern for HoMo$_6$S$_8$. Data taken at 1.00 K (above the magnetic ordering temperature $T_M$) have been subtracted from the data taken at 0.05 K. The new Bragg peaks which develop below $T_M$ coincide with the positions of the HoMo$_6$S$_8$ nuclear peaks, establishing that the transition is to a state of long range ferromagnetic order.
Fig. 11. Temperature dependence of the electrical resistance of HoRh$_4$B$_4$. 

![Graph showing the temperature dependence of the electrical resistance of HoRh$_4$B$_4$.](image)
Scientific Impact

The most important aspect of the work completed under this contract is the discovery of the occurrence of high superconducting transition temperatures in the presence of large localized magnetic moments. This extremely unusual phenomenon gives hope for higher $T_c$'s as well as the expectation now under investigation, that critical field measurements for these superconductors may provide important clues for the achievement of higher critical fields, a development which would be of great technologic significance.
STATEMENT OF WORK      (1 October 1976 - 31 Dec. 1977)

a) Synthesize, measure, and analyze new multicomponent superconductors.

b) Synthesize and measure new metastable superconductors, by somehow circumventing their instabilities.

c) Perform electric and magnetic measurements on superconducting materials at normal and high pressures.

d) Perform low temperature x-ray diffraction measurements on superconductors.
PUBLICATION LIST


38. Low Temperature Crystal Structures and Superconductivity of \((\text{Hf}_{1-x}\text{Zr}_x)\text{V}_2\) Alloys, A. C. Lawson, Phys. Rev. (in press).


43. Re-entrant Superconductivity and Magnetic Ordering in the Pseudoternary System \((\text{Er}_{1-x}\text{Ho}_x)\text{Rh}_4\text{B}_4\), D. C. Johnston, W. A. Fertig, M. B. Maple, and B. T. Matthias, Solid State Communications (in press).


1. High Transition Temperature Superconducting Materials
   a. Bernd T. Matthias, University of California, San Diego, IPAPS
   b. Consultation with other government agencies
   c. Los Alamos Scientific Laboratories, Los Alamos, New Mexico—The research on improving the basic properties of present superconducting materials for use in superconducting cables continues with several groups of researchers at Los Alamos Scientific Laboratories. For the most part, this coupling is still available only in classified form.
   a. Bernd T. Matthias, University of California, San Diego, IPAPS
   b. Conference
   c. Annual Meeting of the Southeastern Section of the American Physical Society
   a. Bernd T. Matthias, University of California, San Diego, IPAPS
   b. Special Lecture Series
   c. "Science in the Public Interest Lecture Series" sponsored by the University of Colorado, Boulder, Colorado

2. New Multicomponent Superconductors
   a. Bernd T. Matthias, University of California, San Diego, IPAPS
   b. APS March Meeting
   c. Announcement of ErRh4B4 superconductor which also exhibits ferromagnetism.
   a. Bernd T. Matthias, University of California, San Diego, IPAPS
   b. Lecture Series
   c. Concepts in Modern Engineering and Technology, State University of New York at Binghamton, New York
   a. Bernd T. Matthias, University of California, San Diego, IPAPS
   b. Distinguished Lecturer
   c. University of Houston, Houston, Texas
3. Other

a. Zachary Fisk, University of California, San Diego, IPAPS

b. Collaboration

c. A. Arko, G. Crabtree, D. Karim, F. M. Mueller, L. R. Windmiller, J. B. Ketterson, Argonne National Laboratories, deHaas van Alphen effect and the Fermi surface of LaB$_6$

a. Robert N. Shelton, University of California, San Diego, IPAPS

b. Collaboration


a. Robert N. Shelton, University of California, San Diego, IPAPS

b. Collaboration


a. Robert N. Shelton, University of California, San Diego, IPAPS

b. Collaboration

c. S. Foner and E. J. McNiff, Jr., MIT National Magnet Laboratory, upper critical magnetic fields on ternary molybdenum selenides

a. Robert N. Shelton, University of California, San Diego, IPAPS

b. Collaboration

c. J. W. Lynn, University of Maryland and D. E. Moncton, Bell Laboratories, Observation of long range magnetic order in ternary molybdenum chalcogenides

a. Robert N. Shelton, University of California, San Diego, IPAPS

b. Collaboration

c. T. F. Smith, Monash University, Australia, Thermal expansion measurements on ternary molybdenum sulfides and selenides

a. David C. Johnston, University of California, San Diego, IPAPS

b. Collaboration

c. B. G. Silbernagel, Exxon Research Laboratories, NMR studies of ternary borides

a. David C. Johnston, University of California, San Diego, IPAPS

b. Collaboration