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A NEW FAMILY OF TERNARY INTERMETALLIC SUPERCONDUCTING/MAGNETIC STANNIDES

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A new family of rare earth-rhodium-tin intermetallic compounds, with the representative formula $(RE)Rh_xSn_y$, has been synthesized in single crystal form. The compounds containing the heavier rare earths are superconducting and those with the lighter rare earths are generally magnetic. The compound $ErRh_{1.1}Sn_{3.6}$ exhibits reentrant superconductivity with $T_c = 0.97$ K and $T_m = 0.57$ K as determined from ac magnetic susceptibility measurements. The synthesis and X-ray characterization of the series are described and the results of electrical resistivity, upper critical magnetic field, magnetic susceptibility, specific heat and neutron scattering measurements on the Er compound are given.

Introduction

Considerable research activity has recently been focused on the interaction between superconductivity and long-range magnetic order.⁽¹⁻⁴⁾ Two classes of ternary compounds exhibiting these phenomena have been reported: the Chevrel phases typified by $RE_xMo_6S_8(5)$ and $RE_xMo_6Se_8(6)$ and the tetraborides such as $(RE)Rh_4B_4$.⁽⁷⁾ In this Letter we report preparative, crystallographic, analytical, and transition temperature data for a new family of compounds. As in the tetraborides, the Er compound displays reentrant superconductivity and for the adjacent members of the RE series the superconducting transition temperature increases to the right and the magnetic transition temperature increases to the left of Er. A comparison of resistivity, upper critical magnetic field, ac magnetic susceptibility, neutron scattering, and heat capacity measurements on the Er compound is presented.

The new family of ternary intermetallic stannides reported here employs no metalloids, and is thus the first class of compounds exhibiting superconductivity and magnetism wherein all constituents are metals. Furthermore all the compounds have been prepared as single crystals. There are three distinct crystal phases which are compositionally similar. The compounds were synthesized as single crystals by crystallization from an excess of liquid tin employed as a solvent. While the use of molten metals as solvents to effect crystallization is not new, this procedure should be a productive way to explore the periodic system for new compounds.

Synthesis and Chemical Analysis

Single crystals of all compounds were grown by dissolving the constituent metals in an excess of tin. The process was carried out in evacuated, sealed fused silica tubes. The tin used was 5 N's purity from Cominco American, Inc.; rare earth metals were of 3 to 4 N's purity obtained from Research Chemicals. Noble metals were of the highest purity obtainable from Engelhard Industries. All other materials used were of at least equivalent purity. A typical growth sequence, say for $ErRh_{1.1}Sn_{3.6}$, was carried out by weighing 0.2788 gms Er, 0.1715 gms Rh, and 5.00 gms Sn into a silica tube 7.0 mm I.D. \times 9.0 mm O.D. The tube was evacuated, sealed off to a length of \sim 8 cm, and supported vertically in a horizontally loaded, resistively heated furnace. Controlled temperature was held at 1050°C for 2 hrs to effect reaction and solution. A cooling rate of 5 to 10°C/hr was initiated and the program continued down to \sim 575°C when the tube was removed from the furnace and allowed to cool to room temperature. This "quench" was done to preserve good crystal surfaces, whereas if slow cooling was carried on to solidification, crystal surfaces were often marred by precipitates. When the solidified boule was placed in concentrated HCl, care was taken to remove the crystals as soon as they were loose, as prolonged exposure to HCl resulted in a black surface rather than the highly polished metallic surface otherwise obtained. We have determined by X-ray diffraction and fluorescence that the black surface material is an amorphous composition of rhodium and tin, the erbium having been leached out by the HCl. Chemical analysis gave a composition for the erbium compound of $ErRh_{1.1}Sn_{3.6}$. Analyses of selected compounds, all of which were done in duplicate, are given in Table I in column 1 in formula form. Crystals ob-

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TABLE I
Properties of MRh_xSn_y

Compound	Structure (Phase)	Lattice Constant Å	Density gm/cc 25°C	Supercond. T _c (K)	Magnetic T _m (K)	Critical Field	Resist. ρ _{300K} μ Ω cm	Resist. Ratio ρ _{300K} /ρ _{10K}
						dH _{c2} dT(T=T _c) KG/K		
LaRh _x Sn _y	I	9.745		3.2-3.0 ^(a)				
CeRh _{1.2} Sn _{4.0}	I	9.710	8.3					
PrRh _x Sn _y	I	9.693					114	21
NdRh _{1.2} Sn _{4.1}	I	9.676	8.4					
SmRh _{1.2} Sn _{4.3}	I	9.657	8.7					
EuRh _x Sn _y	I	9.749			~11 ^(c)			
GdRh _x Sn _y	I	9.638			11.2 ^(b)			
TbRh _{1.1} Sn _{3.6}	III	13.774	8.7		^(e) { 3.8 ^(a) 2.8			
DyRh _{1.1} Sn _{3.6}	III	13.750	8.8		2.08 ^(a)			
HoRh _{1.2} Sn _{3.9}	II		8.9		1.68 ^(a)		310	0.84
HoRh _{1.2} Sn _{3.9}	III	13.750						
ErRh _{1.1} Sn _{3.6}	II		9.1	{ 1.31 ^(a) 1.22 ^(b) 0.97 ^(c)	{ 0.34 ^(b) 0.57 ^(c) 0.61 ^(d)		340	0.85
ErRh _{1.1} Sn _{3.6}	III	13.714						
TmRh _{1.3} Sn _{4.0}	II		9.2	2.3-2.2 ^(a)			286	0.94
TmRh _{1.3} Sn _{4.0}	III	13.701						
YbRh _{1.4} Sn _{4.6}	I		8.9	8.6-8.2 ^(a)		3.5		
LuRh _{1.2} Sn _{4.0}	II		9.6	4.0-3.9 ^(a)		20.3		
YRh _x Sn _y	II			3.2-3.1 ^(a)		21.5	290	1.03
ScRh _x Sn _y	II			4.5-4.1 ^(a)				
ThRh _x Sn _y	I	9.692		1.9-1.7 ^(a)		9.3	140	4.3
CaRh _{1.2} Sn _{4.5}	I	9.702	8.3	8.7-8.6 ^(a)		4	110	8.8
SrRh _x Sn _y	I	9.800		4.3-4.0 ^(a)				

Phase I = Primitive cubic, a₀ ~ 9.7 Å

Phase II = Pseudo-tetragonal, a ~ 13.7, c ~ 9.7 Å

Phase III = Face centered cubic, a₀ ~ 13.7 Å

a = Measured inductively

b = Measured resistively

c = Susceptibility measurement

d = Neutron scattering

e = Two T_m's observed on same crystal

tained by this procedure were typically 1-2 mm on an octahedral edge. We occasionally see a trace of superconductivity at ~ 3.7 K which we believe is due to entrapped Sn. Two different crystallographic phases, (II and III described later), are sometimes found in a single melt possibly due to either compositional gradients too small to detect chemically, or different degrees of sublattice order. Arc-melted samples where the constituents were weighed for the composition ErRh_{1.1}Sn_{3.6}, produced the f.c.c. phase III material only, with weak lines of elemental Sn as determined by X-ray powder diffraction.

Compounds with Co and Ru replacing Rh have been prepared which also fall into this new class. A large number of compounds were also made with Ir replacing Rh. Of these, La, Ca and Sr were of phase I, (described later), and superconducting with T_c's at ~ 2.6, ~ 7.1, and ~ 5.1 K respective-

ly. All of the systems were further permuted by substituting elements such as Ca, Sr, Mg, Cd, Y, Sc, Zn, In or Th for the RE. Partial substitutions for Sn were made using Pb, Bi, and Ge.

X-ray Analysis

Each compound was examined by powder X-ray diffraction using a 114.6 mm Debye-Scherrer camera and filtered Cr K_α radiation. The symmetry was established from precession photographs of the Yb and ErRh_xSn_y compounds using filtered Mo K_α radiation. The crystallographic data for the series are reported in columns 2, 3 and 4 of Table I. Phase I is primitive cubic with a₀ ~ 9.7 Å, and is found in those compounds where RE is La to Gd and also with Yb, Th, Ca or Sr. The YbRh_{1.4}Sn_{4.6} compound is distinguished

from the other compounds of phase I by showing a broadening of some high angle lines in its X-ray powder diffraction photograph, which may be indicative of a degree of disorder. The systematic absences are $hh'l$ with $l \neq 2n$ leading to possible space groups $P43m$ (#218) or $Pm3n$ (#223). Phase II is pseudo-tetragonal, (the apparent tetragonality may be a superlattice), with $a \sim 13.7 \text{ \AA}$ and $c \sim 9.7 \text{ \AA}$. It is found in those compounds where RE is Ho, Er, Tm, Lu and also with Y or Sc. Phase III is face centered cubic with $a_0 \sim 13.7 \text{ \AA}$; here RE can be Tb to Tm. One notes that the lattice parameters of phases I and III are related by $\sqrt{2}$, and that $c/a = 1/\sqrt{2}$ in phase II.

Superconducting and Magnetic Transitions in MRh_xSn_y Compounds

Those transition temperatures above 1.1 K were determined by ac inductance measurements using a frequency of 13 cycles. The results are given in the fifth and sixth columns of Table I. The compounds containing Yb and Ca have superconducting transition temperatures greater than 8 K. There are magnetic transitions for RE compounds containing Eu to Er with T_m decreasing the heavier the rare earth. Superconductivity appears at Er where it is reentrant, and T_c increases toward 4 K at Lu, with the exception of Yb where T_c is at 8.9 K.

In order to further characterize the series, the slope of the upper critical field with respect to temperature just below T_c , $(dH_{c2}/dT)_{T=T_c}$, is shown in column 7 of Table I. Finally, the resistivity at 300 K and the resistivity ratio ($\rho_{300}/\rho_{4.2}$) are given for representative members of the series in the last two columns of Table I. As can be seen the room temperature resistivity is lower and the resistivity ratio higher for the compounds in phase I. This suggests a high degree of disorder in the crystals of phases II and III, but further study will be needed to understand the microscopic origin of this difference.

Reentrant Superconductivity

To establish in more detail the reentrant superconductive behavior of the Er compound, a number of different measurements were made for $0.08 \leq T \leq 1.4 \text{ K}$ including electrical resistivity, upper critical field, ac magnetic susceptibility, neutron scattering and heat capacity; these measurements are displayed in Fig. 1. They clearly establish that at low temperatures the Er compound has fairly long-range ferromagnetic order that destroys the superconductivity; much as is seen in the Chevrel compounds and the RE tetrahydrides.⁽⁸⁻¹¹⁾

The low frequency (15 Hz) ac electrical resistivity measurements in zero and applied magnetic fields and the low frequency (15 Hz) ac magnetic susceptibility measurements were made, respectively, on bars and powders prepared from a single crystal of $ErRh_{1.1}Sn_{3.6}$. The measurements were made at temperatures between 70 mK and 2.0 K in an He^3 - He^4 dilution refrigerator cryostat. The temperatures at which the ac electrical resistance dropped to 50% of its normal state value (taken just above T_c) in each applied magnetic field were used to define the values of T_c and T_m in determining H_{c2} . The χ_{ac} data give the values $T_c = 0.97 \text{ K}$ and $T_m = 0.57 \text{ K}$, while the ac electrical resistivity and upper critical field measurements give $T_c = 1.22 \text{ K}$ and $T_m = 0.34 \text{ K}$. No thermal hysteresis was observed in the transition at T_m in these measurements, in contrast to the behavior previously reported for ternary RE compounds which exhibit reentrant superconductive behavior.⁽¹⁰⁻¹²⁾ A neutron scattering measurement gives $T_m = 0.61 \text{ K}$. The disparity in the values of the transition temperatures may be due to varying degrees of sublattice order.⁽¹³⁾ The neutron scattering measurements were done at the High Flux Beam Reactor at Brookhaven National Laboratory on a crystal 3-4 mm on a side which was mounted in an $hh'l$ scattering plane in an He^3 - He^4 dilution re-

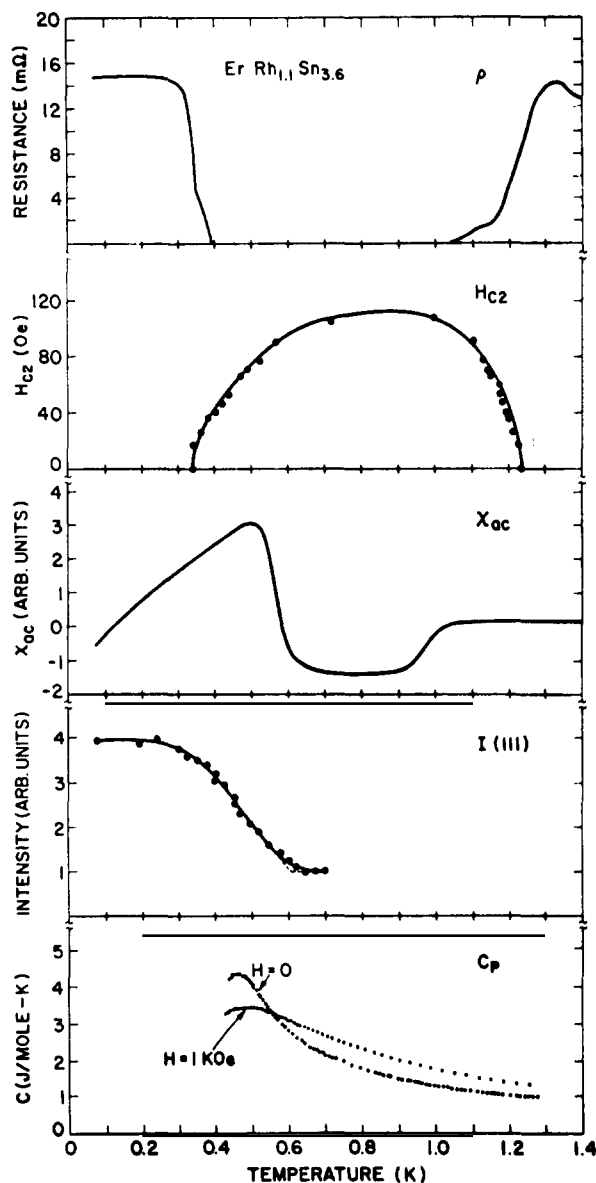


Fig. 1.

frigerator. Bragg intensities were measured in θ - 2θ scans through the various positions with integral h and l , and also some half integral values both at $T = 0.07 \text{ K}$ and 0.8 K . The only magnetic intensity ($I(0.07 \text{ K}) - I(0.8 \text{ K})$) appeared at Bragg positions allowed in the f.c.c. lattice. It is clear therefore that the ordering is ferromagnetic. The intensity of the (111) peak was measured on heating and cooling and the results are shown in Fig. 1. The transition appears to be continuous and no hysteresis could be observed. However, the width of the magnetic contribution to the intensity of the (111) reflection was slightly broader than resolution suggesting that true long-range magnetic order had not developed to temperatures of $T = 0.07 \text{ K}$.

The heat capacity (C_p) data for a single crystal specimen of the Er compound between 0.4 and 1.4 K are shown at the bottom of Fig. 1, (measurements were taken up to 40 K). The measurements were performed with an He^3 calorimeter using a standard heat pulse technique. There is a clear lambda-type anomaly which exhibits a peak at $T = 0.47 \text{ K}$ in

zero applied magnetic field. A rough estimate of the entropy, S , below 3.5 K is consistent with a value $S = R \ln 2$ per mole of Er suggesting that the ground state of the Er^{3+} may be a doublet.

In summary, we have presented the synthesis and characterization of a new class of ternary stannides and have shown that the Er member of this series is a reentrant superconductor with the superconductivity being destroyed by the onset of ferromagnetic correlations. This system is especially attractive for the study of the interaction of superconductivity and magnetism because, unlike the tetraborides and the Che-

vrel phases, large single crystals can be grown. Work on crystal chemistry,⁽¹⁴⁾ X-ray characterization,⁽¹⁵⁾ and X-ray structure determination⁽¹⁶⁾ is continuing and will be reported elsewhere.

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