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MAGNETIC AND SUPERCONDUCTING PROPERTIES OF RARE EARTH OSMIUM STANNIDES

Z. Fisk,* S. E. Lambert,† M. B. Maple†
Institute for Pure and Applied Physical Sciences
University of California, San Diego, La Jolla, CA 92093

J. P. Remeika, G. P. Espinosa, A. S. Cooper, H. Barz
Bell Laboratories
Murray Hill, NJ 07974

S. Oseroff
Departmento de Fisica
Instituto Venezolano de Investigaciones Cientificas, Caracas, Venezuela

We present data on the magnetic and superconducting properties of rare earth osmium stannides. The compounds of Tb and Ho are superconducting only, those of Er and Tm are reentrant superconductors, and those of Gd and Dy appear to exhibit some type of short range magnetic order at low temperatures.

Introduction

The heavy rare earth (RE) rhodium stannides of approximate formula $RERh_{1.1}Sn_{3.6}$ discovered by Remeika et al.[1] crystallize in a cubic structure (phase III, $a_o \approx 13.7$ Å) or a closely related tetragonal structure (phase II, $a_o \sim 13.7$ Å, $c_o \sim 9.7$ Å).[2,3] The Er compound of this series is a reentrant superconductor with an upper superconducting critical temperature (T_{c1}) of 1.3 K and a lower superconducting critical temperature (T_{c2}) of 0.6 K. Below T_{c2}, the Er compound was found to exhibit short range ferromagnetic order. The Tm analogue has a superconducting critical temperature (T_c) of 2.3 K and is reentrant in a magnetic field.[4] There is no indication of magnetic order at temperatures down to 80 mK in the Tm compound.

It has proved possible to prepare the corresponding compounds of Gd through Tm in the Os series.[5] All these materials crystallize in phase III. The properties of the $REOs_xSn_y$ ternary compounds differ substantially from those of either their Rh analogues or the previously investigated $REMo_6S_8$, $REMo_6Se_8$ or $RERh_4B_4$ ternary compounds.

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Experimental

The Os compounds were grown from excess Sn as in ref. 5. Os is only sparingly soluble in Sn, and the clusters of small crystallites recovered contained small amounts of unreacted Os. X-ray analysis revealed no additional phases.

Results

(i) Superconductivity. ac magnetic susceptibility (χ_{ac}) measurements in zero and applied magnetic field (H) were made at temperatures between 70 mK and 2.0 K in a ^3He-^4He dilution refrigerator cryostat. The data obtained are shown in Fig. 1 and summarized in Table 1. The chemical formulae for the compounds in all the figures is abbreviated as $REOs_xSn_y$. Both the Er and Tm osmium stannides exhibit reentrant superconductive behavior in zero field. This is the first reported case in which two pure compounds in a rare earth ternary sequence are reentrant. The reentrant transition at T_{c2} is evidence for the onset of ferromagnetic order, probably of short range, in analogy with the behavior previously reported for $ErRh_{1.1}Sn_{3.6}$. More surprising is the occurrence of superconductivity with no suggestion of magnetic ordering down to 70 mK in the Tb and Ho analogues. No sign of either superconductivity or obvious magnetic ordering down to 70 mK was found for the Gd or Dy analogues. We note that there is some unexplained

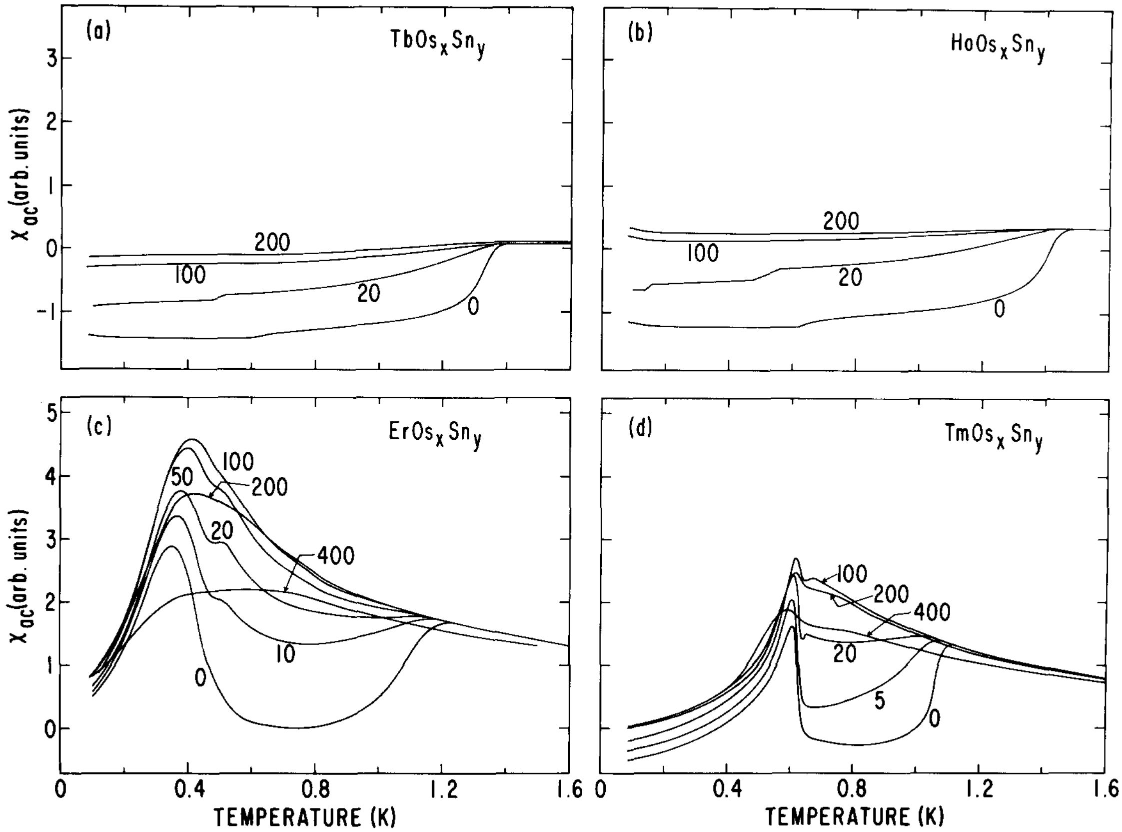

Fig. 1 ac magnetic susceptibility χ_{ac} vs temperature for phase III osmium stannides of Tb, Ho, Er and Tm. The numbers labelling the curves denote the values of the applied magnetic fields in Gauss.

Table 1

Compound[a]	Lattice Parameter	Gram Curie-Constant	Curie Weiss θ(K)	Superconducting Critical Temp. (K)
Gd	13.83_5	8.633×10^{-3}	-10	
$TbOs_{1.5}Sn_{2.6}$	13.81_2	1.378×10^{-2}	-7	1.4
$DyOs_{1.5}Sn_{2.5}$	13.79_2	1.687×10^{-2}	-7	
$HoOs_{1.2}Sn_{2.5}$	13.77_6	1.297×10^{-2}	-2	1.4
$ErOs_{1.1}Sn_{2.7}$	13.760	1.229×10^{-2}	-3	1.3, 0.5
Tm	13.744	7.712×10^{-3}	-1	1.1, 0.6

[a]Gd and Tm compounds not analyzed. Formulae given for other compounds derived from wet chemical analysis.

structure in the χ_{ac} vs temperature curves of the Er and Tm compounds. Part of this may be due to the presence of unreacted Os (T_c = 0.66 K, H_c = 70 Oe) as noted above.

(ii) Static magnetic susceptibility and EPR. The results reported above prompted us to measure the static magnetic susceptibility (χ) of these phase III Os stannides. These measurements were made between 1.4 K and 300 K using a Faraday magnetometer in fields up to 10 kOe. The results obtained are shown in Fig. 2 and partially tabulated in Table 1. We have not computed an effective moment for these compounds due to the inaccuracy with which the formula is known from wet chemical analysis (also given in Table 1). We note that some uncertainty in these analyses arises from the difficulty of dissolving Os.

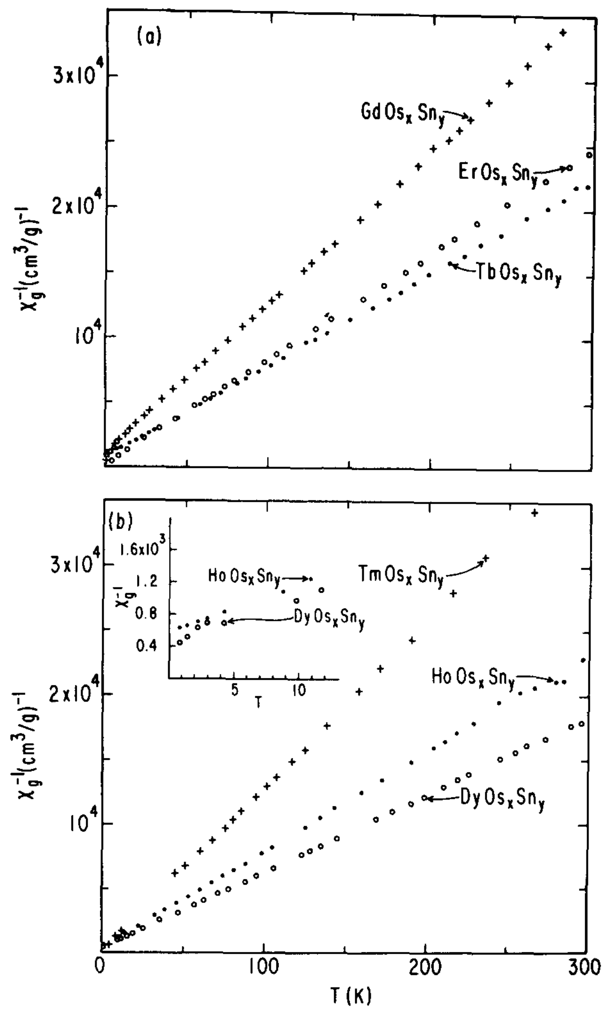

Fig. 2 Inverse gram magnetic susceptibility versus temperature T of the phase III osmium stannides of Gd through Tm. Inset in (b) shows low temperature data for the Ho and Dy compounds.

The points of interest in Fig. 2 are the conformity of the data to a Curie-Weiss law at high temperature with a small value for the Curie-Weiss temperature (θ), and deviations from Curie-Weiss behavior at low temperature for the Tb and Ho compounds that are reminiscent of singlet ground states. This was further investigated using a vibrating sample magnetometer, and these results are displayed in Fig. 3(a). The flattening out of the χ^{-1} vs temperature data for the Tb compound is strongly indicative of a singlet ground state. The situation for the Ho compound is not as clear cut. The site symmetry for the rare earths in these compounds is predominantly 3 m, but there also appears to be some disordering between RE and transition metal sites,[6] a point which we return to below. This symmetry can give a singlet ground state for Tb and Ho.

Magnetization (M) vs H data for the Gd compound measured at 1.6 K in the vibrating sample magnetometer are shown in Fig. 3(b). The nonlinearity of the M vs H curve coupled with the low temperature deviation from Curie-Weiss behavior seen in Fig. 1(a) is suggestive of some type of short range magnetic order. We observed no hysteresis or time dependent effects. The high degree of internal disorder revealed by the poor electrical resistance ratios of the Rh analogues, the occurrence of short range ferromagnetic order below T_{c2} in $ErRh_{1.1}Sn_{3.6}$, and x-ray evidence for structural disorder[6] are all consistent with the possibility of short range magnetic order.

We also shown in Fig. 3(c) EPR data for the Gd compound. The linewidth is very large, and the Korringa constant indicates an extremely small value for the product of the Gd spin-conduction electron coupling constant and the density of states at the Fermi surface. This small value would also be compatible with some type of short range magnetic order.

Finally, we show in Fig. 4 a χ_{ac} vs temperature curve as well as an M vs H curve at 1.6 K obtained with the vibrating sample magnetometer for the Dy compound. There is a feature in the χ_{ac} vs T curve near 4.2 K, below which χ_{ac} rises continuously with decreasing temperature. The M vs H curve is again in this case both nonlinear and nonhysteretic.

Summary

We have studied the magnetic and superconducting properties of six rare earth osmium stannides formed with the heavy rare earth elements Gd through Tm. ac magnetic susceptibility measurements down to 80 mK reveal that the compounds of Tb and Ho are superconducting only, those of Er and Tm are reentrant superconductors, while those of Gd and Dy do not become superconducting. To our knowledge, no other ternary RE system has Tb and Ho com-

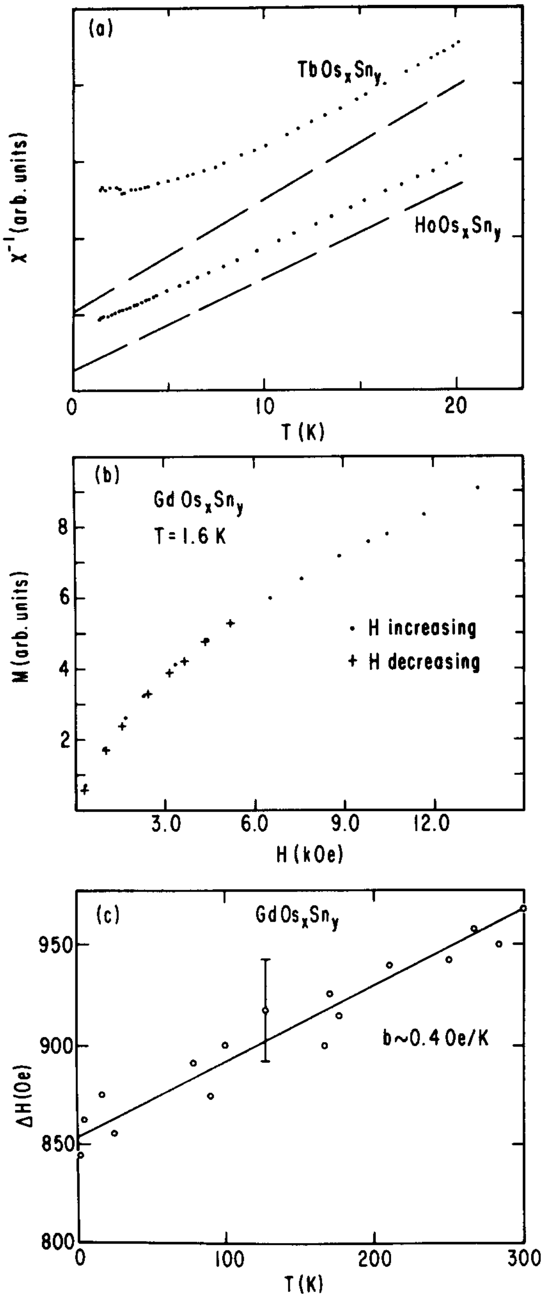

Fig. 3 (a) Low temperature magnetic susceptibilities of the Tb and Ho phase III osmium stannides. These measurements were made with a vibrating sample magnetometer. The susceptibility axis units are arbitrary. Dashed lines show normalized extrapolation of susceptibility from higher temperature data shown in Fig. 2.
(b) Magnetization of phase III GdOs$_x$Sn$_y$ versus applied field H at 1.6 K.
(c) EPR linewidth versus temperature T for phase III GdOs$_x$Sn$_y$.

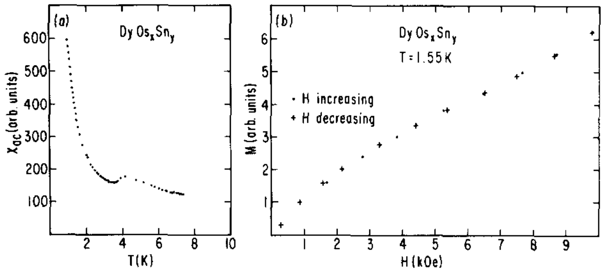

Fig. 4 (a) ac susceptibility of phase III $DyOs_xSn_y$ versus temperature T.
(b) Magnetization of phase III $DyOs_xSn_y$ versus applied field H.

pounds which are superconducting but not magnetically ordered. Magnetic susceptibility measurements indicate that the ground state of the RE ions in the Tb and Ho compounds is a singlet which is consistent with the occurrence of superconductivity and the absence of magnetic order in these two compounds. The reentrant transitions at T_{c2} in the Er and Tm compounds are probably due to the onset near T_{c2} of short-range ferromagnetic order, in analogy to the behavior previously reported for $ErRh_{1.1}Sn_{3.6}$. Magnetic susceptibility measurements suggest that the Gd and Dy compounds display some type of short range magnetic order, not of the usual spin-glass type, that arises from the site disorder and small exchange coupling inferred from the EPR measurements. This short-range magnetic order presumably prevents these two compounds from becoming superconducting.

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