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Journal

Solid State Communications, 39(10)

ISSN

0038-1098

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Publication Date

1981-09-01

DOI

10.1016/0038-1098(81)90205-2

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HIGH PRESSURE SYNTHESIS OF THE MIXED VALENT AND NONSUPERCONDUCTING TERNARY YbRh_4Sn_7 COMPOUND

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Received 28 May 1981 by A. G. Chynoweth

The ternary compound $\text{YbRh}_4\text{Sn}_{4.6}$ with the phase I structure (simple cubic) when subjected to a pressure of 40 kbar at 800°C is found to transform to phase III structure (f.c.c.) with the composition $\text{YbRh}_{1.1}\text{Sn}_3$. The latter compound has a lattice parameter of $a = 13.735 \text{ \AA}$ which suggests that the Yb is in an intermediate valence state. The temperature dependence of magnetic susceptibility suggests that the Yb is in a homogeneously mixed valence state in the pressure synthesized product. In the phase I structure $\text{YbRh}_{1.4}\text{Sn}_{4.6}$ is superconducting at 8.6°K, but in the phase III structure the compound $\text{YbRh}_{1.1}\text{Sn}_3$ is not superconducting down to 0.9°K. It is suggested that superconductivity and mixed valence are incompatible.

AMONG THE NEWLY DISCOVERED ternary metallic superconducting and/or magnetically ordering compounds¹ in the (RE)-Rh-Sn system, the intermetallic compound $\text{YbRh}_{1.4}\text{Sn}_{4.6}$ exhibits the highest superconducting T_c of 8.6°K. The Yb is in the divalent state in the compound and hence any magnetic ordering is ruled out. The compound has the structure designated as phase I, which has been described in terms of a simple cubic lattice.²⁻⁴ By application of high pressure and temperature we have been able to change the valence state of Yb towards higher valence. The valence change shifts the composition and causes a structure change to the phase which has been labeled phase III (the trivalent heavy rare earth stannides crystallize in the phase III structure). The new phase obtained by quenching to ambient pressure exhibits neither superconductivity nor magnetic ordering down to 0.9°K. The lattice parameter and magnetic susceptibility data suggest a homogeneously mixed valence state for Yb. The experiments and results will be discussed in this paper.

The method of preparation^{1,5,6} of the rare earth ternary intermetallic compounds as well as their crystallography,^{2-4,7} magnetic ordering and superconducting transition temperatures⁸⁻¹¹ have appeared in several publications. For the present study single crystals of $\text{YbRh}_{1.4}\text{Sn}_{4.6}$ were powdered, packed into a Ta container and subjected to 40 kbar and 800°C for 2 hours in a piston-cylinder apparatus. After this treatment temperature was brought to ambient and pressure released. Debye-Scherrer X-ray patterns of the treated sample were taken to determine the structural change and lattice parameter. Tests for superconductivity were performed by a.c. inductance measurements. Magnetic susceptibility measurements down to 1°K were also made to determine the magnetic behavior of the sample.

Figure 1 shows a plot of the lattice parameters across the rare earth series for the primitive cubic phase I, while the inset shows the lattice parameters for the face centered cubic phase III. It is to be noted that the lattice parameters of the Eu and Yb compounds are anomalously large, reflecting the divalency of the rare earth in these two compounds. The stability regime of phase I extends from La to Gd; apparently only large ions have the phase I structure. Heavier rare earths starting from Tb crystallize in either the tetragonal phase II or the f.c.c.

phase III structure.^{2,3,7} Also to be noted is the fact that phase II and phase III compounds have a different composition from that of phase I.¹ Lattice parameters for the phase III structure compounds are shown in the inset to Fig. 1. The Yb compound has the phase I structure because of the larger size of the divalent Yb.

It has been demonstrated in several systems involving Sm and Yb compounds that high pressure favors the higher valence state.¹² Hence the Yb in YbRh_4Sn_7 may be expected to transform towards the trivalent state under pressure. Further, a change towards the higher valence state would cause the size of the Yb to become smaller and this would favor phase III. Therefore a valence change may be expected to result in a structure change to phase III. At the same time a shift in the composition may also be expected. These expectations have been fulfilled in our experiments. X-ray studies and chemical analysis reveal that the pressure-temperature treated phase I $\text{YbRh}_{1.4}\text{Sn}_{4.6}$ is converted to that of phase III with the composition $\text{YbRh}_{1.1}\text{Sn}_{3.0}$ (a composition close to phase III compounds of heavy rare earths) as a consequence of the valence change of Yb. Further, we find that the Yb in phase III is not fully in the trivalent state. The lattice parameter of the pressure quenched $\text{YbRh}_{1.1}\text{Sn}_{3.0}$ has the value of $a = 13.735 \text{ \AA}$, which is substantially larger than the value of 13.68 Å predicted by the trivalent line drawn through the data points in the inset to Fig. 1. From this we believe that the Yb is in an intermediate valence state in the compound.

The magnetic susceptibility measurements are shown in Fig. 2. If there had been only trivalent Yb, a Curie-Weiss dependence of the susceptibility and strong divergence at low temperatures are to be anticipated. This is not the case. On the other hand the temperature dependence of susceptibility is similar to that of typical mixed valent systems such as SmS or $\alpha\text{-Ce}$,^{13,14} and the magnetism is quenched in the pressure treated sample (phase III) because of valence fluctuation. The conclusion from this is that the Yb in the pressure quenched product $\text{YbRh}_{1.1}\text{Sn}_{3.0}$ is in a homogeneously mixed valence state. Then the interesting question arises as to what happens to superconductivity; whether superconductivity can coexist with mixed valence. Our measurements down to 1°K do not show any evidence for superconductivity in the pressure quenched

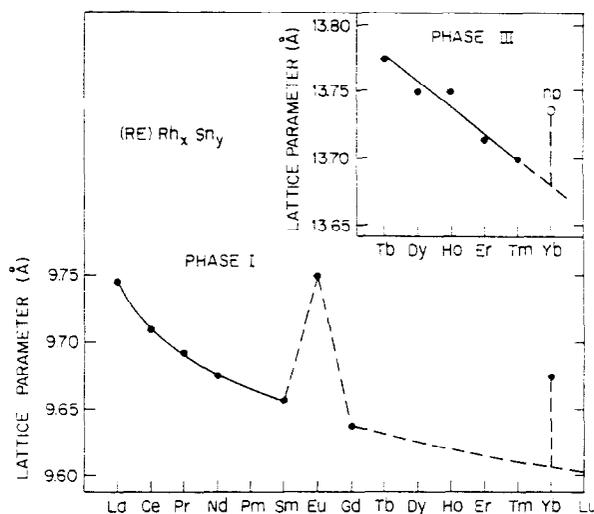


Fig. 1 Lattice parameters for the $(\text{RE})\text{Rh}_x\text{Sn}_y$ system. Eu and Yb compounds have anomalously large values reflecting their divalent nature. Phase I (simple cubic) does not exist for trivalent rare earths heavier than Gd. Inset shows the lattice parameters of phase III (f.c.c.) for the heavier rare earths. The lattice parameter value (open circle) is for the pressure-temperature quenched $\text{YbRh}_{1.1}\text{Sn}_{3.0}$.

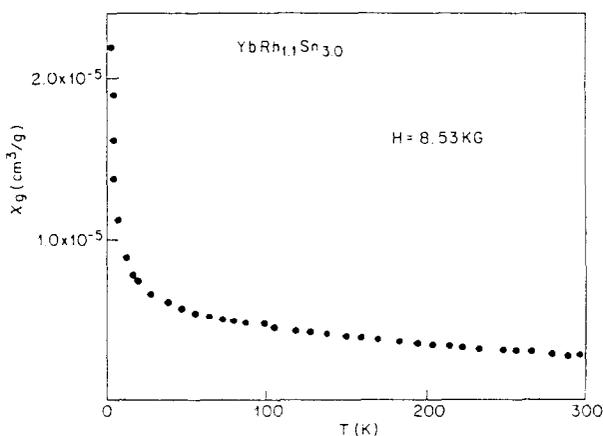


Fig. 2 Temperature dependence of the magnetic susceptibility of pressure quenched phase III structured $\text{YbRh}_{1.1}\text{Sn}_{3.0}$. The susceptibility behavior is similar to that of a mixed valent system.

phase III. The pressure treated material showed traces of superconductivity near 3.7°K , which was identified with the presence of free tin arising from the compositional change of phase I to phase III. When the free tin was eliminated by acid treatment of the sample there was no superconductivity down to 0.9°K , our lower limit. From this it could be stated that possibly mixed valence and superconductivity would not coexist. However it can be argued that the structure change to phase III may have eliminated superconductivity. While this could be true, we believe that the system with a T_c as high as 8.6°K in phase I should exhibit superconductivity within the range $8\text{-}1^\circ\text{K}$

in phase III, if superconductivity and mixed valence can coexist. In fact the Er compound with phase III structure exhibits both superconductivity and magnetic ordering.⁸⁻¹¹ Also, the trivalent nearest neighbors of Yb, namely Tm and Lu rhodium stannides of nearly the same composition, exhibit superconductivity at 2.3 and 4.0°K respectively.¹ Therefore neither the phase III structure nor the composition is unfavorable for superconductivity. Hence we would argue that it is the mixed valence of Yb that kills superconductivity in phase III. Perhaps superconductivity and mixed valence cannot coexist.

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