Coexistence of superconductivity and long-range magnetic order in ErPd$_2$Sn

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Heat-capacity, magnetic-susceptibility, resistivity, and alloying experiments indicate that long-range magnetic order and superconductivity coexist below ~ 1 K in a well-ordered, homogeneous sample of ErPd$_2$Sn. The sample enters the superconducting state at $T_c = 1.17$ K followed by magnetic order at $T_M = 1.00$ K. The superconducting state is retained to 40 mK, the lowest temperature attained.

I. INTRODUCTION

The intermetallic compound ErPd$_2$Sn belongs to a class of materials known as Heusler alloys.[1] These ternary compounds, which have the general composition of RX_2Z, crystallize in the cubic Cu$_2$MnAl-type structure (space group $Fm3m$) and have been widely investigated because of their magnetic properties.[2] Superconductivity was first reported for some Heusler alloys by Ishikawa and co-workers,[3] who focused on the systems RPd$_2$Sn and RPd$_2$Pb where R is a rare-earth metal. In this paper they reported only a magnetic transition for ErPd$_2$Sn at about 0.75 K. Their initial report of both magnetic and superconducting transitions for YbPd$_2$Sn was confirmed by Kierstead et al.,[4] indicating a state of coexistence of these two cooperative phenomena. Additional Heusler alloys were reported to be superconducting by Wernick et al.[5] In previous work,[6] we had observed a superconducting transition for ErPd$_2$Sn in both inductive and resistive measurements. Among rare-earth-metal ternary compounds which exhibit magnetism and superconductivity, erbium is the rare-earth metal most often involved in the phenomenon of coexistence or reentrant superconductivity.[7] Probably the most interesting manifestations of the competition between superconductivity and magnetic order have occurred in ternary rare-earth-metal compounds with Er as the rare-earth element. Confirmation of coexistence in ErPd$_2$Sn permits direct comparison with other Er-containing ternary superconductors such as ErMo$_6$Se$_8$ (Ref. 8), ErMo$_6$S$_8$ (Ref. 9), ErRh$_4$B$_4$ (Ref. 10), Er$_3$Rh$_4$Sn$_{13}$ (Refs. 11 and 12), and Er$_3$Os$_4$Sn$_{13}$ (Ref. 13). Moreover, ErPd$_2$Sn contains a significantly higher percentage (25%) of magnetic constituent than any of these other ternary compounds, yet still becomes superconducting. In this paper we report measurements of the heat capacity, static magnetic susceptibility, and resistivity, all performed on a single sample of ErPd$_2$Sn. This polycrystalline sample is characterized via x-ray diffraction and optical metallographic examinations. Additionally, we examine the systematics of superconductivity in the pseudoternary alloys (Er$_{1-x}$Y$_x$)Pd$_2$Sn.

II. EXPERIMENTAL DETAILS

All samples were prepared from high purity elements (Sn, 99.999 + % pure; Pd, 99.9% pure; Er, Ames Lab, fewer than 30 ppm of any impurity) in a manner described previously.[14] The cubic lattice parameter was determined from powder x-ray patterns by the method of least squares using six reflections including an internal silicon standard ($a = 5.43083$ Å). No impurity reflections were observed. A portion of the approximately 3.1-g sample of ErPd$_2$Sn was polished and examined metallographically. The photos showed a homogeneous, single-phase material with an average grain size of 180 μm. Details of the low-temperature heat-capacity measurement technique may be found in Ref. 15. Static magnetic susceptibility data were taken using a commercial superconducting quantum interference device magnetometer[16] in a field of 2.0 kOe. The ac electrical resistivity was measured on a rectangular parallelepiped of approximate dimensions $5 \times 4 \times 1$ mm^3 using a four-probe technique. Superconducting transition temperatures were determined by both ac susceptibility and resistivity measurements. Temperatures below 1.1 K were obtained in a commercial dilution refrigerator system[17] where the resistivity and ac susceptibility of ErPd$_2$Sn were measured to 40 and 60 mK, respectively.

III. RESULTS AND DISCUSSION

Heat-capacity data for ErPd$_2$Sn between 0.66 and 29.2 K are presented in Fig. 1. The peak corresponding to the onset of magnetic order is evident at $T_M = 1.00$ K. This ordering temperature is slightly higher than the one previously reported.[3] Due to the size of this peak, any superconducting transition in the temperature range 0.5 to 2 K is undetectable by our heat-capacity measurement. To estimate the entropy associated with this magnetic transition, we assume the electronic and lattice contributions to the heat capacity are identical to those of LuPd$_2$Sn, and subtract a parametrization of the normal-state heat capacity of LuPd$_2$Sn from our data. The resulting heat capacity retains the sharp magnetic peak centered at 1.00 K and drops to zero above about 5 K. Integration of this heat capacity up to 5 K yields an entropy associated with the magnetic transition of $S = 0.76R$ which is close to the value expected for a doublet ground state of $S = R \ln 2 = 0.69R$. Our experimental value may be high since we have not accounted for any contribution to the heat capacity due to the electronic Schottky effect from crystalline electric field levels. Based on an analysis of
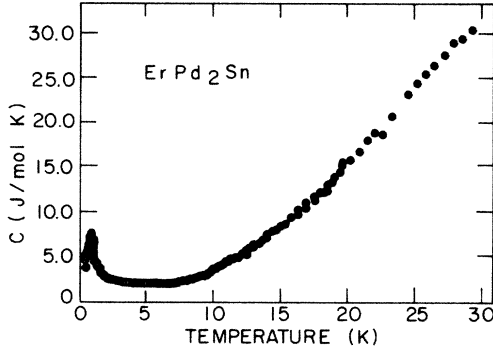
FIG. 1. Heat capacity as a function of temperature for ErPd$_2$Sn.

TABLE I. Cubic lattice parameters and superconducting transition temperatures for sample in the $(Er_{1-x}Y_x)Pd_2Sn$ system.

Composition	a (Å)	T_c (K)
0.00	6.6834(8)	1.17−0.89[a]
		1.23−1.16[b]
0.05	6.6864(8)	1.26−1.08[a]
0.10	6.6873(6)	1.60−1.36[a]
0.20	6.6890(8)	2.08−1.80[a]
0.40	6.6973(6)	2.59−2.37[a]
0.60	6.7024(8)	3.66−3.46[a]
0.80	6.7096(8)	4.38−4.22[a]
1.00	6.7165(8)	5.26−5.04[a]

[a]10—90 % inductive transition.
[b]10—90 % resistive transition.

YbPd$_2$Sn, Kierstead and co-workers[4] predicted a magnetic doublet ground state for ErPd$_2$Sn (Γ_6). Our heat-capacity and magnetic-susceptibility data presented below are consistent with this prediction.

The variation of the inverse molar susceptibility with temperature is presented in Fig. 2. A least-squares fit of the data over the entire temperature range (2.6 to 380 K) was made to the function in Eq. (1), where $C = N\mu_{eff}^2/3k_B$ is the Curie-Weiss constant, N is the Avogadro number, k_B is the Boltzmann constant, Θ is the Curie-Weiss temperature, and X_0 is the temperature-independent susceptibility which represents contributions from Van Vleck paramagnetism, core diamagnetism, and the Pauli paramagnetism of the conduction electrons:

$$\chi_m = \frac{C}{T - \Theta} + X_0 . \tag{1}$$

Values from this fit are as follows: $X_0 = (9\pm5)\times10^{-3}$ emu/mol, $\Theta = -5.8\pm0.4$ K, and an effective paramagnetic moment $\mu_{eff} = (9.57\pm0.20)\mu_B$, where μ_B is the Bohr magneton. Although the uncertainties in the fitting parameters are large, the effective moment obtained by fitting the entire data set is in excellent agreement with the Hund's rule ground state for the free ion Er^{3+}; namely, $\mu_{eff}^{theor} = 9.59\mu_B$. Upon close inspection, however, crystalline electric field effects are evident as curvature in the X_m^{-1} versus T plot. Fitting only data below 30 K to Eq.
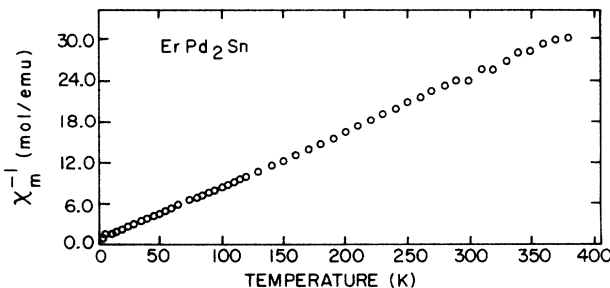
(1) yields a lower effective moment ($\mu_{eff} = 6.59\mu_B$) as well as a Curie-Weiss temperature ($\Theta = -1.8$ K) which is in better agreement with the magnetic ordering temperature ($T_M = 1.00$ K) determined from the heat-capacity data. The negative value for Θ indicates an antiferromagnetic ordering as opposed to ferromagnetism. This hypothesis is strengthened by resistivity and ac susceptibility data presented below which show the coexistence of superconductivity with this magnetically ordered state.

The superconducting transition temperature (T_c) and cubic lattice parameter for eight compounds in the pseudoternary system $(Er_{1-x}Y_x)Pd_2Sn$ are shown in Fig. 3 and are presented quantitatively in Table I. Values of T_c were determined from ac susceptibility measurements on each sample in both the ingot and powder form. No
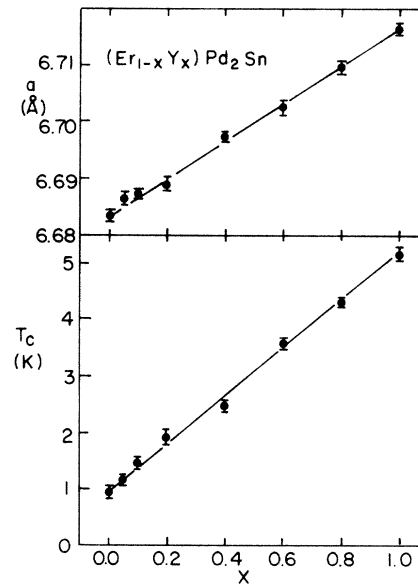

FIG. 2. Inverse molar magnetic susceptibility versus temperature for ErPd$_2$Sn measured in a field of 2.0 kOe.

FIG. 3. Superconducting transition temperature (T_c) and cubic lattice parameter as a function of composition for the pseudoternary system $(Er_{1-x}Y_x)Pd_2Sn$. Error bars indicate transition widths for T_c and experimental uncertainty for the lattice parameter.
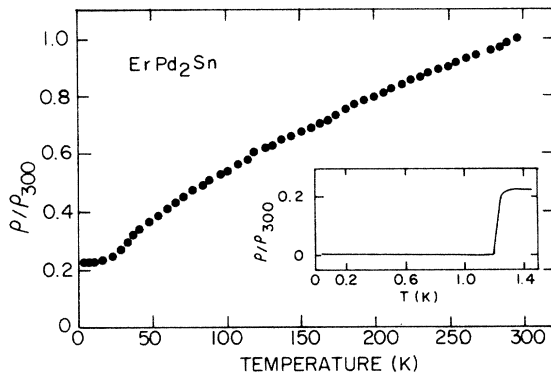
FIG. 4. Electrical resistivity normalized to the value at 300 K versus temperature for $ErPd_2Sn$. The continuous trace in the inset shows the superconducting transition and the low-temperature limit of 40 mK.

difference in T_c or size of signal was observed between an ingot and powder of the same sample. Both T_c and lattice parameter vary in a linear manner between the end members. Our T_c for YPd_2Sn lies within the range of values reported previously.[3] The ac susceptibility for powdered samples of $ErPd_2Sn$ and three pseudoternary compounds with $x = 0.05$, 0.10, 0.20 was measured to 60 mK. All of these samples remained superconducting to this lowest temperature of the experiment. We note that the superconducting transition is completed before the peak in the heat capacity ($T_M = 1.00$ K) is reached. However, as noted previously, the shoulder of the magnetic peak in the heat capacity prevents the detection of the superconducting transition in the calorimetric measurement.

For $ErPd_2Sn$, we have also determined T_c resistively. The resistivity of $ErPd_2Sn$ from 300 K to 40 mK is presented in Fig. 4. At 300 K, the value of the resistivity is 35 $\mu\Omega$ cm. The temperature dependence of the resistivity is metalliclike over the entire temperature range with a residual resistivity ratio of 4.9. As is common, the resistive T_c is slightly higher than the inductive T_c (see Table I). Consistent with the ac susceptibility data, the resistivity remains zero to the lowest temperature attained. Thus, the magnetic transition observed in the heat capacity at $T_M = 1.00$ K does not destroy the superconducting state of $ErPd_2Sn$. Rather, magnetic order and superconductivity coexist in the temperature range between 40 mK and 1.00 K.

IV. CONCLUSION

The combination of heat-capacity, magnetic-susceptibility, and resistivity data show that superconductivity and magnetic order coexist in the Heusler alloy $ErPd_2Sn$. Upon cooling, $ErPd_2Sn$ first enters the superconducting state at 1.17 K. Further lowering of the temperature results in a transition into a magnetically ordered state at 1.00 K while the superconducting properties are retained. Magnetic-susceptibility data indicate that crystalline electric field effects are important at low temperatures, consistent with previous work on $YbPd_2Sn$.[4] This conclusion is also supported by a calculation of the entropy associated with the magnetic transition which favors a ground-

state doublet for $ErPd_2Sn$. Low-temperature neutron diffraction experiments are underway to complete the study of crystalline electric field effects as well as to determine the details of the magnetic structure.

Prior to the discovery of coexistence of superconducting and magnetic states in $ErPd_2Sn$ and $YbPd_2Sn$, only two other crystal structures had yielded compounds showing the coexistence phenomenon;[18] namely, ternary molybdenum chalcogenides with the Chevrel-phase structure and ternary rhodium borides with the $CeCo_4B_4$-type structure. In these two structures, the rare-earth elements (R) are isolated from each other by clusters of Mo_6Se_8 or Rh_4B_4, respectively, yielding large R-R distances of approximately 6.5 and 5.3 Å, respectively. The Heusler alloy $ErPd_2Sn$ presents quite a distinct case, since no autonomous clusters exist and the rare earth is not crystallographically isolated from the other metallic constituents. It will be important to learn whether this distinction is reflected in the details of the magnetic state and the mechanism by which this ordering occurs in the superconducting state of $ErPd_2Sn$.

The competition between the two cooperative phenomena of superconductivity and magnetic order manifests itself in a variety of ternary phases containing rare-earth elements.[7] Across the rare-earth series, Er is most often involved in coexistence or reentrant superconductivity. Three compounds show reentrance due to either long-range ferromagnetic order, $ErRh_4B_4$ (Ref. 19), or short-range ferromagnetic order, $Er_3Rh_4Sn_{13}$ and $Er_3Os_4Sn_{13}$ (Refs. 11—13). Three additional Er-based materials exhibit coexistence; namely, the two Chevrel-phase compounds $ErMo_6Se_8$ and $ErMo_6S_8$ (Ref. 18) and the focus of this study, $ErPd_2Sn$. The frequent appearance of Er in compounds where the free energies of the superconducting and magnetic states are most comparable is probably not a matter of chance. In all of the ternary systems mentioned above, the rare-earth crystallographic site is subjected to symmetry-breaking crystalline electric field effects. Except for Yb^{3+}, which usually has valence instabilities to prevent a pure Yb^{3+} state, Er^{3+} is the heavy rare-earth ion with a Kramers degeneracy to ensure at least a doublet ground state and the magnetic interactions associated with it. Additionally, for systematic magnetic interactions across the rare-earth series, erbium has the possibility of weak, but nonzero magnetic interactions (e.g., consider the de Gennes factor for exchange interactions). The contracted spatial extent of the $4f$ wave functions found in the heavy rare earths keeps the origins of superconductivity (conduction electrons) and magnetism (localized rare-earth metals) distinct, as opposed to heavy-fermion systems where one system of heavy electrons is responsible for both effects. The Heusler alloys $ErPd_2Sn$ and $YbPd_2Sn$ have the distinction as the ternary compounds possessing the greatest concentration of magnetic rare-earth elements that still become superconducting.

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