Coexistence of ordered magnetism and superconductivity in Pd_2YbSn

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The magnetic and superconducting properties of the Heusler alloy Pd_2YbSn have been investigated with heat-capacity, resistivity, and magnetic-susceptibility measurements. The material undergoes a superconducting transition at 2.46 K and a magnetic transition at 0.23 K. The absence of reentrant behavior shows that the magnetically ordered state is coexistent with the superconductivity. A combined analysis of all the data gives the cubic crystalline electric-field parameters $W=-12$ K and $x=-0.65$, implying that the ground state of the Yb^{3+} ion in Pd_2YbSn is a Γ_7 magnetic doublet.

I. INTRODUCTION

Heusler alloys of the general formula A_2BZ crystallizing in the cubic $L2_1$ structure can be formed with d transition elements.[1] Recently, rare earth-containing Heusler alloys of the general form Pd_2RSn (R = heavy rare earth) have been reported in the literature.[2] Some of these have been found to exhibit superconductivity or magnetic ordering.[2,3] In particular, the compounds investigated by ourselves[3] with R = Tb and Dy show antiferromagnetic ordering with T_N of 9 and 15 K, respectively, and no superconductivity down to 1.4 K, the compounds with R = Ho and Er show neither superconductivity nor magnetic ordering in the same temperature range, and the compounds with R = Tm and Yb are found to be superconducting with superconducting transition temperatures $T_c=2.82$ and 2.42 K, respectively. Although previous work[2] had indicated a magnetic transition in Pd_2YbSn at low temperatures, the data were not obtained at sufficiently low temperatures to verify the result. Until now, the nature of the transition was not known, and therefore the question of the coexistence of superconductivity and magnetism in Pd_2YbSn has needed more detailed investigation. Analysis of magnetic susceptibility for the Tm compound has revealed[3] the presence of crystalline electric field (CEF) interactions which result in the Tm ion having a nonmagnetic doublet ground state. As a result, the depression of the superconducting transition temperature by magnetic pair-breaking is suppressed, and the sample has a relatively high T_c. In the case of the Yb compound also, the susceptibility data indicate the presence of CEF interactions,[3] but those data alone were not able to fully specify the ground state.

We present here the results of low-temperature heat capacity and resistivity measurements which serve to clarify many of the above questions. A magnetic transition is verified with $T_M=0.23$ K, coexistent with the superconducting state. This is the first Heusler alloy containing rare earth that shows coexistence behavior. This phenomena had been observed earlier only in some ternary borides and Chevrel phase compounds.[4] In conjunction with the susceptibility data, a detailed analysis has been carried out which fully specifies the CEF ground state.

II. EXPERIMENTAL

The sample was prepared from pure elements by arc melting in Ar gas followed by annealing *in vacuo* for eight days at 900° C. The superconducting transition temperature was determined from ac susceptibility (χ_{ac}), resistivity, and heat-capacity measurements. χ_{ac} was measured using an ac mutual inductance bridge operating at a frequency of 900 Hz. Resistivities were measured on a thin section cut from the arc-melted pellet used for heat-capacity measurements. Current and potential leads were attached with silver paste. Resistances were measured with a Linear Research LR-400 4-wire ac resistance bridge using a current of 300 μa. Susceptibility (dc) measurements were carried out in the temperature range 5–300 K using a superconducting quantum-interference device (SQUID) magnetometer.

Heat capacities were measured in an isothermal calorimeter connected to the mixing chamber of a dilution refrigerator by a mechanical heat switch. Temperatures were measured with calibrated germanium-resistance thermometers obtained from Lake Shore Cryotronics, Inc., using the above-mentioned 4-wire bridge. Heater currents were obtained from a Cryocal CS1000B constant-current source. Voltages were measured on a Keithley model-191 digital voltmeter. Temperature increments were about 10% of the absolute temperature, except near the magnetic and superconducting transition temperatures, where smaller increments were used to enhance the resolution. Curvature corrections were applied, but in most cases they were less than 1%.

III. RESULTS AND DISCUSSIONS

Resistivity, ac susceptibility, and heat-capacity data obtained in the temperature range from 1.5 to 3.0 K are shown in Fig. 1. The susceptibility and heat capacity show a broad superconducting transition centered at $T_c=2.36$ K. The resistivity drops rapidly at somewhat higher temperatures, indicating that some regions of the sample become superconducting at 2.7 K, while the susceptibility shows that some of the material is still normal down to 2.0 K. Reentrant behavior, which would be marked by a return to normal state resistivity, is not seen

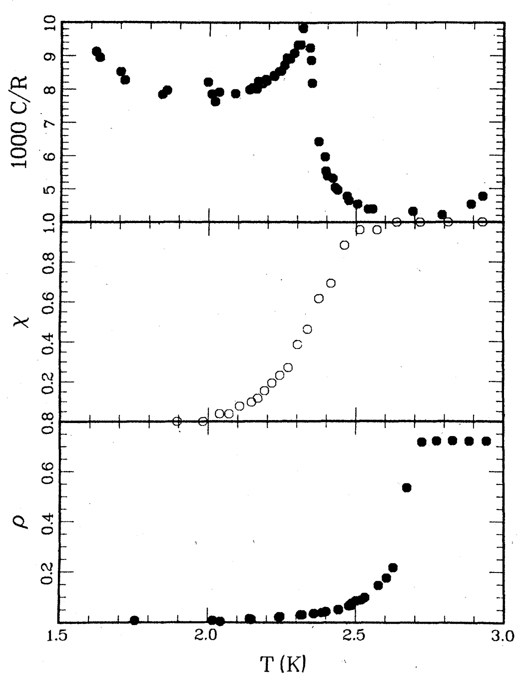

FIG. 1. Resistivity, ac susceptibility, and heat capacity of Pd_2YbSn in the region of the superconducting transition temperature. The resistivity and susceptibility are in arbitrary units.

down to the lowest temperatures measured (0.16 K), showing that no ferromagnetic transitions occur in this region.

Heat-capacity data have been obtained in the temperature range of 0.10 to 20.9 K. Results for temperatures up to 0.4 K are shown in Fig. 2. A clear anomaly corresponding to a magnetic transition is seen with a peak at 0.23 K. In view of the persistence of the superconducting state below 0.23 K as observed from the resistivity data, we conclude that this transition is not to a long-range ferromagnetic state.

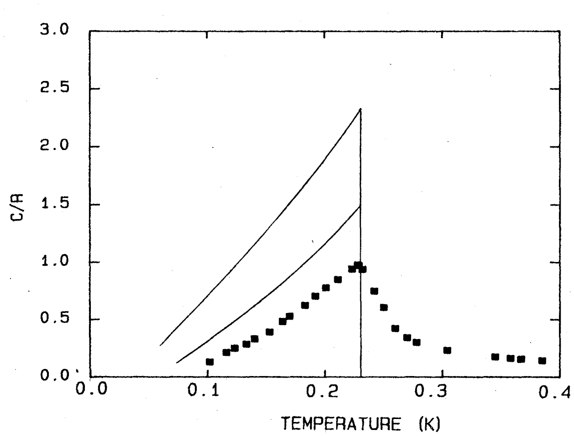

FIG. 2. Heat capacity of Pd_2YbSn showing the magnetic transition at 0.23 K. The upper solid curve shows the mean-field heat capacity for a quartet crystal-field ground state, and the lower solid curve for a doublet ground state.

For the cubic point symmetry of the Yb ions in the Heusler structure, the CEF interactions are commonly described by the parametrization of Lea, Leask, and Wolf:[5]

$$H_{\mathrm{CEF}}=B_4(O_4^0+5O_4^4)+B_6(O_6^0-21O_6^4)$$
$$=\frac{Wx}{F_4}(O_4^0+5O_4^4)+\frac{W(1-|x|)}{F_6}(O_6^0-21O_6^4)\ , \quad (1)$$

where the O_n^m are Stevens operators, B_4 and B_6 are empirical CEF parameters, and F_4 and F_6 have the values 60 and 1260, respectively, for Yb^{3+}. In this case, the CEF ground state can be either a quartet (Γ_8) or one of two doublets (Γ_6 or Γ_7).

The upper solid line in Fig. 2 shows the result of a mean-field calculation of the magnetic heat capacity assuming values of the parameters ($W=-6.38$ K, $x=-0.5$) appropriate for a Γ_8 (quartet) ground state. Similarly, the lower solid line shows the results of the same calculation for a doublet ground state (in this case $W=-10.27$ K, $x=-0.7$, giving a Γ_7 level). The above crystal-field parameters were chosen based on the susceptibility fit[3] from 5 K to 300 K. It is clear that the data are best described by a doublet ground state, although there is an apparent smearing of the magnetic transition which causes the peak height of the heat capacity to be less than that calculated. Integration of the heat capacity up to 2 K gives a magnetic entropy of $S/R=0.632$, very close to the value expected for a doublet ground state of $S/R=\ln 2=0.693$, again indicating a broadened magnetic transition in a doublet ground state. This is consistent with the previous analysis of paramagnetic susceptibility for this material[3] which showed that the ground state was a doublet, but could not distinguish between Γ_6 or Γ_7.

In order to further specify the nature of the CEF splittings, we have carried out a combined analysis of the heat capacity and the magnetic susceptibility above the magnetic transition. Figure 3 shows the heat capacity in the temperature range of approximately 3 to 20 K. This has been analyzed according to

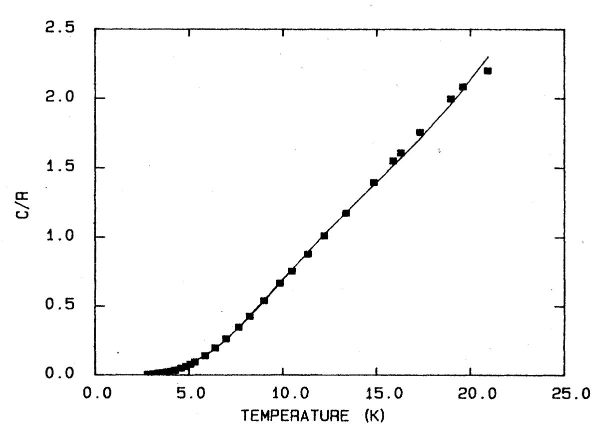

FIG. 3. Heat capacity of Pd_2YbSn in the region above the superconducting transition temperature. The solid curve is a fit to the data including contributions from the electronic heat capacity, the lattice heat capacity, and the electronic Schottky effect from crystalline electric field levels.

$$C=\gamma T+\alpha T^3+C_{\text{Schottky}} , \quad (2)$$

where the three terms correspond to the electronic heat capacity, the lattice heat capacity, and the electronic Schottky effect due to CEF splittings. A least-squares-fit procedure has been used which varied α, γ, and the W and x of Eq. (1), with the latter two parameters falling in the range specified by previous analysis of the susceptibility.[3] The solid line in Fig. 3 shows the best fit to the data, corresponding to the values

$$\alpha=1.80\pm0.03 \text{ mJ}\cdot\text{mole}^{-1}K^{-4} ,$$

$$\gamma=0.1 \text{ mJ}\cdot\text{mole}^{-1}\text{K}^{-2} ,$$

$$W=-12\pm2 \text{ K, and } x=-0.65\pm0.02 .$$

The parameter α, which describes the lattice contribution, is very well determined because it gives the only substantial contribution at the highest temperatures. The value obtained corresponds in a Debye model to a Debye temperature of 114 K. With this value of ϑ_D, the use of a T^3 approximation over the full temperature range may be questionable, but verification of this result will have to await measurements in compounds such as Pd_2LuSn. The electronic coefficient, γ, is quite small, but this parameter is very poorly determined even in order of magnitude because its contribution to the heat capacity is relatively small and comparable in magnitude to the tail of the Schottky anomaly. The crystal-field parameters obtained correspond to a Γ_7 ground state.

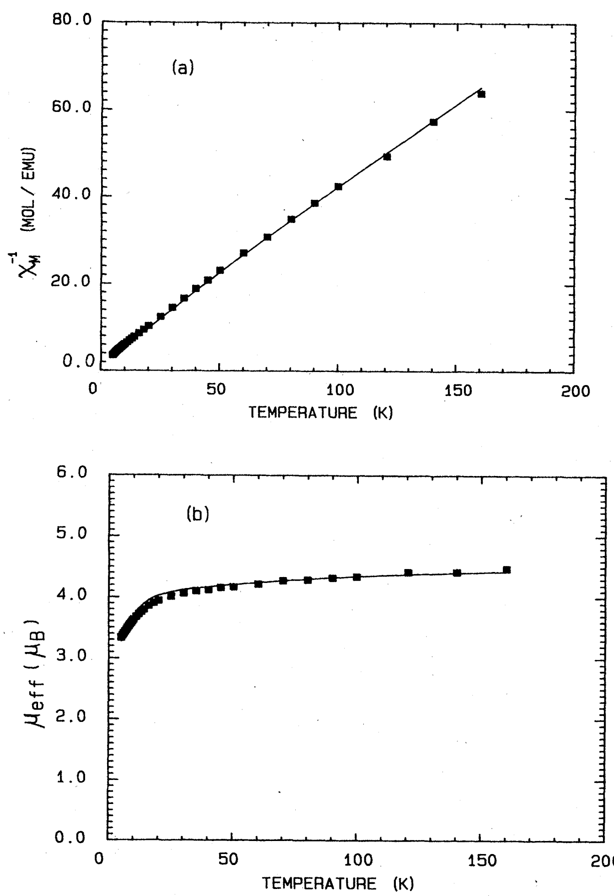

FIG. 4. Magnetic susceptibility showing (a) inverse susceptibility vs temperature and (b) effective paramagnetic moment vs temperature. The solid line includes crystal-field splittings and exchange effects in the mean-field approximation.

Figure 4(a) shows the variation of inverse molar susceptibility (χ_M^{-1}) with temperature for this compound. As previously noted, CEF effects are seen as curvature in the χ_M^{-1} versus T plot. This is seen more vividly in Fig. 4(b), which shows the effective paramagnetic moment, obtained from $\mu_{\text{eff}}^2=3kT\chi_M/N\mu_B^2$, as a function of temperature. For a simple Curie law with no CEF effects, this would be temperature independent. The solid line in each case is obtained by using the above CEF parameters to calculate the susceptibility, χ_{CEF}, and including exchange effects according to

$$\frac{1}{\chi_M}=\frac{1}{\chi_{\text{CEF}}}-\lambda , \quad (3)$$

where λ is an exchange coupling parameter. A least-squares fit to the data gives $\lambda=-0.3307$ mole cm^{-3}. In the simplest molecular field approximation, this constant is related to the magnetic transition temperature T_M according to

$$\chi_{\text{CEF}}(T_M)=|\lambda^{-1}| . \quad (4)$$

Comparison with values of $\chi_{\text{CEF}}(T)$ calculated with the above CEF parameters gives a calculated $T_M=0.36$ K. Agreement with the experimental value $T_M=0.23$ K found from the heat-capacity data is reasonable in view of the fact that the mean-field calculation using a static susceptibility is properly applicable only to ferromagnetic systems.

Using standard procedures, the crystal-field parameters obtained above can be scaled in order to obtain estimates of the electronic ground state in the other Pd_2RSn compounds. This gives values for $R=$Tm of $W=1.93$ and $x=-0.42$, resulting in a magnetic triplet ($\Gamma_5^{(1)}$) ground state with a nonmagnetic doublet (Γ_3) excited state. Other evidence (from Mössbauer studies) indicates that this order should be reversed;[6] however, with these parameters one is in a crossover region of the CEF energy level diagram[5] where small variations in x can invert the order. While this may not be fully resolved at present, one can say that the current parameters are compatible with the Tm results. A similar procedure gives a nonmagnetic ground state for Tb (Γ_3), a magnetic triplet ground state for Ho ($\Gamma_5^{(1)}$), and a magnetic doublet ground states for Dy and Er (both Γ_6). However, it should be noted that a structural phase change occurs in the Tb and Dy compounds at low temperature,[7] which removes the cubic symmetry implicit in the above discussion.

IV. CONCLUSIONS

In conclusion, Pd_2YbSn is the first Heusler alloy containing rare earths in which superconducting and magnetic states have been shown to coexist. By combining data for the heat capacity, resistivity, and magnetic susceptibility, a number of physical properties of this alloy have been obtained. It is shown that this material undergoes a superconducting transition with $T_c = 2.36$ K. At $T_M = 0.23$ K, a transition occurs to an ordered magnetic state, which is coexistent with the superconducting state. Detailed analysis of all the data provides crystalline electric field parameters $W = -12$ K and $x = -0.65$, implying that the ground state of Yb^{3+} ion in Pd_2YbSn is the magnetic doublet, Γ_7.

ACKNOWLEDGMENT

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