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THE HEAT CAPACITY OF THE HEUSLER ALLOY $Pd_2Dy_{0.2}Y_{0.8}Sn$ BETWEEN 0.25 AND 4.2 K *

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ABSTRACT

The heat capacity of the Heusler alloy $Pd_2Dy_{0.2}Y_{0.8}Sn$ has been measured between 0.25 and 4.2 K. The magnitude is very large and can be accounted for over most of the temperature range by the sum of lattice and Schottky type contributions. Evidence is found for two transitions at about $T = 0.4$ and $T = 1.1$ K. The upper one is reasonably consistent with the superconducting temperature reported for an alloy of the same nominal composition.

INTRODUCTION

Some of the Heusler alloys with the general formula Pd_2RSn, where R is a heavy rare earth metal, exhibit superconductivity or magnetic ordering, or both, at low temperatures [1–7]. Compounds containing Tb and Dy appear to order magnetically at low temperatures [1,3] while compounds with Y, Sc, Tm, Yb and Lu exhibit superconductivity. Coexistence of superconductivity and ordered magnetism has been found for Pd_2YbSn below 0.23 K [5] with no reentrant behavior. However, reentrant behavior showing a return to the magnetic phase without superconductivity has been reported for $Pd_2Dy_{0.2}Y_{0.8}Sn$ at $T = 0.75$ K in a field of 1000 gauss [7]. Recently, the effect on T_c of replacing some of the Y in Pd_2YSn by other magnetic rare earth metals has been investigated down to $T = 1.2$ K [6].

At the suggestion of Professor C.V. Stager, we undertook measurements of the heat capacity of the alloy $Pd_2Dy_{0.2}Y_{0.8}Sn$ with the aim of examining the behavior of the alloy to somewhat lower temperatures. While the data yield evidence for two transitions at 0.4 and 1.1 K, the surprising result is that the total heat capacity turns out to be so large.

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* Dedicated to Professor Syûzô Seki in appreciation of his friendship and of his many contributions to Calorimetry and Thermal Analysis.

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EXPERIMENTAL

The specimen (5.45 g/0.0125 mol) was prepared by arc melting the appropriate amounts of the constituent elements under an atmosphere of argon. It was not annealed. Neutron activation analysis of five small chips from different parts of the specimen yielded a dysprosium content of 5.2 ± 0.5 mol%. For mounting the specimen on the tray calorimeter [8,9], one of its surfaces was polished flat. Thermal contact between the specimen and the tray was made through a film of silicone grease.

Two series of measurements were made from 0.28 to 4.2 K and from 0.2 to 1.2 K. They agreed well except for three points in the lower transition region which indicated some possible supercooling of the transition. The average equilibrium time of the calorimeter after an increment of energy had been supplied was about 10 min. This was surprisingly long for such a simple system.

RESULTS AND ANALYSIS

The experimental heat capacities are plotted as points in Fig. 1 and are connected by the solid curve. No distinction is made between the results of the two series of measurements. The other curves in Fig. 1 refer to the analysis of the results and are discussed below.

To establish the scale of the results, the heat capacity of $Pd_2Dy_{0.2}Y_{0.8}Sn$ is larger than that of Pd_2YSn [1] by a factor of 27 at $T = 2$ K and by a factor of 5 at $T = 4$ K. A closer comparison cannot be made because a table or sensitive plot of the primary results for Pd_2YSn [1] was not published.

With regard to analysis of the results, at least four possible contributions to the heat capacity can be envisaged: from lattice vibrations, from elec-

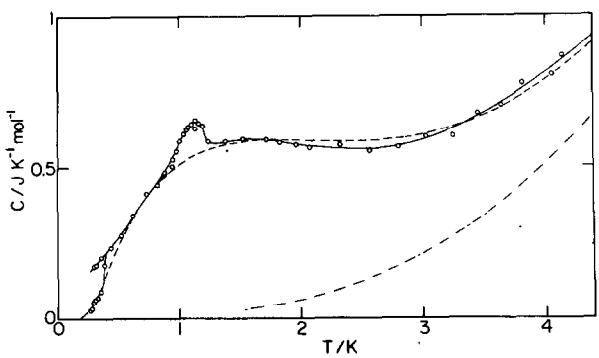

Fig. 1. Heat capacity of $Pd_2Dy_{0.2}Y_{0.8}Sn$ as a function of temperature. (O——O) Experimental data, (- — - —) C_l ($\theta_D = 100$ K), (- - - - -) C_e, (— — —) $C_l + C_e$. (See text for details.)

tronic states, from low-lying energy states and from magnetic and/or superconducting transitions. In this age of the computer, it is relatively easy to put in various assumed contributions to the heat capacity and to seek a best fit to the experimental data. There is, however, the difficulty of producing a unique and convincing interpretation in this way. We choose a simpler approach which has less precision but which has the merit of keeping the analysis closer to the reality of the physical system.

For the alloy Pd_2YSn, the electronic contribution to the heat capacity has been estimated [1] to be about 1.2 T mJ K^{-1} mol^{-1}. If C_{el} for $Pd_2Dy_{0.2}Y_{0.8}Sn$ is of a similar magnitude—which seems to be a reasonable assumption—it is very small compared to the total heat capacity (Fig. 1) and can be neglected. Thus, we conclude that the major contributions to the heat capacity are made by the lattice vibrations and low-lying energy states and we shall try to estimate them.

For the lattice vibrations, the experimental temperature range corresponds to a low temperature regime where the lattice contribution to the heat capacity is given by the asymptotically convergent series

$$C_l = aT^3 + bT^5 + cT^7 + \ldots \tag{1}$$

For a system of a limited array of energy levels, the contribution to the heat capacity is given by the well-known Schottky expression [10]. In the region $T > \epsilon/k$, where ϵ is the separation of the energy levels, the heat capacity can be expressed in series form [11]:

$$C_\epsilon = \frac{A}{T^2} + \frac{B}{T^3} + \frac{C}{T^4} + \ldots \tag{2}$$

Here, the constants A, B, etc., are related to the separations and degeneracies of the energy levels.

If we assume that the experimental temperature range corresponds to low temperature for the lattice vibrations and to high temperature for the other levels, the total heat capacity can be expressed as

$$C = C_l + C_\epsilon$$

$$= aT^3 + bT^5 + \ldots + \frac{A}{T^2} + \frac{B}{T^3} + \ldots \tag{3}$$

Thus, from a plot of CT^2 against T^5 for the experimental data, it is possible to obtain estimates of the constants a and A. Such a plot is shown in Fig. 2 and, from the limiting slope of the curve at the higher temperatures (dashed line in Fig. 2), we obtain $a = 8 \times 10^{-3}$ J K^{-4} mol^{-1}. This corresponds to a Debye characteristic temperature $\theta_D = 100$ K which is somewhat smaller than has been estimated for Pd_2YSn ($\theta_D = 165$ K) [1].

Given this estimate of C_l for $Pd_2Dy_{0.2}Y_{0.8}Sn$, C_ϵ was found by trial-and-error. The final results are illustrated in Fig. 1. The calculated C_ϵ corresponds to an array of six equally spaced levels ($\epsilon = 1.8$ K) and to a

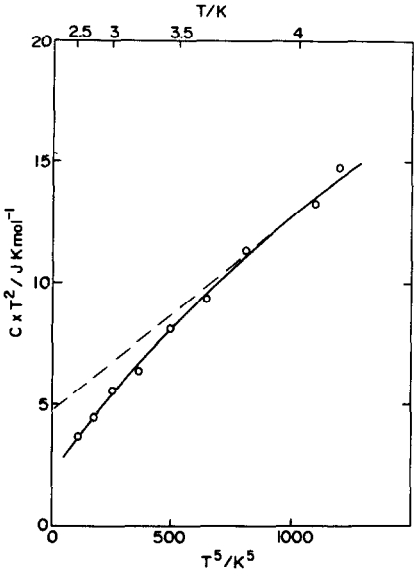

Fig. 2. A plot of CT^2 against T^5 for experimental data in the range $T > 2.5$ K.

dysprosium content of 4.5 mol%. The sum of C_l and C_ϵ accounts for the magnitude and temperature dependence of the observed heat capacity remarkably well. The value of ϵ is nearly two orders of magnitude larger than that found for pure dysprosium metal [12,13]. This suggests that the contribution C_ϵ observed here does not arise from nuclear hyperfine interactions.

The difference between the measured heat capacities and the calculated $C_l + C_\epsilon$ is plotted in Fig. 3. We interpret the excess heat capacities as arising from two transitions at $T = 0.4$ and $T = 1.1$ K. The depression of T_c for the alloy Pd_2YSn by the addition of other magnetic rare earth metals has been

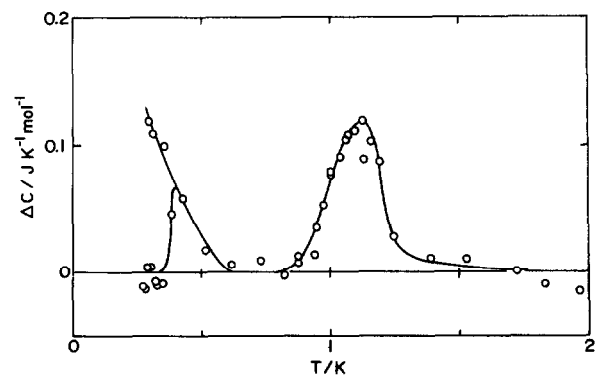

Fig. 3. Excess heat capacity attributed to phase transitions.

TABLE 1

Thermodynamic parameters for the phase transitions

	T_c (K)	ΔH (J mol^{-1})	ΔS (J K^{-1} mol^{-1})
Lower transition	0.4	0.008 ± 0.001	0.019 ± 0.002
Upper transition	1.1	0.031 ± 0.001	0.028 ± 0.001

measured by Malik et al. [6]. For the alloy $Pd_2Dy_{0.2}Y_{0.8}Sn$, they find $T_c = 1.4$ K. This agrees reasonably well with our results that $T_c = 1.1$ K, especially since Malik et al. [6] find that T_c is extraordinarily sensitive to additions of Dy.

Little can be said about the lower transition other than it is likely to be of magnetic origin. Estimates of thermodynamic parameters for the transitions are given in Table 1.

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