Depression of the superconducting transition temperature of the Heusler alloy Pd_2YSn with the addition of magnetic rare-earth metals

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The compound Pd_2YSn, having the cubic Heusler $L2_1$ structure, is superconducting with a transition temperature (T_c) of 4.55 K. The effect on T_c of replacing Y by other magnetic rare-earth metal has been investigated in the series $Pd_2Y_{1-x}R_xSn$ (R = Gd, Dy, Ho, Er, Tm, and Yb). The depression in T_c is the largest with Gd substitution. The initial rate of depression of T_c shows deviation from the de Gennes function. The results of T_c measurements are analyzed in terms of Abrikosov-Gor'kov theory, taking into account the effects of crystalline electric fields acting on rare-earth ions. Values of the density of states times the exchange constant, $[N(0)J_{sf}^2]$, are derived from these measurements.

I. INTRODUCTION

Intermetallic compounds having the general formula A_2BZ which crystallize in the cubic $L2_1$ structure are called Heusler alloys. These alloys have been traditionally known to form with A and B as d transition metals and Z as an sp metal and have been extensively investigated in regard to their magnetic properties.[1] Recently, the formation of Heusler alloys containing rare-earth metals, such as Pd_2RSn (R = Tb to Lu and Sc and Y), has been reported in the literature.[2] In the Pd_2RSn series, the compounds containing Tb and Dy are ordered magnetically at low temperatures[2,3] while the compounds with Y, Sc, Tm, Yb, and Lu exhibit superconductivity with the Y-containing compound having the highest superconducting temperature of 4.55 K. The compounds with Er and Ho investigated in our laboratory are neither magnetically ordered nor superconducting down to 1.2 K. It is interesting to note that the compounds containing Tm and Yb, both being rare earths with an unfilled $4f$ shell, are superconducting. It has been shown recently[3] that crystalline-electric-field (CEF) effects are important in these two compounds and the ground state of the Tm^{3+} ion in Pd_2TmSn is either a nonmagnetic doublet or a triplet which does not suppress superconductivity. In the case of the Yb^{3+} ion, the crystalline-electric-field-split ground state is a magnetic doublet with a reduced moment and this, coupled with the fact that its de Gennes factor is small, does not lead to suppression of superconductivity. However, this compound shows coexistence of ordered magnetism and superconductivity at 0.23 K.[2,4]

The study of ternary superconducting systems with magnetic atoms occupying regular lattice sites has been of great interest. In the well investigated RRh_4B_4 and RMo_6S_8 (R = rare earth) series,[5,6] interesting magnetic and superconducting properties arise because of (i) the localized nature of the $4f$ electrons which are well shielded by the outer $5s$ and $5p$ electrons and (ii) the low exchange interaction constant J_{sf}, between the conduction electron spins and the rate-earth spins. One way of estimating the exchange constant in an isostructural series of compounds is to study the rate of decrease of the superconducting transition temperature, T_c, when magnetic ions are substituted into the nonmagnetic superconductor. In this paper we report the results of such measurements on Pd_2YSn in which Y is replaced by small amounts of other magnetic rare-earth ions. The results have been analyzed in terms of Abrikosov-Gor'kov theory[7] taking into account the effects of crystalline electric fields. These measurements enable us to obtain the values of $N(0)J_{sf}^2$.

II. EXPERIMENTAL

The compounds $Pd_2Y_{1-x}R_xSn$ with R = Gd, Dy, Ho, Er, Tm, and Yb and x ranging from 0 to 1, and Pd_2ScSn and Pd_2LuSn were prepared by melting appropriate amounts of the high purity constituent elements in an arc furnace in a continuous flow of purified argon atmosphere. The ingots were turned over and repeatedly melted to ensure homogeneity. Subsequently, these were annealed in vacuum at 800°C for 7d. Powder x-ray-diffraction studies were carried out using Cu $K\alpha$ radiation which showed that all the compounds are single-phase materials having the cubic Heusler $L2_1$ structure

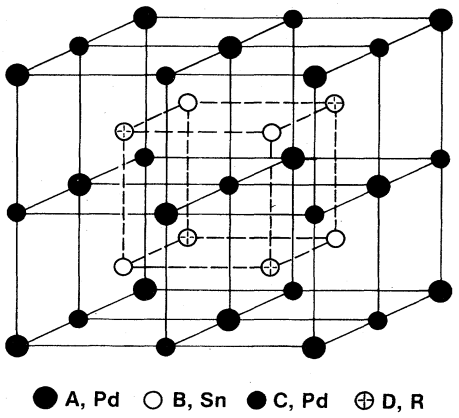

FIG. 1. The Heusler $L2_1$ structure of Pd_2RSn compounds.

TABLE I. Lattice parameter (a) and superconducting transition temperature (T_c) of Pd_2ScSn, Pd_2LuSn, and $Pd_2Y_{1-x}R_xSn$ alloys for different rare-earth metals and for various values of x.

Compound	a (Å)	T_c (K)
Pd_2ScSn	6.503	2.05
Pd_2LuSn	6.644	3.05
Pd_2YSn	6.716	4.55
$Pd_2Y_{0.98}Gd_{0.02}Sn$	6.716	3.24
$Pd_2Y_{0.95}Gd_{0.05}Sn$	6.717	2.41
$Pd_2Y_{0.9}Gd_{0.1}Sn$	6.722	a
$Pd_2Y_{0.9}Dy_{0.1}Sn$	6.716	3.46
$PD_2Y_{0.85}Dy_{0.15}Sn$	6.718	2.80
$Pd_2Y_{0.8}Dy_{0.2}Sn$	6.718	1.40
$Pd_2Y_{0.7}Dy_{0.3}Sn$	6.722	a
$Pd_2Y_{0.9}Ho_{0.1}Sn$	6.715	4.06
$Pd_2Y_{0.9}Er_{0.1}Sn$	6.715	3.87
$Pd_2Y_{0.8}Er_{0.2}Sn$	6.714	3.73
$Pd_2Y_{0.7}Er_{0.3}Sn$	6.714	3.80
$Pd_2Y_{0.6}Er_{0.4}Sn$	6.711	2.77
$Pd_2Y_{0.95}Tm_{0.05}Sn$	6.716	4.12
$Pd_2Y_{0.9}Tm_{0.1}Sn$	6.710	4.12
$Pd_2Y_{0.75}Tm_{0.25}Sn$	6.703	3.73
$Pd_2Y_{0.5}Tm_{0.5}Sn$	6.690	3.65
$Pd_2Y_{0.25}Tm_{0.75}Sn$	6.681	3.06
Pd_2TmSn	6.670	2.82
$Pd_2Y_{0.9}Yb_{0.1}Sn$	6.713	4.37
$Pd_2Y_{0.7}Yb_{0.3}Sn$	6.704	4.03
Pd_2YbSn	6.658	2.42

[a]No superconducting transition down to 1.2 K.

shown in Fig. 1. The crystal structure consists of three interpenetrating face-centered-cubic lattices. The rare earth occupies a site of cubic symmetry. An internal standard was used in x-ray-diffraction studies to obtain accurate lattice parameters which are listed in Table I. The lattice parameter changes in a linear way between any two end members, which is expected for a tight-bound fcc lattice.

Superconducting transition temperatures were measured down to 1.2 K using an ac bridge operating at 900 Hz. In some cases the four probe ac resistive technique was used. The T_c values reported here are defined as 50% of the total transition. Typical transition widths were of the order of 0.2 K.

III. RESULTS AND DISCUSSION

The results of the T_c measurements along with the lattice parameters for the compounds $Pd_2Y_{1-x}R_xSn$ for various R and x are given in Table I. Figure 2 shows the plot of T_c versus x on these compounds. The T_c drops rapidly with the addition of Gd; the compound with 10% Gd is not superconducting down to 1.2 K. The depression in T_c becomes successively smaller for the same value of x in going from Gd to Er. However, the depression is less pronounced for Tm and Yb substitutions because, in this case, the end members Pd_2TmSn and Pd_2YbSn are themselves superconducting. The depression in T_c is almost linear in x for all the rare-earth metals with some scatter

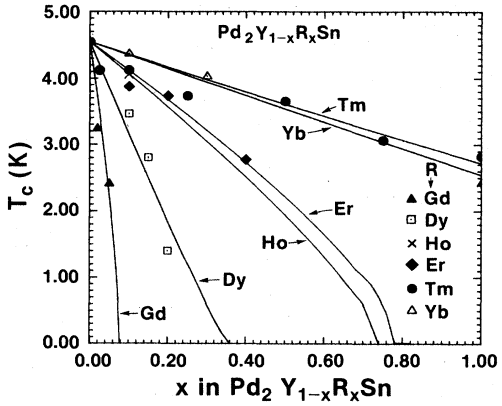

FIG. 2. Variation of superconducting transition temperature as a function of the rare-earth concentration x in $Pd_2Y_{1-x}R_xSn$ (R = Gd, Dy, Ho, Er, Tm, and Yb) compounds. The solid lines are fit to the data based on AG theory and including crystalline electric field effects.

of data. In some cases the superconducting transition temperature was found to be sample dependent.

The exchange interaction between the conduction electron spin $\mathbf{s}$ and the $4f$ (or the rare-earth) spin $\mathbf{S}$, which is responsible for the pair breaking, is given by the Hamiltonian

$$\mathcal{H} = -2J_{sf}\mathbf{S}\cdot\mathbf{s} , \tag{1}$$

where J_{sf} is the exchange constant for the above interaction. The theory for the effect of paramagnetic impurities, such as the rare earths with unfilled $4f$ shells, on superconductivity was given to second order in J_{sf} by Abrikosov and Gor'kov (AG).[7] Qualitatively, one may understand the effect of magnetic impurities in terms of the pair breaking. The exchange interaction given by Eq. (1) has the effect of breaking Cooper pairs by acting differently on the two paired electrons. According to AG theory, in the presence of randomly oriented magnetic impurities, and isotropic exchange interaction, the superconducting transition temperature is given by the following expression:

$$\ln(T_c/T_{c0}) = \psi(\tfrac{1}{2}) - \psi[\tfrac{1}{2} + (2\pi T_c \tau_s)^{-1}] , \tag{2}$$

with

$$\tau_s^{-1} = 2\pi n_I N(0) J_{sf}^2 (g_J - 1)^2 J(J+1) , \tag{3}$$

where n_I is the concentration of impurity rare-earth ions, T_{c0} is the transition temperature in the absence of magnetic impurities (i.e., $n_I = 0$), ψ is the digamma function, $N(0)$ is the density of states at the Fermi level per atom per spin direction, g_J is the Lande' g factor of the impurity rare-earth ion and J its total angular momentum.

According to the AG theory, for small concentration n_I of magnetic impurities, T_c decreases linearly with n_I and the initial rate of depression of T_c, (dT_c/dn_I), is given by the equation

$$\left.\frac{dT_c}{dn_I}\right|_{n_I\to 0} = 4\left.\frac{dT_c}{dx}\right|_{x\to 0} = -\frac{\pi^2 N(0) J_{sf}^2 (g_J-1)^2 J(J+1)}{2k_B} . \quad (4)$$

[For Heusler alloys with four atoms per unit cell we define $dT_c/dx=(\frac{1}{4})dT_c/dn_I$ where x is the fraction of rare-earth atoms in the $Pd_2Y_{1-x}R_xSn$]. The rate of depression of T_c with concentration (dT_c/dx) in $Pd_2Y_{1-x}R_xSn$ series as a function of rare-earth ion is plotted in Fig. 3. The observed dT_c/dx is found to deviate from the de Gennes factor[8] $(g_J-1)^2J(J+1)$ as given by Eq. (4). The expected behavior of dT_c/dx according to AG theory is shown by a dashed line in Fig. 3 after normalizing to the value in Gd. The observed data points, except for Yb, lie below the expected line in general. This may be due to the fact that either $N(0)$ or J_{sf} or both may be slightly changing across the series or due to crystal-field effects. Similar behavior has been observed in the study of magnetic rare-earth substitution in superconducting $LuRh_4B_4$ and $LaAl_2$.[9] The anomalous behavior of Yb has been attributed to the negative sign of J_{sf} due to strong hybridization of conduction-electron states with $4f$ states.[10] Using the experimental value of $dT_c/dx=-44$ K/atom fraction of Gd substitution in Pd_2YSn, we obtain from Eq. (4) a value of 1.83×10^{-4} eV for $N(0)J_{sf}^2$. Since the band structure and hence the density of states is not known in these alloys, exact values of J_{sf} cannot be obtained at present. However, if we take a typical value of $N(0)=0.3$ states/eV atom spin in Pd_2YSn we get $|J_{sf}|=0.025$ eV.

We have also analyzed the complete dependence of T_c on x in $Pd_2Y_{1-x}R_xSn$ for various rare earths in terms of AG theory taking into account the effects due to the CEF. As remarked earlier, the CEF effects have been found to be appreciable in Pd_2TmSn and Pd_2YbSn, the two compounds which have been investigated in detail from susceptibility and/or heat-capacity measurements.[3,4] The crystal-field parameters for these two compounds have been estimated and are consistent with each other in sign and very nearly in magnitude. We assume that the CEF effects are also present in the other isostructural compounds of the Pd_2RSn series. However, in the absence of any direct information on the CEF parameters for the remaining compounds, we have scaled the values from the Tm and Yb compounds to obtain a first approximation of the CEF parameters in these compounds. These experimentally estimated or scaled parameters for the heavy rare earths in the Pd_2RSn series along with the ground state, the first excited state, and their energy separations are listed in Table II, which should be regarded as tentative.

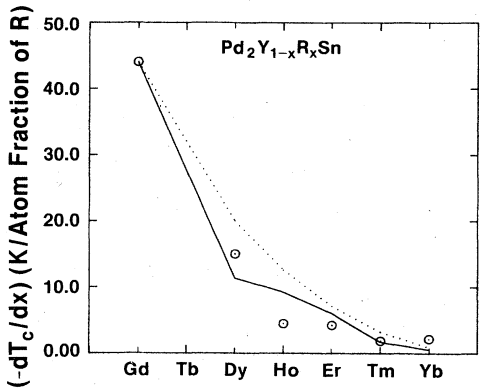

FIG. 3. Initial suppression of T_c with x ($-dT_c/dx$) as a function of rare-earth ion in $Pd_2Y_{1-x}R_xSn$ (R = Gd, Dy, Ho, Er, Tm, and Yb) compounds. The dotted line is based on de Gennes function after renormalizing to the value for Gd. The solid line is based on AG theory with the inclusion of crystalline electric field effects and with $N(0)J_{sf}^2=1.83\times10^{-4}$ eV, the value derived for the Gd substituted system.

The theory of the suppression of T_c in the presence of the CEF has been given by Fulde *et al.*,[11] and by Keller and Fulde.[12] In the dilute impurity limit, in the presence of CEF interaction (including magnetic pair breaking but in the absence of aspherical Coulomb interaction) the superconducting transition temperature is given by the following expression:[13]

$$\ln\left[\frac{T_c}{T_{c0}}\right] = -\sum_{i,j}\frac{\pi p_j}{8T_c\tau_{ij}^s}\left[1+\frac{\tanh x}{x}-\tanh x+\frac{B(x)-A(x)}{\tanh x}\right], \quad (5)$$

where $x=(\delta_{ij}/2T_c)$; $\delta_{ij}=(E_i-E_j)$ is the energy separation between the two crystal-field-split levels $|i\rangle$ and $|j\rangle$,

TABLE II. Experimentally estimated and/or scaled crystalline electric field parameters for various rare-earth ions in Pd_2RSn compounds. For cubic symmetry $B_4^4=5B_4^0$ and $B_6^4=-21B_6^0$. The ground state, the first excited state, and their energy separation (in K) are also given.

R (in Pd_2RSn)	B_4^0 (10^{-2} K)	B_6^0 (10^{-4} K)	Ground state	First excited state (at energy in K)
Dy	−0.61	0.38	Γ_7	$\Gamma_6(26)$
Ho	0.32	0.41	$\Gamma_5^{(1)}$	$\Gamma_3^1(112)$
Er	−0.39	−0.60	$\Gamma_8^{(3)}$	$\Gamma_6(215)$
Tm	−0.014	1.48	$\Gamma_5^{(1)}$	$\Gamma_3(28)$
Yb	0.13	−33.0	Γ_7	$\Gamma_8(38)$

$$p_j = \exp(-E_j/k_B T) \Big/ \sum_j \exp(-E_j/k_B T)$$

and

$$(\tau_{ij}^s)^{-1} = 2\pi n_I N(0)(g_J - 1)^2 \mid \langle i \mid \mathbf{J} \mid j \rangle \mid^2 .$$

and the functions $A(x)$ and $B(x)$ have the same meaning as in Ref. 13 [Eqs. (59) and (60), respectively].

The initial depression of T_c in the presence of CEF interaction is given by

$$\left.\frac{dT_c}{dn_I}\right|_{n_I \to 0} = -\frac{\pi^2 N(0) J_{sf}^2 (g_J - 1)^2}{4k_B} \sum_{i,j} p_j \mid \langle i \mid \mathbf{J} \mid j \rangle \mid^2 \left[1 + \frac{\tanh x}{x} - \tanh x + \frac{B(x) - A(x)}{\tanh x} \right] . \tag{6}$$

Keller and Fulde have given the exact expressions for the T_c for any arbitrary concentration of magnetic impurity and have also shown that for T_c/T_{c0} not too small, the effect of CEF interaction can be approximated by replacing the temperature independent pair-breaking term in Eq. (2) by the temperature-dependent pair-breaking term involving the effects due to CEF. In order to do this one may replace τ_s^{-1} in Eq. (2) by its temperature-dependent analogue given by

$$\tau_s^{-1} = \pi n_I N(0) J_{sf}^2 (g_J - 1)^2 \sum_{i,j} p_j \mid \langle i \mid \mathbf{J} \mid j \rangle \mid^2 \left[1 + \frac{\tanh x}{x} - \tanh x + \frac{B(x) - A(x)}{\tanh x} \right] . \tag{7}$$

Note that in the absence of any CEF interaction $x = 0.0$, $p_j = 1/(2J+1)$, the term in square brackets in Eqs. (6) and (7) becomes unity, and

$$\sum_{i,j} p_j \mid \langle i \mid \mathbf{J} \mid j \rangle \mid^2 = 2J(J+1)$$

and Eqs. (6) and (7) reduce to the corresponding Eqs. (4) and (2) in the absence of CEF effects.

We have numerically calculated T_c's using this theory and the CEF parameters given in Table II. The initial suppression of T_c with the inclusion of CEF effects and assuming $N(0)J_{sf}^2$ to be the same as in the Gd substituted compounds, is shown as a solid line in Fig. 3. This curve is somewhat closer to the experimental values than the curve given by the de Gennes factors. The solid lines in Fig. 2 are the best-fitted lines to the complete data with $N(0)J_{sf}^2$ as an independent parameter. The differences from the AG theory are not very pronounced if the ground state is a Kramer's doublet or more generally a degenerate magnetic state. The values of $N(0)J_{sf}^2$ so obtained are listed in Table III. It is noted that the $N(0)J_{sf}^2$ shows some dependence on the rare-earth ion involved. It may be remarked that the compound Pd_2DySn undergoes a structural transformation[14] at low temperatures to a phase of lower than cubic symmetry. It is assumed that the small addition of Dy does not cause a structural transition in $Pd_2Y_{1-x}DySn$ compounds.

Considerable deviation in the $N(0)J_{sf}^2$ values is observed in the Yb compound and to some extent in the Tm compound compared to the values in other $Pd_2Y_{1-x}R_xSn$ compounds. Part of this may be due to the fact that the T_{c0} may be concentration dependent and some suppression may occur due to nonmagnetic effects. This can be seen by plotting the T_c of Pd_2RSn compounds as a function of lattice parameter (Fig. 4) for nonmagnetic R = Sc, Y, and Lu. T_c is found to vary from 2.05 K for Pd_2ScSn to 4.55 K for Pd_2YSn, although all the rare-earth ions involved are nonmagnetic. One may have to take into account such dependence of T_c on the lattice parameter. This does not cause much of a problem in dilute alloys of Gd, Dy, Ho, and Er because T_c is suppressed very rapidly due to magnetic impurities while the lattice parameter remains essentially unchanged. However, for Tm and Yb compounds there is a large change in the lattice parameters. In order to take this into consideration we have also performed calculations by defining a different T_{c0} for each concentration of Tm and Yb. The T_{c0}'s corresponding to the lattice parameters of these compounds are taken

TABLE III. Values of $N(0)J_{sf}^2$ obtained from the suppression of T_c data in $Pd_2Y_{1-x}R_xSn$ (a) for free rare-earth ion, (b) with crystalline electric fields, and (c) with crystalline electric fields and different T_{c0} for different concentration. The error based on experimental results is ±20%.

Impurity rare earth	$N(0)J_{sf}^2$ (10^{-4} eV) (a)	(b)	(c)
Gd	1.83	1.83	1.83
Dy	1.23	2.29	2.29
Ho	0.75	1.21	1.21
Er	1.15	1.64	1.64
Tm	1.18	2.08	1.04
Yb	4.48	6.77	3.23

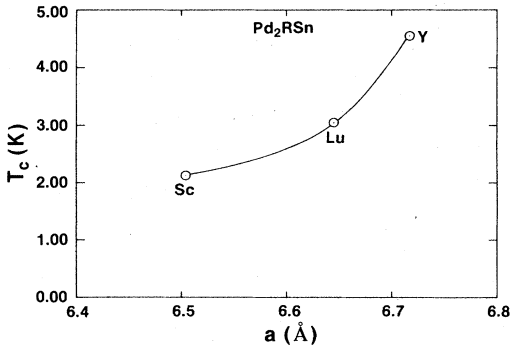

FIG. 4. Superconducting transition temperature versus lattice parameter for Pd_2RSn (R = Sc, Lu, and Y) compounds.

from Fig. 4. This is an assumption and certainly all the change in T_{c0} is not due to changes in the lattice parameters alone. In any case this procedure has the effect of reducing $N(0)J_{sf}^2$ causing some discrepancy in the value for Tm compound but acting in the right direction for the Yb compound. The values of $N(0)J_{sf}^2$ so obtained are given in Table III. As remarked earlier, the somewhat larger value of $N(0)J_{sf}^2$ in the Yb compound may be due to the presence of a Kondo-type interaction. We find that to reproduce the T_c values of Pd_2TmSn and Pd_2YbSn with CEF effects and with $N(0)J_{sf}^2 = 1.83 \times 10^{-4}$ eV, we need T_{c0} values of 4.43 K and 3.35 K, respectively. We would like to suggest that pressure-dependent investigations on these systems may help resolve some of the above questions.

The values of $N(0)J_{sf}^2$ in $Pd_2Y_{1-x}R_xSn$ obtained from the present studies are comparable in magnitude to those in RRh_4B_4 series of compounds[5] and somewhat larger than those estimated in Chevrel-phase compounds[6] RMo_6S_8. With only four atoms in the unit cell of the Heusler structure, the superconducting T_c is depressed very rapidly with the addition of magnetic rare earths and hence no superconductivity is observed in the magnetic rare-earth compounds of this series except for Tm and Yb compounds. It has been shown that the crystalline electric fields are appreciable in Pd_2TmSn and Pd_2YbSn. As a result of the lifting of the degeneracy of the ground J manifold by CEF, the ground state is either a nonmagnetic doublet or a triplet in the case of Tm^{3+}. The ground state of a Yb^{3+} ion is a magnetic doublet Γ_7 but with the moment considerably reduced from its free-ion value. Therefore, in spite of the large value of $N(0)J_{sf}^2$, the superconducting state in Tm and Yb compounds is not suppressed.

In conclusion, the depression of the superconducting transition temperature of a new rare earth containing Heusler alloy Pd_2YSn has been investigated as a function of the concentration of magnetic rare-earth ions substituted in place of Y. Deviations from the de Gennes—type behavior are observed in the initial suppression of T_c. The results have been analyzed on the basis of AG theory taking into account the CEF effects. The values of the density of states times the exchange constant, $[N(0)J_{sf}^2]$, for exchange interaction between conduction-electron spins and rare-earth spins have been estimated.

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